

Anonyme. The Journal of physical chemistry. Published at Cornell university [puis Published under the auspices of the American chemical society, the Chemical society and the Faraday society]. 1896 [I]-. 1922.

1/ Les contenus accessibles sur le site Gallica sont pour la plupart des reproductions numériques d'oeuvres tombées dans le domaine public provenant des collections de la BnF. Leur réutilisation s'inscrit dans le cadre de la loi n°78-753 du 17 juillet 1978 :

\*La réutilisation non commerciale de ces contenus est libre et gratuite dans le respect de la législation en vigueur et notamment du maintien de la mention de source.

\*La réutilisation commerciale de ces contenus est payante et fait l'objet d'une licence. Est entendue par réutilisation commerciale la revente de contenus sous forme de produits élaborés ou de fourniture de service.

Cliquer [ici](#) pour accéder aux tarifs et à la licence

2/ Les contenus de Gallica sont la propriété de la BnF au sens de l'article L.2112-1 du code général de la propriété des personnes publiques.

3/ Quelques contenus sont soumis à un régime de réutilisation particulier. Il s'agit :

\*des reproductions de documents protégés par un droit d'auteur appartenant à un tiers. Ces documents ne peuvent être réutilisés sauf dans le cadre de la copie privée sans l'autorisation préalable du titulaire des droits.

\*des reproductions de documents conservés dans les bibliothèques ou autres institutions partenaires. Ceux-ci sont signalés par la mention Source Gallica.BnF.fr / Bibliothèque municipale de ... (ou autre partenaire). L'utilisateur est invité à s'informer auprès de ces bibliothèques de leurs conditions de réutilisation.

4/ Gallica constitue une base de données, dont la BnF est producteur, protégée au sens des articles L341-1 et suivants du code la propriété intellectuelle.

5/ Les présentes conditions d'utilisation des contenus de Gallica sont régies par la loi française. En cas de réutilisation prévue par un autre pays, il appartient à chaque utilisateur de vérifier la conformité de son projet avec le droit de ce pays.

6/ L'utilisateur s'engage à respecter les présentes conditions d'utilisation ainsi que la législation en vigueur, notamment en matière de propriété intellectuelle. En cas de non respect de ces dispositions, il est notamment passible d'une amende prévue par la loi du 17 juillet 1978.

7/ Pour obtenir un document de Gallica en haute définition, contacter [reutilisation@bnf.fr](mailto:reutilisation@bnf.fr).

***Journal of physical  
chemistry***

**Tome 26**

**Volume 26**

***Washington* 1922**



IX-3

20154

CPgh

**THE JOURNAL  
OF  
PHYSICAL CHEMISTRY**

*Editor*

**WILDER D. BANCROFT**

*Associate Editors*

<b>S. L. BIGELOW</b>	<b>J. JOHNSTON</b>	<b>H. SCHLUNDT</b>
<b>F. K. CAMERON</b>	<b>L. KAHLBERG</b>	<b>E. P. SCHOCH</b>
<b>G. H. A. CLOWES</b>	<b>W. L. MILLER</b>	<b>S. E. SHEPPARD</b>
<b>E. C. FRANKLIN</b>	<b>J. E. MILLS</b>	<b>H. B. WEISER</b>
<b>G. A. HULETT</b>	<b>T. B. ROBERTSON</b>	<b>S. W. YOUNG</b>

**VOLUME XXVI 26**

ITHACA, N. Y.  
THE EDITOR

**1922**





CONTENTS OF VOLUME XXVI

1. JANUARY

<b>J. N. Pearce and L. B. Miller,</b>	Some Colloidal Properties of Pleistocene Clays and Their Bearing on the Chemical Theory of the Formation of Gumbotil, . . . . .	1
<b>E. O. Holmes, Jr. and W. A. Patrick,</b>	The Action of Ultra-violet Light on Gels, . . . . .	25
<b>N. A. Clark,</b>	The Rate of Formation and the Yield of Yeast in Wort, . . . . .	42
<b>S. S. Bhatnagar,</b>	The Water-proofing Efficiency of Some Bi- and Trivalent Salts of Higher Fatty Acids and Their Adsorption by the Fibres of Paper, . . . . .	61
<b>F. B. Kenrick,</b>	The Scattering of Light: Note on Wolski's Paper on Optically Empty Liquids, . . . . .	72
<b>W. H. Martin and S. Lehman,</b>	The Scattering of Light by Dust-free Liquids. II, . . . . .	75
<b>New Books,</b>		89

2. FEBRUARY

<b>P. F. Sharp and R. A. Gortner,</b>	Physico-chemical Studies of Strong and Weak Flours, . . . . .	101
<b>P. C. Alsgaard,</b>	Electrolytic Production of Sodium Perborate . . . . .	137
<b>V. Lenher, G. B. L. Smith and G. G. Town</b>	The Vapor Pressure of Selenium Oxochloride, . . . . .	156
<b>O. W. Brown and C. O. Henke,</b>	Catalytic Preparation of Aniline, . . . . .	161
<b>New Books,</b>		191

3. MARCH

<b>E. J. Witzemann,</b>	The Transition from Crystalloid to Colloid Properties within Homologous Series, . . . . .	201
<b>F. H. Getman,</b>	A Spectrophotometric Study of Solutions of Cupric Chloride, . . . . .	217
<b>L. H. Milligan,</b>	The Mechanism of the Dehydration of Crystalline Aluminum Hydroxide and of the Adsorption of Water by the Resulting Alumina, . . . . .	247
<b>H. W. Smith,</b>	The Nature of Secondary Valence. V, . . . . .	256
<b>O. W. Brown and C. O. Henke,</b>	Catalytic Preparation of Aniline. II, . . . . .	272

W. W. Paddon,	The Effect of Light on Fibres dyed with a Mixture of Chrysaniline and Fuchsine, .	288
New Books,		292
4. APRIL		
K. L. Wismer,	The Pressure-Volume Relation of Superheated Liquids, .	301
W. E. Hughes,	Studies on the Electro-deposition of Lead from Mathers' Perchlorate Bath. I, .	316
C. O. Henke and O. W. Brown,	Catalytic Preparation of Azobenzene and Aniline, .	324
H. W. Smith,	The Nature of Secondary Valence. VI, .	349
F. W. Bergstrom,	The Vapor Pressure of Sulfur Dioxide and Ammonia, .	358
F. H. Getman,	A Study of the Absorption of Light by Solutions of Cupric Lithium Chloride, .	377
W. W. Paddon,	Dyeing of Deaminated Wool, .	384
New Books,		390
5. MAY		
H. B. Weiser,	Hydrous Oxides. III, .	401
J. C. Witt,	The Oxidation of Oxalic Acid in the Absence of Other Acids, .	435
Wilder D. Bancroft,	Mordants. I, .	447
W. H. Martin,	The Relation between Light-Absorption and Light-Scattering for Liquids, .	471
O. W. Brown, S. V. Cook and J. C. Warner	Effect of Grinding upon the Apparent Density of Lead Oxides, .	477
R. P. Sanyal and S. S. Joshi,	The Formation of a Water-in-Oil Type Emulsion by the Concentration of the Oil Phase, .	481
New Books,		487
6. JUNE		
Wilder D. Bancroft, Arne Westgren and Josef Reitstötter,	Mordants. II, .	501
J. B. Ferguson,	On the Coagulation of Colloids, .	537
	The Melting Interval of Certain Undercooled Liquids with a Note on the Use of Liquid Air as a Refrigerant, .	549
B. S. Neuhausen,	The Solubility of Gases in Liquids, .	553
R. B. Elder,	Note on the Measurement of Surface Tensions, .	558
J. F. G. Hicks with Wallace A. Craig,	Relations in Fused Salt Media. II, .	563
A. T. Rabinovich,	On the Conductivity of the Latent Image .	577
New Books,		591

*Contents of Volume XXVI*

iii

7. OCTOBER

M. L. Huggins, J. B. Ferguson,	Electronic Structures of Atoms, . . . . .	601
	The Melting and Freezing Point of Sodium Chloride, . . . . .	626
C. O. Henke and O. W. Brown,	Catalytic Preparation of Azobenzene and Aniline. II, . . . . .	631
E. Q. Adams,	The Role of Hydrogen- and Hydroxyl-Ion Diffusion in Nerve and Muscle Ac- tion, . . . . .	639
W. O. Robinson, H. B. Weiser, New Books,	The Absorption of Water by Soil Colloids, .	647
	Hydrous Oxides. IV, . . . . .	654
		687

8. NOVEMBER

P. B. Ganguly and N. R. Dhar,	Coagulation of Manganese Dioxide Sol by Different Electrolytes, . . . . .	701
O. W. Brown and C. O. Henke, O. F. Tower and Martha C. Cooke,	Catalytic Action of Copper, . . . . .	715
	On the Preparation of Colloidal Solutions of Nickel and Cobalt Hydroxides and Some Other Compounds of these Metals, . . . . .	728
Wilder D. Bancroft, Neil E. Gordon and E. E. Reid, W. W. Paddon, New Books,	Mordants. III, . . . . .	736
	The Solubility of Liquids in Liquids, . . . . .	773
	The Mordanting of Wool with Potash Alum, . . . . .	790
		794

9. DECEMBER

R. H. Bogue,	Hydrogen-ion Concentration and the Prop- erties of the Emulsion Colloids, . . . . .	801
J. G. Thompson, M. L. Huggins, P. B. Ganguly and N. R. Dhar,	The Preliminary Study of Zirkite Ore, Boron Hydrides, . . . . .	812 833
	Adsorption of Ions by Freshly-precipitated Manganese Dioxide, . . . . .	836
T. R. Briggs and A. W. Bull, F. W. Bergstrom, New Books, Name Index, Index to New Books, Subject Index,	The Physical Chemistry of Dyeing, . . . . .	845
	The Boiling Points of Ammonia, Sulfur Dioxide and Nitrous Oxide, . . . . .	876
		895
		901
		904
		906





## SOME COLLOIDAL PROPERTIES OF PLEISTOCENE CLAYS AND THEIR BEARING ON THE CHEMICAL THEORY OF THE FORMATION OF THE GUMBOTIL

BY J. N. PEARCE AND L. B. MILLER

In a paper on "The Origin of the Gumbotil," Kay and Pearce<sup>1</sup> have presented the geological evidence for and the chemical theory of the formation of the gumbotil from the original glacial drift material. The present paper deals with some of the colloidal properties of the gumbotil and of its related strata. In order to define clearly the object of this work and to bring out the relations involved it will be necessary to discuss briefly both the geological evidence and the chemical theory proposed in the original paper.

A study of the glaciated regions of the United States shows that during the Pleistocene age five great glaciers have moved southward over what now constitutes the North Central States. These are known as the Nebraskan, the Kansan, the Illinoian, the Iowan, and the Wisconsin. Since all five of these are exposed to view in Iowa, this state offers an exceedingly favorable place for the study of glacier drifts, their orientation, their materials. As each glacier advanced from the North it gathered up and carried southward vast amounts of rock material which varied in nature from huge granite boulders to rock flour, some clays and former soil. This southward movement was halted at those points where the melting of the ice kept pace with the advancing glacier. In time the temperature of the whole region rose, the ice melted, the glacier receded and this rock debris was deposited in the form of broad, deep, and comparatively level plains.

Between the recession of one ice-sheet and the on-coming of the second there were long interglacial periods during which

<sup>1</sup> Jour. Geology, 28, 89 (1920).

NOTE: G. F. Kay, Professor of Geology and Dean of the College of Liberal Arts, The State University of Iowa; Director of the Iowa Geological Survey.

a soil was formed, a flora developed and a fauna appeared. In time erosion began and continued with the development of a new topography.

The succeeding glacier bearing down upon this surface, razed the hills and filled the valleys, and on melting laid down another deep deposit of rock material. The process of soil formation and the development of plant and animal life began again.

An extensive field study of these glaciated regions by Kay<sup>1</sup> has shown that the three older drifts, viz., Nebraskan, Kansan and Illinoian, are uniformly alike in structure and conformity. These similarities are best observed, in section, in deep recently made railroad cuts.

When erosion has not been too severe and the parts remain in place these drifts show five distinct strata. The top stratum, which lies just below the soil, consists of a loess, a wind-blown material, or of a loess-like clay, possibly related to the drift. The second stratum is that commonly known as the gumbo. This is a "gray to dark colored, thoroughly leached, non-laminated, deoxidized clay, very sticky when wet, very hard and tenacious when dry." Below the gumbo is a narrow stratum of a yellow to chocolate colored clay, containing a few siliceous pebbles and sand lenses, but leached with respect to calcium and magnesium. This narrow, oxidized-leached stratum is always found just below the gumbo and, except for the color, they appear to be closely related. The fourth stratum is a yellow oxidized-unleached clay. It contains many pebbles and small boulders, and also many calcareous concretions due to infiltration from above. The bottom layer is the unoxidized-unleached, unweathered original drift material.

The two yellow clays have, I believe, always been considered a part of the drift. Opinion as to the origin of the gumbo has been varied. Leverett<sup>2</sup> favored the view that

---

<sup>1</sup> Bull. Geol. Soc. Amer., 27, 115; Iowa Geological Surv., 26, 215 (1917).

<sup>2</sup> U. S. Geol. Surv., Monograph, 38, 28 (1899).

the gumbo is the result of aqueous deposition following the submergence of the region. Bain<sup>1</sup> presents the view that the gumbo suggests a quiet water deposit which has been compacted or puddled by water. A somewhat similar view is held by Arey.<sup>2</sup> Udden<sup>3</sup> states that it is probably an old loess which has been clogged by the interstitial deposition of fine ferruginous material through the agency of ground water, or perhaps, a fluvial deposit made at a stage of semi-stagnant drainage.

As the result of an extensive field study Kay has been lead to the conviction that this so-called gumbo is in reality a part of the original drift,—that it is the residuum left after the complete weathering and leaching of the drift materials. In order therefore that the name might the more explicitly suggest both its origin and its relation to the drift, he has preferred to call it the "Gumbotil."<sup>4</sup>

This new theory regarding the formation of the gumbotil involves the assumption that, following the laying down of each original drift a very long period elapsed during which chemical weathering and leaching took place; that the upper layers are the residua left by these processes. After these processes had continued for a long time diastrophic movements occurred, erosion began and then continued until the general topography existing at the ends of the interglacial periods had been developed.

#### **Field Evidence Supporting the Theory**

In any cut showing all of the five strata in place these points may be noted. The lines of demarkation between any two strata do not conform to the shape of the hill, but run directly and almost horizontally to the edge of the hill upon both sides. Considering any two adjacent cuts, it will be observed that the lines of demarkation are symmetrically placed, the

<sup>1</sup> Iowa Geol. Surv., 18, 292 (1907).

<sup>2</sup> Ibid., 20, 511 (1909).

<sup>3</sup> Ibid., 11, 258 (1900).

<sup>4</sup> Science, 44, 637 (1916).



continuity being broken only by the valley between. Except at the boundary between the oxidized-leached and the oxidized-unleached strata, the surfaces of separation are not as distinct as they would be, if one stratum were laid down directly upon another. They dove-tail, so to speak, into each other, and in these dove-tailings we may follow the processes of weathering and oxidation.

The variation in the size of the pebbles offers strong evidence in support of the theory. The pebbles found are quartz, chert, flint, quartzite, granite, basalt and greenstone, feldspar, sandstone, etc., the proportions of each in any pebble count decreasing in the order named. This, however, is practically the reverse of the order of their hardness and solubility. In the upper loess-like clay the pebbles are exceedingly rare and very minute. Passing downward through the gumbotil and the oxidized-leached strata the pebbles gradually increase not only in frequency, but also in size. In the oxidized-leached stratum we frequently find the disintegrated remains of huge granite boulders. They consist chiefly of fine sand grains; they are the residue left after all of the soluble weathered material has been leached away. In the oxidized-unleached stratum and in the original drift material they are often massive in size, but they still retain their original form and structure.

#### **The Role of Water in Geo-Chemical Changes**

The dominant factor in all the geo-chemical changes here involved is water,—more especially the aerated rain-water. When rain falls upon the ground one part, the "run-off,"<sup>1</sup> flows over the surface and escapes. This is the cause of erosion. A second part, the "fly-off," immediately evaporates into the air. A third part, the "cut-off," enters the soil and, moving downward with considerable speed, carries with it the dissolved mineral matter. Of these the cut-off water is the only form which is directly effective in soil formation and in the theory of the formation of the gumbotil.

<sup>1</sup> Cameron: *Jour. Phys. Chem.*, 14, 340 (1910).

When a relatively small quantity of water is added to a dry solid or soil the water spreads over the surface in the form of a film. With addition of water the apparent volume of the solid increases until a maximum is reached. Still further additions of water will not increase the thickness of this water film, but will produce free-water in the soil interstices, and in some cases this often leads to puddling.

The film-water is held tenaciously by the soil particles. In dry seasons it is practically a saturated solution of the dissolved rock and soil materials. When the surface becomes flooded, as in wet seasons, or during heavy rains, the free- or cut-off water in its downward movement extracts and carries away a part of the mineral content of this film-water solution. Once the free water is removed, the saturation of the film repeats itself. In this water are the dissolved rock materials, the carbon dioxide, oxygen, nitrogen, humus material and the soil bacteria. Between these are evolved all the processes leading to the disintegration of the rocks and the formation of the soil and its sub-strata.

The rock materials transported by the glaciers were of igneous origin, viz., feldspars, amphiboles, pyroxenes, micas, quartz, some clay and other previously weathered materials. These are silicates, salts of a very weak acid,—silicic acid, with various base-forming elements, the alkalies, calcium, magnesium, iron and aluminum. Like all salts of strong bases and weak acids, these silicates when dissolved hydrolyze to form the free ionized bases,—the hydroxides of sodium, potassium, calcium and magnesium, some iron and either the free un-ionized silicic acid, or some simpler silicates. The latter will in turn continue to hydrolyze and there will result still other products, and in the end simpler silicates, perhaps kaolin, or even silica as sand or quartz.

If the reaction products are not removed by leaching, a state of saturated solution equilibrium is attained and the solution process ceases. Under these conditions the decomposition products from different sources may react with each other to form more or less complex silicates of a secondary

origin. Let the saturated solution be removed and fresh water added, the various solution equilibria are disturbed and the solution processes begin again.

In the soil solution thus formed, the dissolved materials will at the proper concentrations react with the carbon dioxide of the soil atmosphere to form the soluble, highly ionized, carbonates of sodium and potassium, and the soluble acid carbonates, or the insoluble carbonates of calcium and magnesium. The insoluble carbonates crystallize out as the calcareous concretions so frequently found in the clay subsoils. In the presence of a sufficient excess of carbon dioxide the insoluble carbonates pass into the form of the soluble acid-carbonates and are leached away by the downward moving free-water. Ferrous silicates upon hydrolysis give ferrous ions. These react with the ions of the soil solution to form the relatively slightly soluble ferrous hydroxide or carbonate, or, as is more likely the case, they may be oxidized immediately to ferric ions and then precipitated as the insoluble ferric hydroxide. The aluminum remains for the most part in the form of silicates. The soil solution contains other elements and compounds, but their proportions are relatively slight and subject to considerable variation. The consideration of these is not needed in this paper.

In summarizing, we may divide the mineral matter of the soil solution into two classes. The more easily diffusible are the soluble alkali bases and salts, the soluble acid-carbonates of calcium and magnesium, the slightly soluble ferrous compounds and the semi-colloidal sodium and potassium silicates. The less easily diffusible are the colloidal forms of gelatinous silicic acid, the hydrated silicates and the hydrated ferric oxide.

According to Julien<sup>1</sup> the solvent action of the alkaline soil solution and of the humic acids, aided by the abrasive effects of the earth's displacements, slowly but surely transforms the quartz pebbles into colloidal silica. Under the influence of

---

<sup>1</sup> Proc. Am. Assoc. Adv. Sci., 1879, 311.

the decaying organic matter the ferric compounds are reduced, temporarily at least, to ferrous compounds. While the existence of ferrous compounds in contact with the soil atmosphere must obviously be a short one, the alternate oxidation and reduction permits the slow downward transportation of the iron. The decomposition of the aluminum silicates leads ultimately to the formation of the colloidal hydrated aluminum silicates. These are the most complex, most resistant, the least soluble and the least mobile of all of the decomposition products produced by the disintegration of the silicate rocks. It is obvious, therefore, that the aluminum compounds will not be subject to appreciable removal by capillary flow.

Hence, in the leaching of the weathered products of the original glacier drift material we should expect to find a gradual increase in the proportion of the soluble diffusible materials as we pass downward from the surface. On the contrary, conditions permitting, we should expect to observe a gradual decrease in the proportion of alumina. These relations are exactly what we do find from the results of a series of chemical analyses of a series of strata in any single complete cut.

#### **Chemical Analyses of the Clays**

The samples of clay used for analysis were taken from deep and recently made railroad cuts. Each sample was taken from the middle of the stratum and from the bottom of deep holes dug horizontally into the side of the cut. This latter precaution was taken in order to avoid as far as possible any contamination due to surface water. The air-dried samples were carefully powdered, without grinding, and sifted through a clean dry 20-mesh copper sieve. Since we are chiefly concerned with the weathered material only, the arbitrary choice of a mesh of this size gives us a uniform standard for the uniform fineness of the glacier flour for all clays.

The sifted material was then ground in an agate mortar until every trace of it passed through a 100-mesh sieve. It

was then thoroughly mixed on a mixing cloth and preserved in glass-stoppered bottles.

All of the analyses were made exactly as prescribed by Hillebrand in his classic work on "Carbonate and Silicate Analysis." Since we are concerned only with the less mobile constituents no attempt was made to make a complete analysis of any stratum. The results are given in two forms: (a) the percentage composition with respect to the less mobile constituents, (b) the parts by weight of these constituents per 100 parts of the more resistant  $Al_2O_3$ .

Only the analyses of the samples taken from the localities at "A," "B," "C" and "D" will be reported in this paper. They represent the three older drifts and are typical of the many analyses made.

The three localities "A," "B" and "D" show the gumbotil underlying the loess or loess-like clay and covered by a thin layer of soil. At "C" the Nebraskan gumbotil lies below the soil with no intervening loess or loess-like clay. The loess or loess-like clay are of great interest but are not being considered except incidentally in this paper. In places these materials are clearly eolian in origin. In other places the loess-like clay may be closely related in origin to the gumbotil. The presence of loess or loess-like clay above the gumbotil might be expected to have some slight effect upon the present chemical composition of the gumbotil, and in fact may explain the few percentages in the analyses which might seem to contradict the theory proposed.

It is assumed that the composition of the flour of the unoxidized and unleached till is now the same as when laid down by the glacier. The possibility exists, however, that it may have received a small amount of leached material from above, or that it may have lost to the strata above by capillary flow slight quantities of the more easily diffusible dissolved materials. It is not to be expected that its composition will be similar to that of the overlying materials which have been subjected to marked chemical changes, to leaching, or to infiltration.

TABLE I

## A. Chemical Analyses of Samples of Kansan Drift Materials taken in Monroe County, Near Foster, Iowa

	(a) Percentage composition				
	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO
Gumbotil (Kansan)	72.03	4.18	12.27	1.33	2.29
Glacial till, oxidized-leached	73.11	4.62	11.57	1.66	2.56
	(b) Parts per 100 parts Al <sub>2</sub> O <sub>3</sub>				
	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO
Gumbotil (Kansan)	587.0	34.10	100.0	10.84	18.68
Glacial till, oxidized-leached	631.9	39.92	100.0	14.35	22.18

TABLE II

## B. Chemical Analyses of Samples of Kansan Drift Materials taken in Clarke County, near Murray, Iowa

	(a) Percentage composition				
	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO
Gumbotil (Kansan)	70.46	4.17	12.04	1.21	0.55
Glacial till, oxidized-leached	71.84	4.62	10.86	1.29	0.72
Glacial till, oxidized-unleached	68.56	4.40	11.13	4.48	0.79
	(b) Parts per 100 parts Al <sub>2</sub> O <sub>3</sub>				
	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO
Gumbotil (Kansan)	585.2	34.7	100.0	10.05	4.57
Glacial till, oxidized-leached	661.5	42.5	100.0	11.87	6.66
Glacial till, oxidized-unleached	616.0	39.5	100.0	40.30	7.16

TABLE III  
C. Chemical Analyses of Samples of Nebraskan Drift Materials  
taken in Carroll County, Near Manning, Iowa

	(a) Percentage composition				
	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO
Gumbotil (Nebraskan)	71.59	4.35	12.79	1.26	0.93
Glacial till, oxidized-leached	66.85	5.92	11.65	3.67	0.78
Glacial till, oxidized-unleached	66.52	4.80	11.18	4.28	1.43
	(b) Parts per 100 parts Al <sub>2</sub> O <sub>3</sub>				
	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO
Gumbotil (Nebraskan)	559.7	34.0	100.0	9.90	7.31
Glacial till, oxidized-leached	573.8	50.7	100.0	31.51	6.71
Glacial till, oxidized-unleached	594.5	42.9	100.0	38.30	12.81

TABLE IV  
D. Chemical Analyses of Samples of Illinois Drift Materials taken  
in Lee County, near Fort Madison, Iowa

	(a) Percentage composition				
	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO
Gumbotil (Illinoian)	71.07	4.24	14.91	0.79	0.85
Glacial till, oxidized-leached	72.24	7.43	11.65	0.61	0.95
Glacial till, oxidized-unleached	72.30	3.47	8.59	4.13	1.28
	(b) Parts per 100 parts Al <sub>2</sub> O <sub>3</sub>				
	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO
Gumbotil (Illinoian)	476.0	28.44	100.0	5.34	5.68
Glacial till, oxidized-leached	620.1	63.80	100.0	5.26	8.22
Glacial till, oxidized-unleached	841.2	40.39	100.0	48.10	14.95

A study of Tables I to IV will bring out several interesting facts. In all of the series here represented the percentage of  $\text{Al}_2\text{O}_3$  decreases downward from the gumbotil through the oxidized and leached stratum. Except in the case of "B" (Table II), this decrease continues also through the oxidized and unleached stratum.

TABLE V  
Comparative Analyses of Strata from Various Localities and Drifts

Locality	A	B	C	D
	$\text{SiO}_2$			
Gumbotil	72.03	70.46	71.59	71.07
Glacial till, oxidized-leached	73.11	71.84	66.85	72.24
Glacial till, oxidized-unleached	.....	68.56	66.52	72.30
	$\text{Fe}_2\text{O}_3$			
Gumbotil	4.18	4.17	4.35	4.24
Glacial till, oxidized-leached	4.62	4.62	5.92	7.43
Glacial till, oxidized-unleached	....	4.40	4.80	3.47
	$\text{Al}_2\text{O}_3$			
Gumbotil	12.27	12.04	12.79	14.91
Glacial till, oxidized-leached	11.57	10.80	11.65	11.65
Glacial till, oxidized-unleached	.....	11.13	11.18	8.59
	$\text{CaO}$			
Gumbotil	1.33	1.21	1.26	0.79
Glacial till, oxidized-leached	1.66	1.29	3.67	0.61
Glacial till, oxidized-unleached	....	4.48	4.28	4.13
	$\text{MgO}$			
Gumbotil	2.29	0.55	0.93	0.85
Glacial till, oxidized-leached	2.56	0.72	0.78	0.96
Glacial till, oxidized-unleached	....	0.79	1.43	1.28

Perhaps the most important evidence in favor of the leaching theory is to be gained from a study of the relative proportions of  $\text{CaO}$  and  $\text{MgO}$  in the various horizons. In



practically every series the proportions of these two constituents show a pronounced increase downward. Apparent contradictions for both might be considered for MgO in Table III and for CaO in Table IV. Field relations will show in these instances either that the gumbotil is overlaid by material containing a higher proportion of these constituents, or that erosion began before the leaching process in the gumbotil was completed. Assuming that the loess or the loess-like clay is a subsequent formation, it also will have been leached of some of its CaO and MgO. This means a slight increase in the proportions of these two in the stratum below, the leaching of which has not been completed.

The silica and the iron are less diffusible and hence less subject to leaching than are the carbonates of calcium and magnesium, and a much longer time is required for complete leaching. In every instance the proportion of iron in the gumbotil is less than it is in the oxidized and leached stratum just below. Except for the case of the Nebraskan (Table III), the proportion of SiO<sub>2</sub> is greater in the oxidized and leached stratum than in the gumbotil. It should be observed that the Nebraskan at the locality "C" underlies the Kansan, and the apparent discrepancy may be accounted for in the transference of the alkaline silicates from the Kansan into the upper strata of the Nebraskan below. On the basis of parts per 100 parts of Al<sub>2</sub>O<sub>3</sub> not only CaO and MgO but also SiO<sub>2</sub> show distinct evidence of leaching even in the oxidized and leached stratum, and this is true for practically every series. On the same basis the evidence points to a leaching of the iron into the oxidized and leached stratum from gumbotil, but the time allowed was not sufficiently long for the subsequent leaching of the iron from the oxidized and leached stratum into the one below.

#### **The Leaching Process**

We are now in a position to picture the weathering and leaching processes as they occurred long ago. The oxygenated and carbonated water falls upon a uniformly level,

more or less uniformly constituted, blue to blue-black drift. Percolating downward it dissolves a portion of the rock material. Hydrolysis follows, and there are liberated successively the hydroxides of sodium or potassium, then of calcium or magnesium, and finally the more or less difficultly soluble hydroxides of ferrous and ferric iron, depending on the nature of the iron in the original silicate. The ferrous iron throughout the depth penetrated by the dissolved oxygen is immediately oxidized and the deposit assumes the typical iron color of the yellow clays.

The calcium and magnesium hydroxides combine with the carbon dioxide of the soil atmosphere to form the insoluble carbonates which crystallize out as calcareous concretions. The soluble alkalis and their salts and the alkaline silicates are carried downward by the moving free water. The negative colloidal silicates and the silicic acid are coagulated and rendered motionless by the electrolytes of the soil solution. As hydrolysis proceeds the mass of the insoluble material thus formed increases and probably does continue to increase until all of the easily available, hydrolyzable materials are used up or removed.

Obviously those insoluble materials which are most easily attacked will be the first to be leached away. These are the carbonates of calcium and magnesium. Although only very slightly soluble, the dissolved portions of these combine with the carbonic acid of the soil solution to form the soluble acid-carbonates. These are carried downward to lower levels where in fissures and crevices they again crystallize as irregular concretions. In this way were formed all of those concretions which are found in the oxidized stratum.

According to the Law of Mass Action, the activity, or the solvent effect of the carbon dioxide will be greatest at those points where its concentration is a maximum. This obviously will be at the upper level of the initially unleached calcareous zone. Owing to its diffusion power some of the carbon dioxide may escape combination at the upper level only to combine at a slightly lower level. Ultimately there will

be a lower limit beyond which the carbon dioxide entering from the atmosphere will not penetrate, or its concentration in the soil solution will be too slight to produce any appreciable chemical effect. These limits of maximum and minimum activity represent the boundaries of the dynamic zone of carbonic acid activity—the oxidized and leached stratum. As time goes on the concentrations at the upper level disappear, and the levels of maximum and minimum activity move downward simultaneously.

This dynamic zone has played an important rôle in all drift transformations. It spreads horizontally like a thin sheet of more or less uniform thickness. It is found always directly upon the oxidized-unleached stratum and always directly below the gumbotil. In the Nebraskan drift it is thin, less than two feet to somewhat more than four feet. The oxidized-leached stratum of the Kansan drift averages about five feet, attaining in a few places a thickness of seven feet. That of the Illinoian has an average thickness not to exceed six feet. In the Iowan it has reached a maximum of three and one-half feet, yet in those areas where the Iowan has been exposed it has not yet left the surface. The Wisconsin drift shows no leached stratum at any point. The original granite boulders of this glacial drift lie directly upon the oxidized-unleached material. Our assumption is that the time which has elapsed since the laying down of the Wisconsin has not been sufficiently long to permit these changes. The areas of Iowa covered by the Wisconsin are so flat and level that even the drainage channels already formed are insufficient to carry away the excess surface water. There is, therefore, a relatively large excess of cut-off water: the existing conditions favor leaching. Hence, we may safely assume that if the present existing conditions continue sufficiently long, this drift also will show not only the oxidized-leached stratum, but also, possibly, the gumbotil lying on top of it.

This downward movement of the oxidized-leached zone did not cease until after disatrophic movements had occurred. Then erosion began and, instead of percolating downward, the

falling aerated rain-water escaped over the surface.

After the leaching of the calcium and magnesium—perhaps simultaneously—there follows a second step. When the concentrations of the precipitating ions have been leached below their critical coagulating values new processes occur within the leaching zone. The coagulated iron passes into solution either as colloidal ferric hydroxide by peptization or deflocculation by the emulsoidal humus material, or as ferrous compounds through reduction by organic matter. Thus either by colloidal flow, by alternate reduction and oxidation, or through the medium of its slightly soluble salts, the iron is leached and slowly passes downward. The silica either in the form of the colloidal silicic acid or as the soluble alkaline silicates also moves downward. Likewise, through various peptizing influences the colloidal clays begin to swell and deflocculate. Ultimately some of these pass into suspension of colloidal particles; they are also caught in the downward current and carried by it to lower levels where they are again coagulated. Only a slight amount of this material is leached away.<sup>1</sup>

The properties of the gumbotils are largely those which one might predict from a knowledge of the colloidal chemistry of clays. The characteristic color changes of the gumbotil are those imparted to it by the colloidal clays, perhaps by the kaolin contained in it, the color of the colloidal material being sufficiently strong to mask the reddish yellow color of any oxidized iron which may be present. This doubtless is responsible for the belief held by some that the iron in the gumbotil is deoxidized or reduced, a condition which could hardly be possible in the presence of the oxygenated soil solution.

The chemical analyses of the gumbotils from different drifts and localities show, with respect to certain constituents, a striking similarity. This is especially true for the iron and the silica and, as we might expect, for the calcium. Slight

<sup>1</sup> Note: The writer is well aware of the extremely slow diffusion speeds of colloids. To transport appreciable quantities of such material would require long periods of time. These we have when we count time by geological periods.

fluctuations may be expected due to differences in the original rock materials, to the amount of rain-fall, or to leaching from above. It may be concluded, therefore, that all gumbotils have a common origin, viz., "the chemical modification by weathering of the glacial till."

Furthermore, the chemical analyses, as arranged in Table V, show a slightly less striking similarity between the gumbotil and the yellow oxidized and leached clay just below. Naturally one should expect to find a slightly greater concentration of the diffusible material in the leached zone. One should expect also to find a slight variation in the proportion of any one constituent between the top and the bottom of any single zone. Each level in any single stratum is still slightly unleached with respect to another level close to and above it.

The proportions of most of the constituents present in the oxidized-leached and gumbotil strata differ in most cases by only a few tenths of one percent. When greater deviations than this occur it can be shown by field observations that one or more of the upper strata have been removed before the leaching process was completed. The distinguishing features between these two strata are, therefore, due primarily to differences in the physical properties, and these properties are chiefly the colloidal properties of the clay itself. It is possible that two forms of the same material are here being dealt with, namely, the gumbotil, a highly colloidalized form, and the oxidized-leached material, the non-colloidalized form, which in the presence of certain electrolytes is incapable of assuming certain colloidal properties.

#### **Some Colloidal Properties of These Glacial Clays**

In what has preceded we have attempted to give a chemical explanation of the origin of the gumbotil. The theory proposed has been substantiated by the results of chemical analyses. According to this theory we should expect to find a more or less pronounced increase in the colloidality of the clay of any drift sheet as we pass upward from the lower strata.

To test this point Mr. Miller has made a rather extensive study of certain colloidal properties.

Since the properties of colloids are primarily surface properties any process which would determine the extent of surface development may be considered a measure of the colloidal content of the material. Keppler<sup>1</sup> has found that the hygroscopicity of clays varies in the same order as their plasticity. Ashley<sup>2</sup> states that when clays are classified according to their colloidal content they are also classified according to their plasticity. He has also studied the adsorptive power of clays for certain dyes and he has found that the adsorption of dyes by clays furnishes a means of measuring the relative specific surface of the clays.

We have used the measurements of hygroscopicity and adsorptive power for dyes as a means of determining the relative surface development of the various strata of Pleistocene clays produced by the weathering and leaching process.

The clay samples used throughout this work were from the same original samples as those used for the analyses above. Unfortunately some of the original samples were entirely used up in the previous work, thus leaving a lack of continuity in the data from some localities. It was thought better however to work with the incomplete set of samples rather than to obtain fresh samples of the missing strata upon which no chemical analyses had been made.

#### **Preparation of the Clay Samples**

In order to reduce the clays to a condition of uniform fineness and homogeneity about one pound of each clay was stirred into a large volume of water; the lumps were broken up by gently rubbing between the fingers and the whole mass was then washed through a 200-mesh sieve. For all clays used only a very small amount of each sample failed to pass through the sieve during this treatment. An excess of 1 N hydrochloric acid was then added to destroy any carbonates

<sup>1</sup> Sprechsaal, 46, 445 (1912).

<sup>2</sup> Bull. U. S. Geol. Survey, No. 388.

which might be present. After stirring vigorously for some time the clay suspension was allowed to stand for twenty-four hours, during which sedimentation became complete. The supernatant liquid was then removed as completely as possible by means of a siphon filter, more water was added, the clay was vigorously stirred and then allowed to stand for another twenty-four hours, when the liquid was siphoned as before. This procedure was continued until the filtrate gave only a very slight opalescence when tested for chlorides. At this point the spontaneous dispersion of the clay made it impossible to wash further without the loss of some suspended colloidal material. The clay was then filtered with the aid of suction through a hardened filter, the small portions of the material which passed through in the first filtrates being refiltered through the mass until the filtrate became clear. The clay was then sucked as dry as possible and the drying completed in an electric oven at  $110^{\circ}$ . The dried material was carefully reduced to a fine powder without rubbing and then carefully mixed on a mixing cloth to insure homogeneity.

#### Hygroscopicity Measurements

As here used hygroscopicity is a measure of the power of the clay to absorb water from the atmosphere. Three five-gram samples of each clay were accurately weighed into tared glass-stoppered weighing bottles and heated at  $110^{\circ}$  until successive weighings of each sample checked to  $\pm 0.0015$  gram. This corresponds to an error of about  $\pm 0.03$  percent on the basis of the weight of clay taken, a closer check being impossible since the hygroscopic tendency of the clays varied greatly from day to day with changes in the humidity of the atmosphere. The weighed samples were then placed in the vapor from a large volume of 10 percent sulphuric acid contained in a large sealed jar immersed in a large Freas water-thermostat and kept constantly at  $25^{\circ} \pm 0.005$ . The dilute sulphuric acid was used since its lower vapor pressure prevents the formation of droplets on the inner walls of the vessels containing the clay. The sample was then allowed to take up water va-



por until the change in the weight of the sample between successive readings taken on every second day became negligibly small.

The results of the hygroscopic determinations are given in Table VI. In the first column are the various drift strata arranged in the order of their occurrence in the drift. The remaining columns represent the hygroscopic water for the various samples taken from localities A, B, C, etc., each expressed in percentage by weight of the dried clay.

TABLE VI  
The Hygroscopicity of Certain Pleistocene Clays

Locality	A	B	C	D	E
Gumbotil	11.7	.....	11.6	13.05	12.33
Oxidized-leached	7.6	10.63	....	11.10	.....
Oxidized-unleached	....	9.05	8.8	9.86	.....
Unoxidized-unleached	....	6.63	....	.....	.....

The blank spaces occurring at the bottom of the vertical columns indicate that for these localities these strata were not exposed. When the blank space occurs at the top, as in B, that stratum has been entirely eroded away. The remaining samples in E were entirely used in the former research.

A survey of the data obtained for any locality shows a gradual decrease in the hygroscopicity of the clays as we pass from upper to lower strata. This would indicate for the gumbotil, as predicted, a greater surface development, i. e., a greater specific surface. A, B and C represent three widely separated localities in the Kansan. The gumbotils at A and C show nearly identical hygroscopic powers. These values are slightly less than the corresponding values for the Nebraskan (D) and the Illinoian gumbotil (E). The high hygroscopicity of the oxidized-leached stratum (B) is to be accounted for by the fact that the upper stratum has been removed and colloidalization has proceeded even after erosion has taken place. The samples of the oxidized-unleached material from different localities exhibit very similar hygroscopic properties.



**Total Water Capacity**

The total water capacity as here used is the number of grams of water which when added to one gram of clay is just sufficient to cause it to flow. Ten-gram samples of each clay were placed in large flat tared weighing-bottles, each containing a small glass stirring rod. Each sample was then heated to constant weight at 110°. Water was then added drop by drop from a burette, with careful stirring of the clay, until a furrow made by the glass rod immediately filled with clay and water, i. e., until the clay ran. The bottle was tightly stopped wiped clean, then placed in the balance case for a time and finally weighed. A part of the water was allowed to evaporate from the clay and the former procedure was repeated until three successive readings did not differ by more than  $\pm 0.04$  percent. This corresponds to an accuracy of one small drop of water, or a mean variation of about 0.4 to 0.8 percent on the basis of the water taken up. The values given in Table VII represent the amounts of water taken up in percentage by weight of the dried clay. Each value is the mean of three determinations of the total water capacity made upon one single sample of clay.

TABLE VII  
The Total Water Capacity of Pleistocene Clays

Locality	A	B	C	D	E
Gumbotil	73.9	....	65.0	79.3	70.5
Oxidized-leached	36.3	68.9	....	64.4	....
Oxidized-unleached	....	63.2	51.2	44.1	....
Unoxidized-unleached	....	51.5	....	....	....

**The Free Water Capacity**

Cameron<sup>1</sup> defines "free" water as the water in the soil which is not held adsorbed upon the surface of the soil particles. It is the excess water in the soil above that which is just necessary to produce optimum swelling. In this work the free water capacity is taken as the difference between the hygroscopic water capacity and the total water capacity. The free water

<sup>1</sup> Jour. Phys. Chem., 14, 340 (1910).

capacity of the different clays expressed in percentage by weight of the dried clay are given in Table VIII.

TABLE VIII  
The Free-Water Capacity of Pleistocene Clays

Locality	A	B	C	D	E
Gumbotil	62.2	....	53.4	66.3	58.2
Oxidized-leached	46.5	58.3	....	53.3	....
Oxidized-unleached	....	42.2	54.4	34.2	....
Unoxidized-unleached	....	44.9	....	....	....

The free water capacity is a measure of the interstitial space in the clay rather than of the specific surface. The total water capacity is a measure of the film water plus the free water. The data of Table VII show that the gumbotil possesses the greatest power to take up water. Its high total water capacity probably accounts for the ease with which it slides in exposed cuts or on the hill sides. It may also account for the fertility of glacial soils, since when not eroded away, the stratum most capable of holding water is found close to the surface soil. The gumbotil has the property of taking up and retaining great quantities of water during the rainy seasons, thus forming during dry seasons a store house of moisture which by capillary flow keeps the surface soil moist and into which the longer roots of the plants penetrate directly.

It should be observed in passing that both the free water capacity and the total water of these clays decrease from the gumbotil downwards.

#### The Humic Acid Content of These Clays

The question as to whether the humic acids might be found in these strata, and if so the belief that they too should decrease in content as we pass downward from the surface lead us to determine the humic acid content of each clay. The method used was that prescribed by Wiley.<sup>1</sup> The actual quantities found did not in any case exceed a few milligrams

<sup>1</sup> "Principle and Practice of Agricultural Analysis," p. 331.

in a twenty-five gram sample of the clay. This would indicate that in these strata the humus material has been completely oxidized by the soil atmosphere.

#### **The Adsorption of Dyes by Glacial Clays**

On the basis of the leaching theory for the formation of the gumbotil the colloidal nature of the clays should decrease from the surface downward. These clays in their colloidal form are negatively charged. They should, therefore, show a pronounced adsorption power for positive dyes. On the other hand, we should expect but slight adsorption for negative dyes. To test this point we have studied the adsorption of the positive dyes, methylene blue and methyl violet, and of the negative dye, eosin. These were carefully purified by several crystallizations from the proper solvents.

Various solutions of the dyes of the desired concentration were carefully prepared in accurately calibrated flasks at 25°. Two exactly one-gram samples of each clay were weighed into separate 100-cc glass-stoppered bottles. To each pair of samples were added exactly 100 cc of one of the dye solutions. The bottles were then sealed with paraffin, placed in a shaker immersed in a large water thermostat and rotated for twenty-four hours at 25°. The bottles were then taken from the shaking apparatus and allowed to stand in the bath until the clay had completely settled. Accurately measured volumes of the supernatant dye solution were withdrawn from each bottle, accurately diluted to a convenient color intensity and the amount of dye in one cc determined colorimetrically by means of a Duboscq colorimeter. From the data obtained the amount of dye adsorbed by one gram of the clay is easily determined.

In order to obtain an idea of the relative adsorption powers of the different clays in any one drift sheet a duplicate series of adsorption experiments were made involving all of the various samples at our disposal. To each gram of clay we added 100 cc of a solution containing exactly one gram of dye per liter. The mean weights of dye adsorbed by one

gram of clay for the various strata and localities are collected in Tables IX and X.

TABLE IX

A Comparison of the Adsorption Power of the Various Clays for Methylene Blue

Locality	A	B	C	D	E
Gumbotil	0.09989	.....	0.09948	0.09994	0.09897
Oxidized-leached	0.04399	0.08672	.....	0.09991	.....
Oxidized-unleached	.....	0.06684	0.06761	0.05717	.....
Unoxidized-unleached	.....	0.06900	.....	.....	.....

TABLE X

A Comparison of the Adsorption Power of the Various Clays for Methyl Violet

Locality	A	B	C	D	E
Gumbotil	0.09957	.....	0.09937	0.09998	0.09673
Oxidized-leached	0.05643	0.09094	.....	0.09965	.....
Oxidized-unleached	.....	0.09275	0.09857	0.08080	.....
Unoxidized-unleached	.....	0.07926	.....	.....	.....

As was predicted, the adsorption of the negative eosin by all of the clays is relatively slight and therefore somewhat irregular. For this reason the data found will not be inserted.

A survey of the data presented in these two tables for the adsorption of methylene blue and methyl violet shows that the gumbotils exhibit practically the same adsorption powers, which indicates that the extent of surface development of this stratum from different drifts and localities is very similar.

Some geologists have considered the gumbotils to be mainly of fluvioglacial origin, some believe they are an aqueous deposit, and still others have considered them as related to the loess. These theories would not necessitate a similarity

in the gumbotils from different drifts or from different localities in the same drift. According to Kay and Pearce (loc. cit.), however, the gumbotils, being the residuum from the weathering and leaching of more or less similar igneous drift material, should be similar from whatever drifts or localities they are obtained. The data herein exhibited support the theory proposed.

*Physical Chemistry Laboratory  
The State University of Iowa*

## THE ACTION OF ULTRA-VIOLET LIGHT ON GELS\*

BY EDWARD O. HOLMES, JR. AND WALTER A. PATRICK

### Introduction

The present investigation was undertaken with the idea of explaining certain phenomena that have been observed in connection with the action of light upon gels. It is known that exposure to light is sufficient to bring about marked changes in the properties of many gels; as examples: the hardening of gelatine and the embrittling of celluloid under the influence of light may be cited. It occurred to us that possibly the explanation of these phenomena was, in all cases, due to the loss of solvent and not to a specific chemical reaction that was brought about by the light. In other words, it was our belief that the action of the light simply effected a change that produced a loss of associated solvent, and it was due to the loss of the latter that the change in the properties was brought about.

### Historical

The mechanism of this loss of solvent as produced by the action of light was suggested by experiments on the adsorption of sulphur dioxide by silica gel.<sup>1</sup> It was found that the presence of a small amount of air reduced the amount of sulphur dioxide adsorbed by the gel. This point is best made clear by reference to the adsorption isotherms which are here reproduced.

In Figure 1<sup>2</sup> Curves (A) and (B) show the adsorption of sulphur dioxide in the presence of small amounts of air while those in Figure 2 indicate the adsorption in the absence of air. It is to be noted that the curves in Figure 2 are reversible; that is, the removal of sulphur dioxide follows the same path as the adsorption. In the case of the removal of

\* Contribution from the Chemical Laboratory of Johns Hopkins University

<sup>1</sup> MacGavack and Patrick: Jour. Am. Chem. Soc., May, 1920.

<sup>2</sup> Ibid.

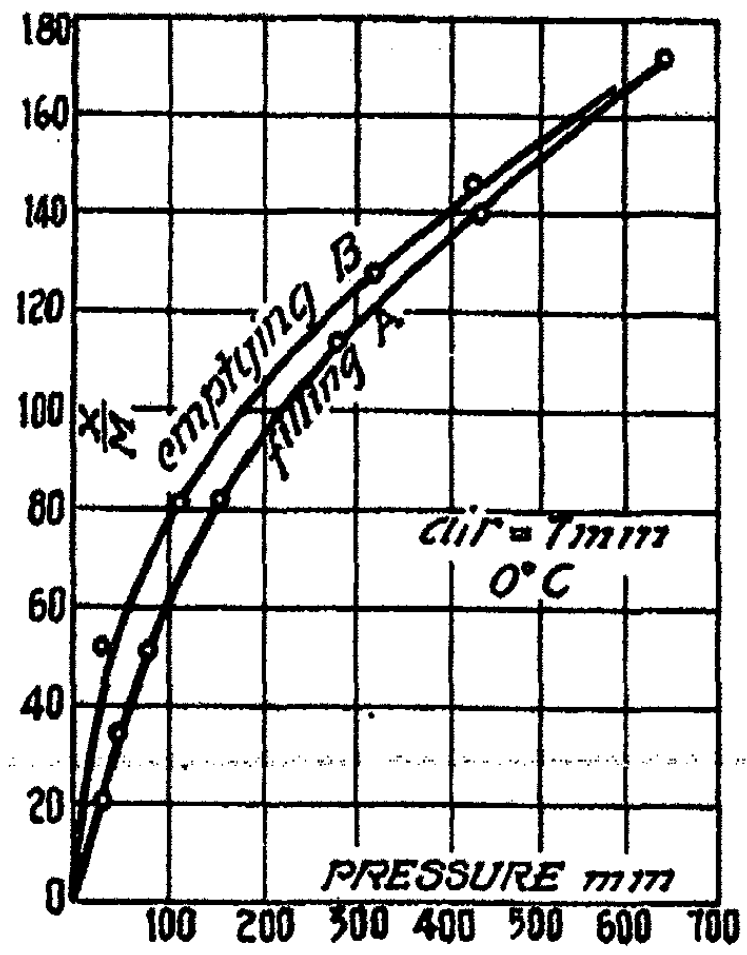


Fig. 1

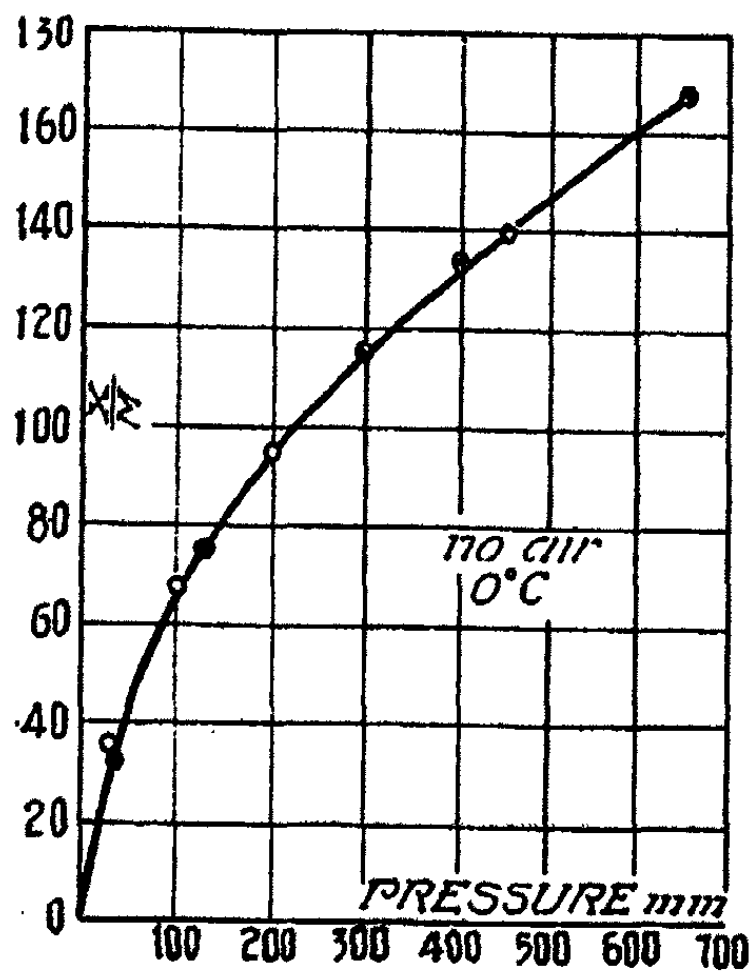


Fig. 2

sulphur dioxide after adsorption in the presence of air (Curve B in Figure 1) the path coincides with that of the reversible curves. From these curves it is easily seen that the adsorbent under the same partial pressure of sulphur dioxide will retain more of the latter in the absence of air.

This effect has been explained by the assumption that the presence of permanent gases prevents complete wetting of the pores by the adsorbed vapors. In order to test this theory it was thought that gels containing liquids that could be decomposed by ultra-violet light with the formation of permanent gases should show a loss of liquid when exposed to the light.

With the foregoing in mind the purpose of the following research and the method of attack may be outlined more clearly. We first attempted to prove that ultra-violet light caused a loss of solvent from those gels that contained liquids decomposable by this light; that furthermore, this loss of solvent was not simply the results of the decomposition of the solvent itself but that the production of the permanent gases in the pores of the gels caused the solvent to escape. Upon proof of the above we then proposed to extend the study to other organic gels and see if the same explanation was sufficient to account for the observed effects.

#### **Description of Apparatus**

The principle of the apparatus is simply that of a tensi-meter: namely, a means of reading the difference in pressure between two bulbs containing portions of the same sample of gel, one of which is being exposed to the ultra-violet light, the other being shielded from it.

In order to keep the temperature of the two bulbs the same, both bulbs were immersed in a water bath which was constantly stirred by air. The ultra-violet light was generated by an iron arc, passed thru a quartz window in the side of the water bath and into the quartz reaction flask where it hit the gel. The compensation bulb was of glass and was protected from the light by a metal screen. Fig. 3 shows an iron arc



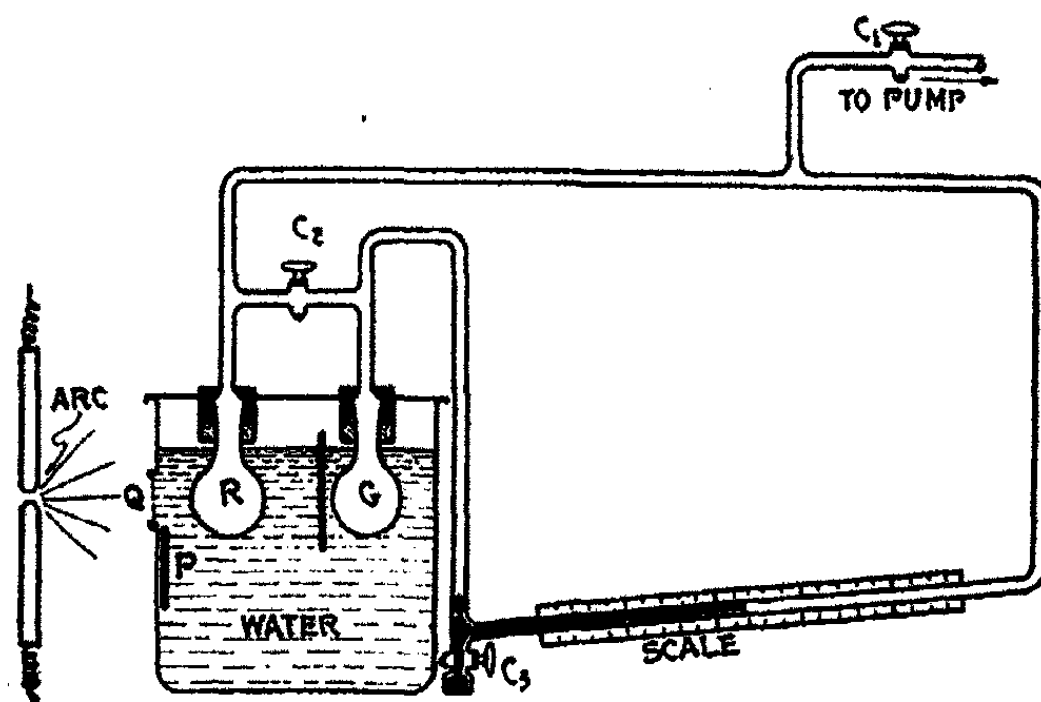


Fig. 3

giving our ultra-violet light, which passes thru the quartz window (Q) in the bath. The light traverses the quartz bulb (R) and strikes the gel contained therein. A metal plate protects the bulb (G) from any scattered rays. This bulb (G) is the same size as the bulb (R) and contains the same amount of the same sample of gel as is placed in bulb (R)—functioning merely as a compensating bulb.

The two bulbs are connected with a manometer having a long, gently-sloping straight arm which makes the manometer very sensitive. Behind this arm is a scale, the movement of the mercury along one division of which represents  $\frac{1}{100}$  mm. The two arms of the manometer are connected by a tube which contains a mercury sealed stopcock ( $C_2$ ).

The whole system is connected to a barometer column, a mercury pump and an oil pump thru stopcock ( $C_1$ ). The cock ( $C_3$ ) at the bottom of the manometer is placed there to facilitate replacing the mercury and cleaning the arms in case the mercury be attacked by the gases liberated by the action of the light on the gel.

#### Description of Runs

The gel was originally made up for use in gas masks and contained about nine percent of water. This was partially

replaced by immersing the gel four times in fresh portions of the desired liquid during which the water is replaced by the liquid used to about fifty percent. This gel is now dried in an air bath until it has no appreciable vapor pressure.

Each bulb was filled with the same quantity of dry gel. After attaching the bulbs to the apparatus thru a mercury-sealed joint, the whole was evacuated, the stopcocks being opened. When the apparatus was completely evacuated these cocks were closed and the system allowed to stand to be sure that no vapors escaped from the gel. If any increase in pressure in the system was observed, the whole was re-exhausted and allowed to stand once again. It was necessary to have the vapor pressure of the gel in the two bulbs the same and below one millimeter to avoid any "air effect" which is described later.

When the manometer had not moved after long standing, which showed that the gel in each bulb was in equilibrium with that in the other and that the apparatus did not leak, the arc was started and the readings of the mercury column in the long arm of the manometer taken at certain intervals.

#### Preliminary Runs on Liquids and Air

It became necessary to know what effect any air left in the bulbs would have upon the readings; so that a run was made in which the bulbs contained nothing but forty millimeters air pressure. The arc was started and the curve rose immediately, giving the air curve No. 1 in Fig. 4. When the arc was stopped, the pressure fell rapidly to zero. This "air

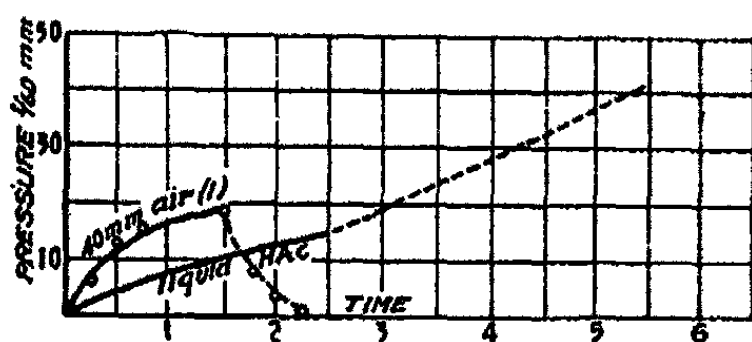


Fig. 4

Curves for Liquid Acetic Acid and Air

effect" was regarded as purely thermal and showed the necessity of excluding air from all runs.

A great many organic liquids can be decomposed by ultra-violet light; but two were chosen to impregnate the gel which were easily decomposed and readily attainable: namely, acetone and acetic acid.

In order to obtain some data as to the rate of decomposition of these liquids, a run was made by filling both bulbs with glacial acetic acid and exposing in the usual manner. Curve No. 2 in Fig. 4 was obtained. It should be noticed that even after the light is turned off the curve continues to rise for some time. This is due to the lag caused by the time it takes the gaseous decomposition products formed in the liquid to migrate to the vapor space above and hence to the manometer. On account of this lag, it was decided to find curves for the rate of decomposition of the vapors of the liquids to be used.

#### Rate of Decomposition of the Vapor

This was found by filling the bulbs about one-quarter full of the liquids to be used and then boiling under reduced pressure until only a small amount remained in the bottom, so as to expel all the air. The arc was started and readings taken.

In Fig. 5, Curve No. 1 shows the results obtained with acetic acid. The curve is a straight line as would be supposed, flattening out when the light is shut off.

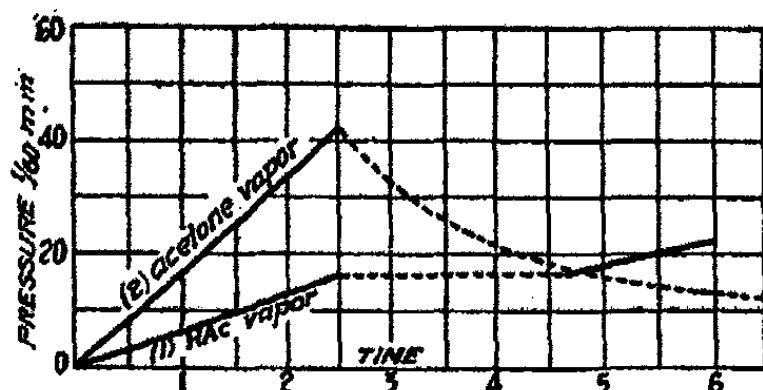


Fig. 5  
Curves for Acetone and Acetic Acid Vapor

Curve No. 2 shows the results with acetone. This curve has a greater slope than that of the acetic acid curve and drops when the arc is shut off. The difference in slope is due to the fact that at the temperature used, acetone has a vapor pressure sixteen times that of acetic acid. However, the slope of the acetone curve is only four and three-tenths times that of the acetic acid curve, indicating that acetic acid is more readily decomposed than acetone. On the other hand, this is contrary to the literature on the subject and is accounted for by the fact that on photo-chemical decomposition, acetic acid gives carbon monoxide, carbon dioxide and hydrogen,—three molecules; whereas acetone gives only carbon monoxide and ethane, or a smaller number of molecules.

#### **Runs of Impregnated Gels**

This chapter is divided into two parts: the first titled "Total Illumination" and the second, "Partial Illumination." In the first part, the whole of the quartz reaction flask was exposed to the light, which hits the gel as well as the vapors above the gel. However, it became necessary in order to prove certain points to make similar runs exposing sometimes the solid gel, sometimes the vapor above, or even as before, both; so that this second part was headed "Partial Illumination."

In the following runs, we endeavored to keep a constant source of light, but this could only be done approximately, as we used a powerful source of ultra-violet light,—an iron arc taking eight amperes at two hundred and twenty volts. For a single run, it was much easier to keep the arc constant than to have it the same in two runs; hence the slopes of the curves are not strictly comparable to one another as the amount of decomposition depends on the amount of light absorbed, and this, other things being the same, on the intensity.

The temperature of the bath gradually rose during the run due to the heat absorbed from the arc. However, as both bulbs were kept at the same temperature, they compensated each other for any change in vapor pressure of the gel.

**(A) Total Illumination  
Water Gel**

In order to show that if any increase in vapor pressure resulted on exposure of an impregnated gel it was not due to the water in the gel, a sample containing water (9.73%) was exposed in the apparatus. Curve No. 1 in Fig. 6 shows the

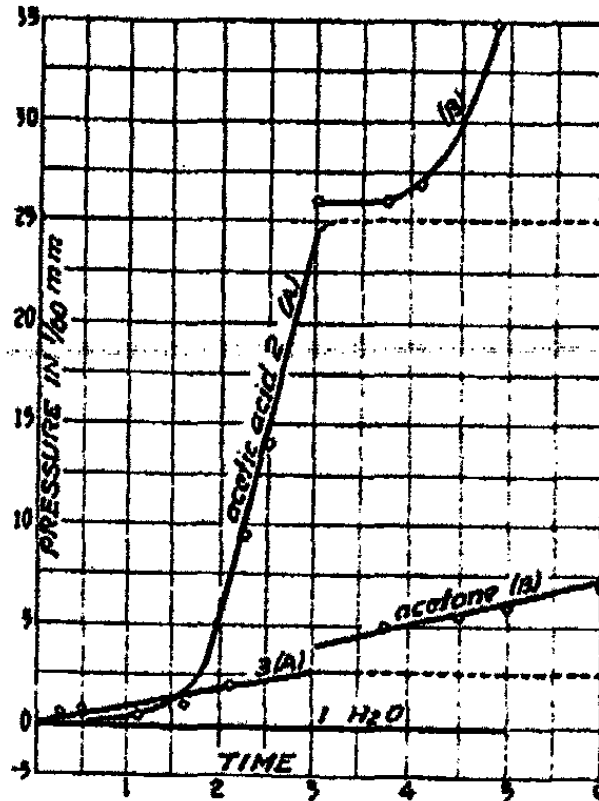


Fig. 6

flat line obtained, proving that there was no water vapor given off by the gel. This result was anticipated inasmuch as the light was of wave length not short enough to decompose water, and therefore no gas could be generated which would prevent the absorbed water from wetting the surface of the pore.

**Acetic Acid Gel**

A gel containing twenty-one percent volatile matter, about half of which was acetic acid, was run and quite different results obtained, as is shown in Curve No. 2, Fig. 6. The Curve consists of two parts (A) and (B). Part (A) was run one day and (B) the following, allowing the apparatus to stand overnight. For the first two hours of exposure, the pressure increases slowly, the rate becoming constant during

the next hour. The arc was shut off and the curve gradually flattened out in the manner of an exponential curve. At this point, the apparatus was allowed to stand undisturbed overnight.

That part of the curve showing a gradual increase was the result of two factors: firstly, the arc was gradually increasing in intensity; and secondly, there was the natural lag of the apparatus—namely the time necessary for the molecules of liquid liberated to diffuse to the manometer. The latter of these explains the rise in the curve after the light was shut off.

The next morning the run was continued, forming part (B) of the curve. However, this time the arc was brought to full intensity before the gel was exposed, which accounts for the much quicker rise in pressure.

The gel filled about two-thirds of the reaction bulb and the vapors the remaining third. Hence the ultra-violet light played upon both the gel and the vapors above it.

#### Acetone Gel

In place of the acetic gel, a gel containing about seventeen percent of volatile matter, half of which was acetone and the other water was introduced into the apparatus. This run was carried out in a similar manner to the previous one,—namely in two parts, (A) and (B). The pressure rose very slowly as can be seen from Curve No. 3 in Fig. 6, the curve becoming flat when the arc was shut off. The next morning the curve was continued and gave another straight line,—part (B).

These three curves show that when a gel impregnated with some organic substance which can be decomposed by ultra-violet light is exposed to the same, some sort of vapor is set free which causes the manometer to show a reading. However, as yet, there is no evidence as to whether this vapor consists of the solvent itself or the gases formed by the photochemical decomposition of the solvent.

#### (B) Partial Illumination

In the following runs, a lead screen (seen on the diagram) was added to the apparatus, and if the bulb was half-

filled with gel, by moving the screen, the gel itself, the vapors above, or both could be illuminated as desired.

**Acetic Acid Gel**

The gel used in this case was from the same large sample as that used in the former run under this title, only re-dried at a higher temperature and for a much longer time, thereby reducing the content of total volatiles to nine and one-half percent. However, recent work has shown that a larger fraction of this residual solvent was acetic acid than that in the gel used in the preceding run with acetic acid. The bulb was only half-filled with the gel.

The run consists of three parts (A), (B), and (C) which followed one another consecutively without the apparatus being disturbed, save the lead window. The results of this run are plotted in the form of a discontinuous curve in Fig. 7.

When the system had come to equilibrium as usual, the space above the gel was exposed to the light for one and one-half hours with no result; then the screen was removed and

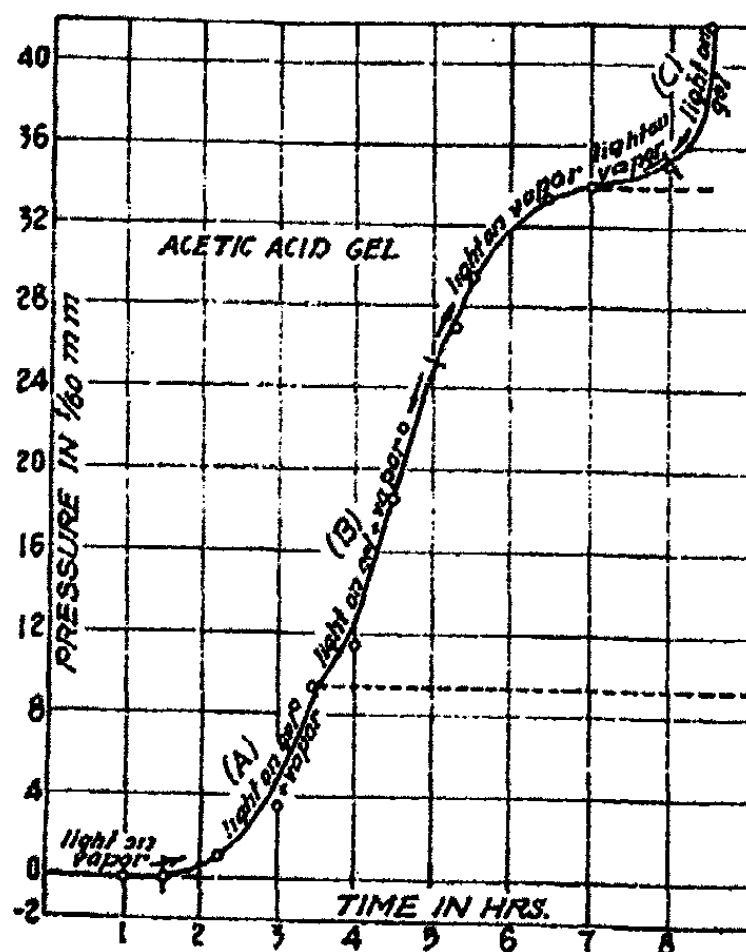


Fig. 7

the gel also exposed. The rate of decomposition grew to a constant value, as was the case in the preceding run. When the arc was shut off, the curve flattened out immediately.

The following day the arc was started again, the gel and the space above it being exposed until the rate of increase of pressure reached a constant value. At this point, the lead screen was placed in such a position that the light fell on the vapor only. The pressure continued to rise for some time; the rate falling off and finally becoming zero. Then the arc was turned off and the pressure remained constant overnight.

With the lead window still allowing the vapors only to be hit by the light, the arc was lighted and a small rate of increase observed. However, when the screen was lowered allowing the gel itself to be hit by the light, the pressure rose rapidly and the curve regained its usual slope as was obtained in the first two parts of this run when the light hit the gel itself.

The important feature of this curve (the upper half of part B) is that after the gel and the vapor above it have been exposed for some time and the increase in pressure has become constant, when the lead screen is so placed that only the vapor is hit by the light, the pressure still continues to rise at a gradually decreasing rate. This has only one meaning which is that there must be some substance present in the vapors above the gel that can be decomposed by the light. Obviously this substance cannot be the gaseous decomposition products from the pores of the gel and therefore must be acetic acid itself which has been liberated intact. As this acetic acid vapor is gradually broken up by the light the curve flattens out, there remaining in the gaseous phase only the decomposition products consisting chiefly of carbon monoxide, carbon dioxide and hydrogen.

#### Acetone Gel

In order to check this point, a similar run was made with the acetone gel used in the former run, and the results of this run are shown in Fig. 8.



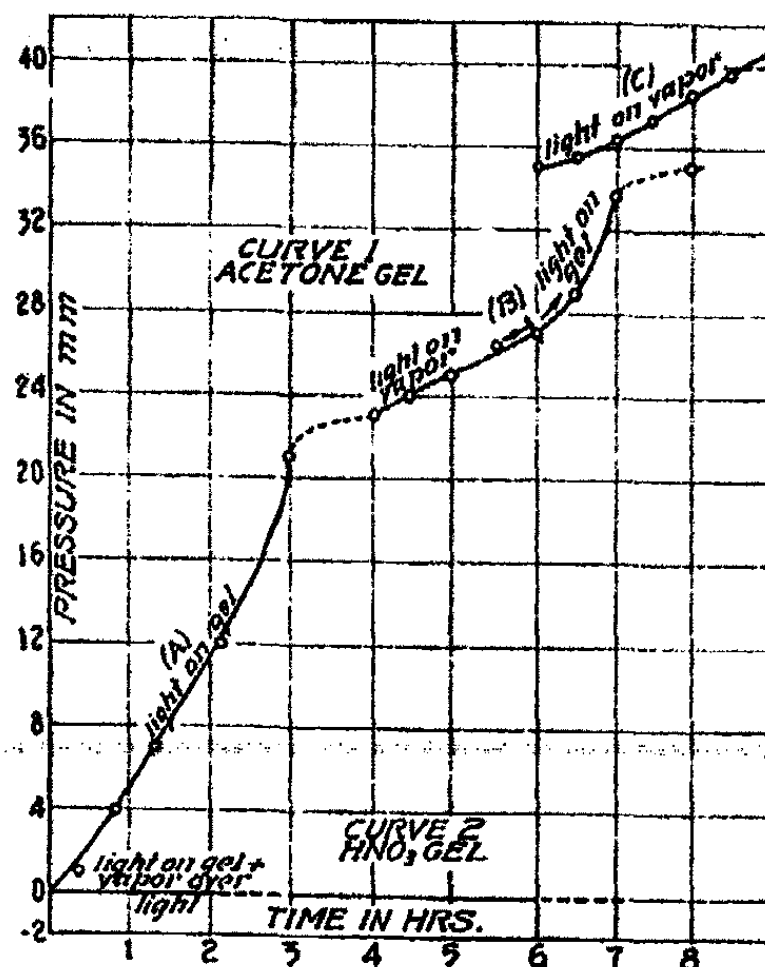


Fig. 8

(Ordinates are  $\frac{1}{100}$  mm and not mm.)

The curve consists of three parts (A), (B), and (C). The light was allowed to hit the gel only until a constant rate of decomposition was attained. When the arc was turned off, the curve rose for a short time and then flattened. This completed part (A) of the acetone curve. The fact that the curve flattens proves that the gases liberated by the action of the light are not reabsorbed by the gel.

Now the light was allowed to strike the vapor above the gel only, which produced the lower part of section (B). Then the position of the screen was so shifted that the light struck the gel only, and the same steep slope was obtained as under similar conditions in part (A). The light was now turned off and the curve flattened as usual, completing part (B) of the curve.

The next morning the run was resumed with the light on the vapor above the gel and another straight line was obtained which constitutes part (C) of the curve.

We have now proven that our results are perfectly reproducible, and that the organic liquid with which the gel is impregnated is set free intact when ultra-violet light plays upon the gel, and also that neither it nor the gaseous decomposition products are reabsorbed by the gel.

#### Nitric Acid Gel

It was now thought advisable to impregnate silica gel with an inorganic liquid which would be decomposed by the light. For this purpose some original gel was exposed to the fumes of concentrated nitric acid in a vacuum desiccator for several days. The gel was dried until it had no appreciable vapor pressure and was found on analysis to contain five per cent nitric acid.

The curve obtained, No. 2 in Fig. 8, consists of a straight line parallel to the abscissa,—in other words, no pressure at all was generated.

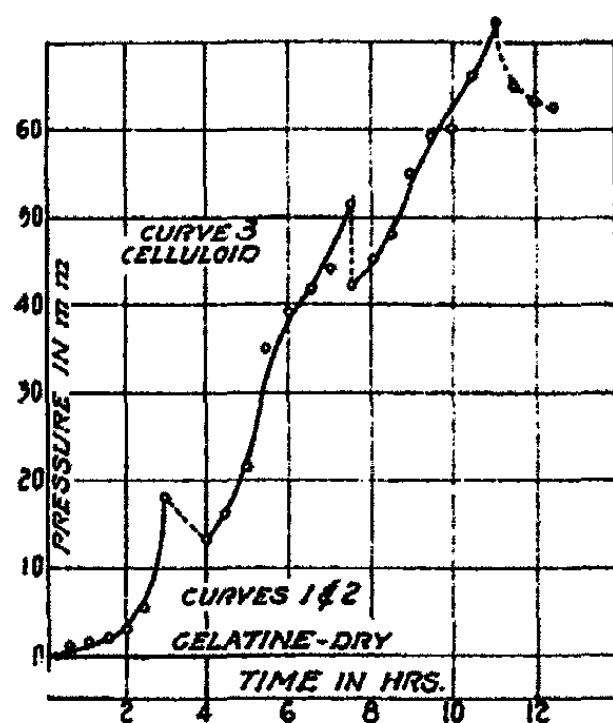


Fig. 9

(Ordinates are  $\frac{1}{100}$  mm and not mm.)

At first, this result may seem strange as nitric acid is easily decomposed by light. However, when it is considered that silica gel adsorbs oxides of nitrogen very strongly, which are the photo-chemical decomposition products of the nitric

acid, it is not remarkable at all that nitric acid gels show no pressure under the influence of the ultra-violet light. As fast as the nitric acid is decomposed the products are adsorbed and thus there is no gas which will prevent wetting of the surface of the pores by the nitric acid solution.

### Celluloid

As the embrittling and the discoloring of celluloid by light furnished the original idea of the problem, it was now an opportune time to try the effect of ultra-violet light on celluloid itself. Inasmuch as the gel structure as well as the solvent are both easily decomposed by the light, celluloid could not be used for a study of the mechanism of the process but a gel having a stable structure was necessary—silica gel.

A run on celluloid was made by cutting the celluloid up into small pieces and dropping them in the necks of the bulbs, until each bulb contained the same amount and was approximately full.

The celluloid in the quartz bulb was exposed to the light and Curve No. 3 in Fig. 10 obtained. The rate of decom-

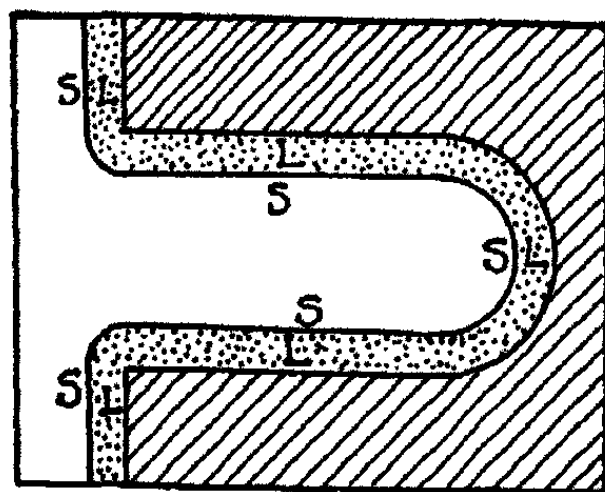


Fig. 10

position increased to a constant value. The products are undoubtedly gases from the decomposition of the nitrocellulose and its solvent, and also the undecomposed solvent itself.

When the arc is shut off, the curve drops rapidly, finally coming to a constant reading.

This drop can be the result of two things; the thermal effect, or more likely the re-adsorption of the oxides of nitrogen. The curve is made up of the results of three similar runs made at different times, the apparatus being undisturbed in between. The second and third sections show a peculiar twist which cannot be accounted for in light of the present knowledge on the subject.

**Mechanism of the Liberation of the Solvent from the Gel**

Let us suppose a number of tiny pores or cells to be in a completely evacuated space. For simplicity, consider one cell as pictured in figure No. 10. Now introduce into this space a gas such as sulphur dioxide which can be adsorbed. Immediately, some will enter the pores or cells and be condensed on the surface forming a liquid film (L)—the phenomena of adsorption. The surface (S) of this film will tend to become smaller due to the force of surface tension. This tension is very great and puts the liquid under a negative pressure which reduces its vapor pressure to a very small value.

As the pressure in the surrounding space is above that of the liquid in the pores, more gas will condense in the liquid surface and tend to make this smaller, which decreases the negative pressure and in turn causes an increase in the vapor pressure of the liquid film. Obviously, the process will continue until the vapor pressure of the film is equal to that of the surrounding space.

This same state can be reached from the other direction,—that is by filling the pores with a liquid and evacuating the space around, which causes the liquid to evaporate from the pores and thereby reduce its vapor pressure. In this manner the gels used in the previously described runs were brought to a condition of equilibrium with the apparatus.

Hence by either of these two processes, we have a large number of pores partly filled with the adsorbed substance under great negative pressure and therefore having a very low vapor pressure. The negative pressure on the film is caused by the surface tension acting along the sides of the pores and around their circumference.

If by any means, this force of surface tension is reduced the vapor pressure of the liquid film becomes greater than that of the surrounding space and some of the liquid evaporates in order that equilibrium shall be restored. Now ultra-violet light does reduce this force by decomposing the liquid of the

film with the formation of gas bubbles, which prevent the film from completely wetting the surface of the pore, resulting in a decrease in negative pressure and subsequently an increase in the vapor pressure of the adsorbed substance. Inasmuch as the vapor pressure of the film is now above that of the surrounding space some of the liquid evaporates.

This same mechanism will explain the liberation of gases by celluloid under the influence of ultra-violet light only here we have the complication that the light decomposes the structure of the gel itself (cellulose nitrate) as well as the solvent in the pores. Therefore the reason for celluloid turning brown and becoming brittle under the action of the ultra-violet light of the sun is quite evident.

Thus in the case of sulphur dioxide where there is residual air present, as already cited, the air prevents the adsorbed sulphur dioxide from completely wetting the surface (for small pressures) and therefore the adsorbed film has a higher vapor pressure than if it completely wet the surface. This is a case of what might be called "mutual adsorption." Recent work of Patrick<sup>1</sup> and Ryerson on the adsorption of bromine by silica gel in air shows that when the concentration reaches a certain point, the air no longer exerts an influence and is squeezed out or removed in some such way.

However, on emptying the pore, the air is swept out alone with the adsorbed substances, and so when equilibrium is obtained at any point on this curve, the surface can be completely wet,—the air having been removed from the pore. Hence the explanation of the irreversible curves obtained for the adsorption of sulphur dioxide when air is present, which was revealed by our work on the action of ultra-violet light on impregnated silica gel.

#### Summary

(1) Silica gel impregnated with certain organic liquids will, on exposure to ultra-violet light, give off gaseous prod-

---

<sup>1</sup> To be published.

ucts, provided the liquid can be decomposed photo-chemically into gases which are not adsorbed by the gel.

(2) The gaseous products consist of a mixture of the vapor of the organic liquid itself along with those gases resulting from the photo-chemical decomposition of the liquid.

(3) Celluloid acts in a similar way under the influence of ultra-violet light.

(4) The mechanism of the liberation of the adsorbed liquid is explained.

(5) These results show in a very striking way the manner in which gas bubbles in the pores affect adsorption, which accounts for the irreversibility of the sulphur dioxide isotherms obtained by MacGavack and Patrick.

(6) The embrittling of celluloid is also due to this effect.

781 / 38

## THE RATE OF FORMATION AND THE YIELD OF YEAST IN WORT

BY NORMAN A. CLARK

In 1892, while studying the effect of varying environment on the reproduction of yeast cells, Adrian J. Brown<sup>1</sup> noticed that "when any fermentable nutritive solution, such as malt wort or a solution of dextrose in yeast-water, is inoculated with a "high" fermentation yeast, and kept at a temperature favorable to yeast growth, the cells reproduce themselves rapidly for a time, and then their (rapid) reproduction ceases, and that the fermentation of the solution may still be carried on by the continued life of the cells already formed . . . and that, although different liquids may cause yeast to increase to a differing extent, yet the same liquid, providing all the conditions, such as agitation, etc., are kept constant, appears to cause an increase in the number of cells to about the same maximum, no matter how the amount of yeast added to start the fermentation may vary." When the number of cells added to start the fermentation was considerably greater than this maximum, "not the slightest sign of increase, or growth in size, of the cells could be detected at any time, although the fermentation of the liquid in which they were, proceeded with great rapidity." When the amount of yeast added was not very largely in excess of the maximum the liquid was capable of developing, and the cells in the flask were examined with the microscope at the commencement of fermentation, "some of them did show an inclination to increase by budding, but the buds only developed to such a small extent that it was impossible to consider them as complete cells when enumerating the individuals present at the end of the experiment."

Suitable experiments shewed that this cessation of reproduction was not due to lack of food (sugar), nor to the toxic effect of the products of fermentation (carbond ioxide, alcohol,

<sup>1</sup> Jour. Chem. Soc., 61, 369 (1892); 65, 911 (1894).

etc.) in the quantities in which they were present when active reproduction ceased. A subsequent investigation,<sup>1</sup> in which carbon dioxide, hydrogen, and air, respectively, were passed through the wort during fermentation, convinced the author that the cessation of reproduction was due to exhaustion of the oxygen dissolved in the wort, and that in the presence of a continuous air supply, the number of cells produced depends only on the food available.

In 1913, A. Slator, working with a Burton yeast, shewed that until the yeast crop reached about ten million cells per cubic centimeter (a "count" of 40), the rate of increase at any moment is proportional to the number of cells then present; whence

$$\log_{10} C/C_0 = k(t-t_0).$$

"Growth after this time is measurably retarded."

In the same year, T. Carlson<sup>2</sup> deduced a more complicated relation between  $C$  and  $t$  from the assumption that, besides being proportional to the number of cells present, the rate is also proportional to the square of the concentration of the foodstuff remaining available in the wort. Carlson's formula thus provides for a decrease in the rate of reproduction as the fermentation advances, and is therefore better fitted to represent the experimental results over a long range than is the simple logarithmic expression. In the absence of any direct evidence in support of the fundamental assumption, however, the expression must be regarded only as a more or less convenient interpolation formula. Such evidence—for or against—would be furnished by experiments on the rate of reproduction in diluted wort; there is no record of any such experiments, but determinations of the total yield of yeast when water is added to a constant quantity of wort shewed that addition of water increases the crop. This result is ascribed by Carlson to the dilution of the alcohol formed during the fermentation.

<sup>1</sup> Jour. Chem. Soc., 87, 1395 (1905).

<sup>2</sup> Biochem. Zeit., 57, 313 (1913).



In 1914 Horace T. Brown<sup>1</sup> determined the rate of reproduction of yeast when grown in mixtures of air-saturated wort with wort from which all air had been removed by boiling in an atmosphere of hydrogen. "The main facts which have been established experimentally, with regard to the reproduction of yeast cells in a nutrient liquid containing dissolved oxygen, and an excess of all the mineral and organic substances requisite for their full nutrition, may be summarized as follows:

"(1) When the available oxygen is limited to that initially contained in the liquid, the number of yeast cells per unit volume tends to attain a maximum which is independent, or nearly so, of the number of cells of seed-yeast per unit volume, but is conditioned in the first instance by the initial amount of this dissolved oxygen.

"(2) 'Within certain limits of oxygen supply' (up to about 60 or 65 percent of complete saturation of the liquid with atmospheric oxygen) the maximum reproduction is strictly proportional to the initial amount of this oxygen.

"(3) 'The rate of reproduction under these conditions is not logarithmic, but is a linear function of the time.' (The explanation offered is that "at each subdivision the oxygen charge of the mother-cell must be halved, consequently the time required for the next subdivision of the mother- and daughter-cell will be double that required for the previous subdivision.")

"(4) The dissolved oxygen does not remain as such in the liquid during the reproductive period, but is rapidly absorbed by the seed-yeast before cell-budding commences." Experiments in which yeast cells were suspended in air-saturated water showed that the absorption of oxygen progresses as a linear function of the time, and that with a "count" of 48 (12 million cells per cc), all the dissolved oxygen is absorbed in two and a half hours.

The explanation put forward by Adrian Brown for the limited yeast crop obtained by him when working under the

<sup>1</sup> "Annals of Botany," 28, 197 (1914).

ordinary conditions (top yeast, nutrient liquid fermenting in a flask with limited access of oxygen), viz: that reproduction is limited by the initial supply of oxygen, thus seems to be borne out by the subsequent work of Horace Brown. In some of Adrian Brown's experiments, however, air was bubbled through the liquid while the fermentation was taking place; with initial counts of 280 to 360, no increase in the number of cells was observed after 3 hours at 19° C, 3.25 hours at 23° C, 24 hours at 7° C, or 23 hours at 9° C. The "lack of oxygen" explanation seems inapplicable to cases such as these, and the experiments described in the present paper show that still another factor must be taken into consideration.

#### **Material, Apparatus and Methods**

The yeast used was a "bottom" yeast, and therefore probably less sensitive to oxygen than those experimented with by Slator, Carlson and the Browns; it was obtained from Fleischmann's yeast-cake by plating and growing in wort as described by Fulmer.<sup>1</sup> When used as seed, the cells were filtered from the wort, washed, and suspended in distilled water to a suitable count, and one cc of the suspension added to 49 cc of the culture medium. At intervals, one cc of the fermenting liquid was removed by a sterile pipette, and after diluting if necessary, a drop was examined in the haemocytometer; the number of cells over one "large" square ( $4 \times 10^{-6}$  cc), after multiplying by the dilution if any, being recorded as the "Count."

In the experiments on the influence of alcohol, the field was photographed and the counts made at leisure; this made it possible for a comparatively large number of fermentations to be carried out at one time. Most commercial microphotographic outfits are either expensive or shaky; both disadvantages were avoided by standing the microscope on the bottom shelf of a cupboard and sliding the plateholder ( $3\frac{1}{4} \times 4\frac{1}{4}$  glass plates) into position over a hole in the next shelf, a sleeve of black cloth hanging from the hole in the shelf down

<sup>1</sup> Jour. Phys. Chem., 25, 20 (1921).

over the eye-piece effectually cut out stray light, and when all was ready the cupboard door was closed and a 100 watt tungsten lamp turned on for four seconds. The developed negatives were used as lantern slides, the image being thrown on a sheet of paper lying on the writing table; each photograph shewed twelve of the large haemocytometer squares.

In the beginning, the fermentations were carried out in 250 cc Erlenmeyer flasks in the incubator at 25° C. The curves obtained, log C against  $t$ , while fairly straight for part of their course, were not all of the same slope, and when produced to  $t = 0$  usually did not pass through the point corresponding to the count at the moment of seeding. As calculated from the straight part of the curves, the constant  $k$  of the expression  $\log C = k.t + \text{const.}$  varied from 0.12 to 0.20; no relation could be discovered between the value of  $k$  and the amount of yeast used as seed. The maximum crop of yeast also varied, and was much increased by occasionally shaking the flasks.<sup>1</sup> The use of flasks was therefore abandoned, and all the results recorded in the present paper were obtained by use of the "rocker."

The rocker used was that described by Fraser,<sup>2</sup> but my tubes were of somewhat smaller diameter than his; in each experiment 50 cc of liquid was used; the temperature in all cases was 25° C.

#### Range of the "Logarithmic" Formula

In the experiments recorded in Table 1 the initial count was 1.0; that is, at the moment of seeding each cubic centimeter of the nutrient liquid contained 250,000 yeast cells. After "time" is recorded the number of hours elapsed between the moment of seeding and that at which the count was made, and after "log C" the common logarithm of the count.

<sup>1</sup> The following counts were obtained from flasks which remained in the incubator, undisturbed, from the time of seeding till counted:

Time	1	2	3	4	5	7	9	days of 24 hours.
Count	375	435	545	574	760	831	734.	

The maximum count obtained by A. Brown under similar circumstances, but using a top yeast, was about 450.

<sup>2</sup> Jour. Phys. Chem., 25, 1 (1921).

TABLE I  
(100% Wort)

Time	0	8.9	9.9	10.7	10.9	11.8	12.7	14.2	15.2	16.2
Log C	0	1.34	1.30	1.60	1.62	1.85	2.02	2.25	2.38	2.53
Time		17.5	19.1	20.2	21.2	22.2	23.2	24.0		
Log C		2.66	2.81	2.88	3.03	3.04	3.16	3.09		

When these results are plotted (Fig. 1, 100% wort) it is obvious that the formula  $\log C = 0.16 t$  represents the rate of reproduction while  $\log C$  varies from 0 to 2.6, i. e., while  $C$  varies from 1 to 400, in other words while the number of cells increases from 250,000 to 100,000,000 per cubic centimeter of the nutrient liquid. To test the formula for small seedings, a suspension of yeast in sterile water was made up with a count of  $C = 18$ ; this was diluted geometrically with water and used to inoculate two tubes, each being given nine cells per cc—a count of  $C = 36 \times 10^{-6}$ . After rocking about 40 hours, they were counted with the following results:

TABLE 2

Time	41.2	41.5	42.5	43.5	44.6	hours
Log C	—	240	—	475	—	(Tube I)
Log C	210	—	354	—	594	(Tube II)
$k$	0.164	0.164	0.164	0.164	0.162	

Similar experiments were carried out with initial seedings varying from 5 cells per cc ( $C = 20 \times 10^{-6}$ ) to eight million cells per cc ( $C = 32$ ), and the values of  $k$  were calculated as above from a number of counts varying from  $C = 50$  to  $C = 600$ ; the results are given in Table 3.

TABLE 3

Initial C	$20 \times 10^{-6}$	$36 \times 10^{-6}$	$176 \times 10^{-6}$	0.09	1.0
$k$	0.157	0.164	0.163	0.160	0.160
Initial C	2.5	4.4	14	21	32
$k$	0.160	0.160	0.160	0.160	0.160

To make  $k = 0.160$  for the first three experiments of the table, it must be assumed that the actual number of cells used for

seeding was 3.5 per cc instead of 5, 13 instead of 9, and 56 instead of 44 respectively; bearing in mind that it was a yeast suspension, not a solution, that was being diluted—in the first case over a million fold—this seems the natural assumption to make. Adopting the value  $k = 0.160$ , the number of cells in the culture is doubled every 1.88 hours, that is, in one hour and fifty three minutes.

Thus, under the conditions of our experiments, the rate of reproduction of a bottom yeast in wort is independent of the amount used for seeding; and, until the crop reaches one hundred million cells per cubic centimeter, the relation between count and time is given very closely by the "logarithmic formula"  $\log C/C_0 = 0.160 t$ .<sup>1</sup>

Slator, with a top yeast, found  $k = 0.104$  at 20° C until the crop reached ten million cells per cc; the initial values from Carlson's table IX recalculated, gives  $k = 0.20$  for his top yeast at 30° C.

#### The Artificial Medium

It has long been recognized that beer-wort is the best medium for the culture of yeast. A number of the artificial media commonly recommended, including those of Hansen, Laurent, Stern, Naegeli, and Williams (Fulmer's had not yet been published) were tried, each being made up in duplicate, (a) with cane sugar, and (b) with glucose; no marked difference was found between these two sugars. With an initial count  $C = 1.0$  the crop after 72 hours never reached  $C = 50$ , except in the case of Hansen's medium, which contains peptone; in wort, 24 hours after seeding  $C = 1200$ .<sup>2</sup>

The following recipe was used in what follows:

- (a) 100 cc water; 10 g potassium dihydrogen phosphate cryst.; 5 g magnesium sulphate cryst.; 20 g ammonium nitrate.

<sup>1</sup>  $C_0$  the count at the moment of seeding,  $C$  the count  $t$  hours later, log the common logarithm.

<sup>2</sup> Fulmer (Jour. Am. Chem. Soc., 43, 186 (1921)) obtained a count of 284 with his artificial medium; initial count  $C=1.0$ ; the experiments were carried out in Erlenmeyer flasks at 30° C.

(b) 100 cc water; 1.4 g calcium chloride hexahydrate.

If *a* and *b* are mixed and sterilized a precipitate is formed; they were therefore sterilized separately; 5 cc of each of them, 10 g of cane sugar, and enough water to make up to 100 cc constituted the "artificial medium" of the present paper. Actively budding "normal" yeast, filtered and well washed with water, reproduced in this medium yielding well shaped cells with a strong tendency to form clusters or bunches, which caused difficulty in the counting; it required about four hours to double the initial count, whether that were  $C = 1.0$  or  $C = 30$ , as compared with 1 hour 53 minutes in wort; after 8 hours the reproduction was very slow, and when the initial count was 1.0, the maximum crop was about  $C = 25$ .

**Rate and Yield in Wort diluted with the Artificial Medium**

Addition of a little wort made a great deal of difference; the results of Table 4 were obtained from media prepared by mixing wort and the artificial medium in various proportions; "wort 80%" means a solution made from 40 cc wort and 10 cc artificial; after mixing, the medium was sterilized with live steam for 30 minutes and seeded to a count

TABLE 4

80% Wort		50% Wort		30% Wort		10% Wort	
Hours	Log C	Hours	Log C	Hours	Log C	Hours	Log C
0	0	0	0	0	0	0	0
9.1	1.11	9.2	1.36	9.2	1.42	9.3	1.63
10.0	1.52	10.1	1.48	10.2	1.65	10.2	1.77
10.9	1.80	11.1	1.74	11.1	1.76	11.2	1.79
12.0	1.95	12.1	1.95	12.2	2.14	12.2	2.03
12.7	1.95	12.8	2.26	13.9	2.13	13.0	2.12
14.3	2.32	14.4	2.32	14.5	2.56	14.5	2.32
15.3	2.40	15.4	2.51	16.5	2.71	15.6	2.54
16.3	2.50	16.4	2.70	17.7	2.83	16.6	2.52
17.6	2.72	17.6	2.80	19.5	2.90	17.7	2.67
19.2	2.95	19.3	2.90	20.4	2.89	19.6	2.56
20.2	2.90	20.3	2.98	21.5	2.90	20.5	2.45
21.3	3.00	21.4	3.01	22.5	2.91	21.6	2.79
22.2	3.10	22.5	2.93	23.3	2.96	22.5	2.66
23.2	3.12	23.2	3.10	24.3	2.97	23.4	2.71
24.1	2.98	24.2	2.96	—	—	24.4	2.74

TABLE 4 (Continued)

5% Wort		1% Wort		0.06% Wort	
Hours	Log C	Hours	Log C	Hours	Log C
0	0	0	0	0	0
9.4	1.40	9.5	1.45	9.6	1.04
10.2	1.66	10.3	1.57	10.5	1.04
11.2	1.93	11.3	1.64	11.4	1.11
12.3	2.03	12.4	1.66	12.5	1.45
13.1	2.11	13.1	1.76	13.2	1.15
14.6	2.35	14.7	2.01	14.7	1.38
15.6	2.54	15.7	2.05	15.7	1.04
16.6	2.52	16.7	1.92	24.7	1.28
17.8	2.48	17.9	1.97	36.0	1.23
19.7	2.63	19.8	2.01	—	—
21.6	2.52	20.7	2.05	—	—
22.6	2.50	21.7	2.18	—	—
23.5	2.47	22.7	1.92	—	—
24.5	2.45	23.5	2.03	—	—

of 1.0. The results of Table 1, "wort 100%" are directly comparable with these.

In the case of 0.06% wort, the cells were badly bunched and had already stopped reproducing when first counted; in the 1.0% wort, also, the cells were badly bunched and counting was difficult.

Inspection of the graphs, Fig 1, shews that the initial rate

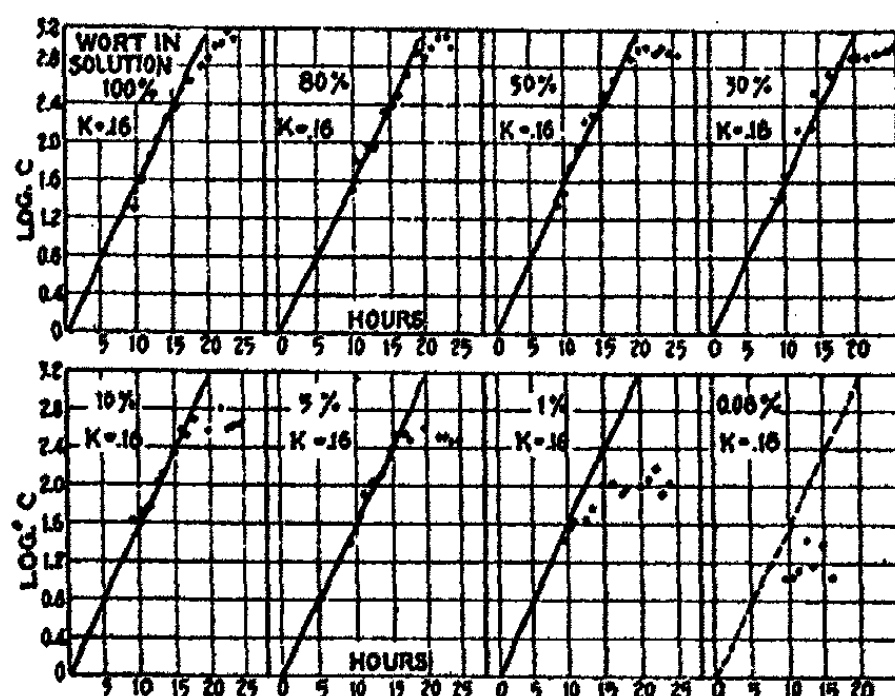


Fig. 1

of reproduction is the same in all the media tested, viz.: from 100% wort to 1.0% wort; and that in every case the maximum yield is reached within 24 hours.

**Retardation due to Alcohol**

In solutions containing 10, 30, 50, 80, or 100 percent wort, the logarithmic formula holds until  $\log C =$  about 2.7, i. e.,  $C =$  about 500; a number of distillations showed that at this point the solutions contain 1.8% alcohol (1.8 g per 100 cc). Measurements of the rate were then undertaken in wort to which various amounts of alcohol had been added before seeding; of course, additional alcohol is formed during the experiments, and no doubt there is some loss from evaporation, but these changes are small. For instance, with an initial count of  $C = 23$  in pure wort, less than 0.5% alcohol was formed in six hours; wort initially containing 1.58% alcohol increased to 1.8% in 5 hours, and when the initial concentration was 3.1%, the concentration after 5 hours was 3.27%.

In the experiments whose results are given in Table 5 and Fig. 2, the medium consisted of 45.5 cc wort, the amount of alcohol named in the table, water enough to bring the volume to 49 cc, and 1.0 cc of a yeast suspension made to give an initial count of  $C = 32$  ( $\log C_0 = 1.505$ ). The object

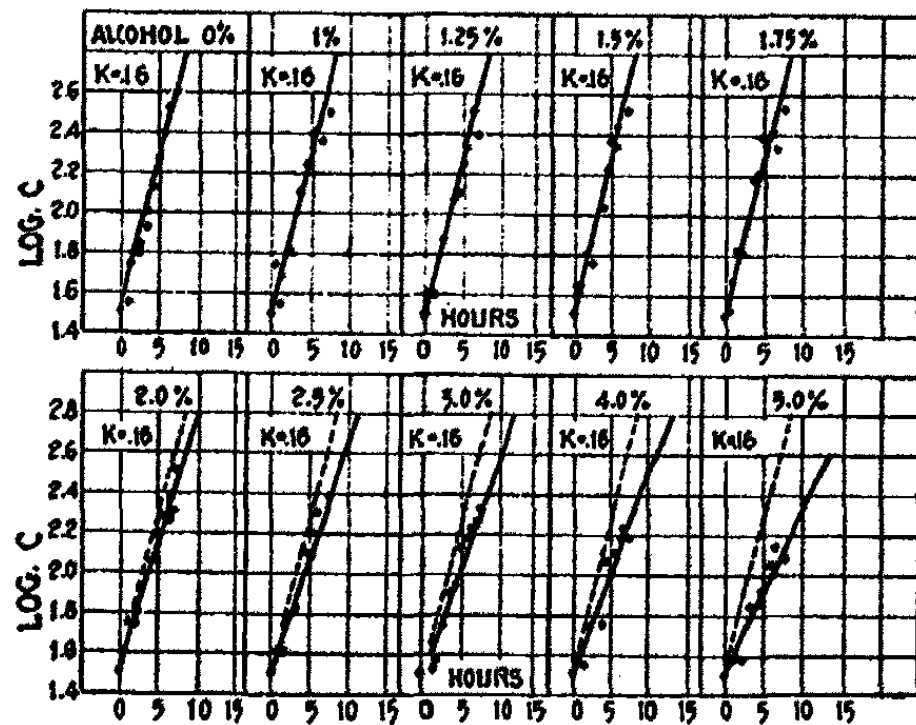


Fig. 2



in using a high count was to avoid trouble from the bunching of the cells grown in the alcoholic solutions; low counts are relatively inaccurate, and large bunches are hard to count and may not be evenly distributed; if the initial number of cells is small and the final count is high enough for accuracy, the number of cells in each bunch is apt to be inconveniently large.

TABLE 5

0% Alcohol		1% Alcohol		1.25% Alcohol		1.5% Alcohol		1.75% Alcohol	
Hours	Log C	Hours	Log C	Hours	Log C	Hours	Log C	Hours	Log C
0	1.51	0	1.51	0	1.51	0	1.51	0	1.51
1.1	1.53	0.6	1.74	0.6	1.61	0.7	1.60	0.8	1.53
1.75	1.74	1.2	1.53	1.2	1.61	1.25	1.65	1.3	1.67
2.5	1.81	1.8	1.68	1.8	1.67	1.9	1.80	2.0	1.85
3.7	2.00	2.5	1.81	2.5	1.87	2.6	1.76	2.7	1.84
4.5	2.12	3.8	2.11	4.0	2.08	4.0	2.05	4.1	2.19
5.0	2.28	4.5	2.25	4.6	2.10	4.6	2.22	4.8	2.22
5.7	2.39	5.1	2.28	5.2	2.25	5.2	2.36	5.3	2.38
6.3	2.52	5.7	2.40	5.9	2.33	5.9	2.33	6.0	2.39
7.0	2.60	6.4	2.36	6.5	2.51	6.5	2.45	6.6	2.32
—	—	7.5	2.49	7.0	2.39	7.2	2.52	7.2	2.51

2.0% Alcohol		2.5% Alcohol		3.0% Alcohol		4.0% Alcohol		5.0% Alcohol	
Hours	Log C	Hours	Log C	Hours	Log C	Hours	Log C	Hours	Log C
0	1.51	0	1.51	0	1.51	0	1.51	0	1.51
0.8	1.56	0.9	1.61	1.0	1.53	1.0	1.57	1.0	1.56
1.4	1.74	1.5	1.60	1.5	1.56	1.6	1.54	1.6	1.58
2.1	1.74	2.2	1.74	2.2	1.70	2.3	1.74	2.3	1.58
2.7	1.80	3.4	1.83	3.5	1.89	3.7	1.74	3.7	1.85
4.1	2.06	4.2	2.12	4.2	1.94	4.3	2.07	4.4	1.86
4.8	2.19	4.8	2.10	4.9	2.14	5.0	2.02	5.0	1.92
5.4	2.26	5.5	2.20	5.5	2.18	5.5	2.10	5.6	2.05
6.0	2.25	6.0	2.30	6.1	2.23	6.2	2.18	6.2	2.13
6.7	2.36	7.3	2.39	6.7	2.26	6.8	2.22	6.9	2.11
6.7	2.31	—	—	7.4	2.32	7.5	2.18	7.5	2.09
7.2	2.51	—	—	—	—	—	—	—	—

Inspection of Fig. 2<sup>1</sup> shews that up to an initial concentration of 1.75% alcohol the constant of the logarithmic formula remains at  $k = 0.16$ , but that with 2.0% alcohol and more it falls (Table 6); in Fig. 3, where  $k$  is plotted against %

<sup>1</sup> The dotted line corresponds to  $K=0.160$ .

TABLE 6

% Alcohol	0	1.0	1.25	1.50	1.75	2.0	2.5	3.0	4.0	5.0
<i>k</i>	0.16	0.16	0.16	0.16	0.16	0.135	0.125	0.113	0.104	0.088

The parabola passing through the three points 1.8, 3.0, and 5.0 has the equation:—  $k = 0.2774 - 0.0806\% + 0.008543 (\%)^2$ .

alcohol, this is brought out clearly. These results shew that with this particular strain of yeast, the concentration of alcohol necessary to affect the rate of reproduction, lies between 1.75% and 2.0%, the retardation in the rate of reproduction in the experiments

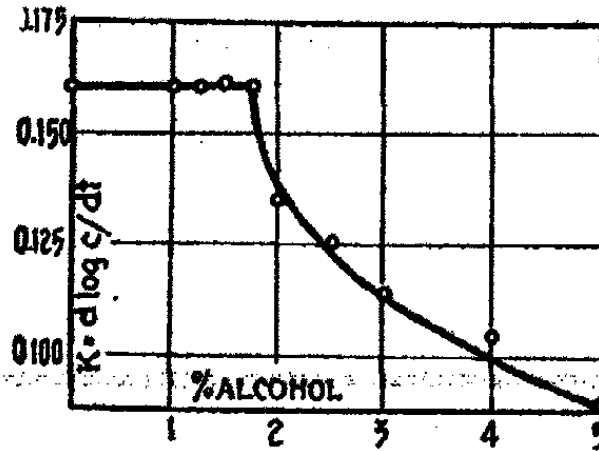


Fig. 3

of Tables 1 and 4, when  $\log C = 2.7$  must therefore be ascribed to the influence of the 1.8% of alcohol formed in these solutions.

Two reasons for this retardation suggest themselves: either (a) the rate of reproduction of each cell is lowered, or (b) some of the cells fail to reproduce; experiments with methylene-blue<sup>1</sup> shewed that none "die" even after 5 hours in 3% or 5% alcohol.<sup>2</sup> Plating experiments were carried out to decide the matter; in these, wort-agar plates containing 2% agar and either 5% alcohol or no alcohol at all, were seeded from the same yeast suspension. On the alcoholic plates the colonies developed uniformly but slowly, and the number, when countable (after four days) was the same as that on the alcohol-free plates (see Table 7), although on the latter the growth was very much faster. The decision therefore is in favour of hypothesis (a).

TABLE 7

Alcohol-free plates	77,77,82,91 colonies, respectively, total 327
5% alcohol plates	80,86,86,85 colonies, respectively, total 337

<sup>1</sup> On the use of this reagent, see Fraser: Jour. Phys. Chem., 24, 741 (1920).

<sup>2</sup> See also Fulmer: Jour. Phys. Chem., 25, 20 (1921).

### Retardation due to Lack of Bios

In solutions containing 5% wort, the logarithmic formula holds up to  $\log C = 2.5$  or  $2.6$  only, and in solutions containing 1.0% wort the retardation begins at  $\log C = 1.7$ , long before the amount of alcohol formed could exert any influence. There was obviously plenty of sugar and salts, and continual aeration was assured by the splashing in the rocker; H. Brown has shewn, moreover, that when the oxygen supply is deficient the logarithmic formula does not hold. To remove all possibility of doubt, experiments were carried out during which filtered air was passed through a tube to the surface of the liquid while rocking, bubbling air through the liquid made too much froth; in these, the cells seemed to shew more tendency to form clusters, but the rate and yield were the same as before. Evidently some new factor is responsible for the retardation and small crop observed in these media.

In a paper entitled "Nouvelle substance indispensable au developpement de la levûre" published in 1901,<sup>1</sup> Dr. E. Wildiers "affirms that yeast-water contains a substance indispensable to the development of yeast,<sup>2</sup> and proposed for it the name "Bios." He established certain of the chemical and physical properties of the new substance, shewed that it was contained in wort, extract of meat, and commercial peptones; and that it disappeared from the culture medium when yeast was grown therein. This last observation was confirmed in 1904 by Amand,<sup>3</sup> who also confirmed and extended the observation of Kossowicz<sup>4</sup> that bios, "or at all events a substance which has the same influence on yeast cultures," is formed in the culture liquids of many microbes. In 1906 Devloo<sup>5</sup> added largely to Wildiers experiments on the behaviour of

<sup>1</sup> La Cellule, 18, 313 (1901).

<sup>2</sup> Bachmann: Jour. Biol. Chem., 39, 235 (1919), finds that different yeasts vary in this respect. Fulmer: Jour. Am. Chem. Soc., 43, 191 (1921), has grown yeast for 10 months in a medium formed from salts, sugar and water.

<sup>3</sup> La Cellule, 21, (2) 327 (1904).

<sup>4</sup> Zeit. landwirtschfl. Versuchswesen in Oesterreich, 1896, and 1903, VI.

<sup>5</sup> La Cellule, 23, 361 (1906).

bios with reagents, and shewed that this substance is contained in the extracts of opium, belladonna, ergot, nux-vomica, quinia, and squills, in commercial lecithin, and in bile. In 1919, Williams<sup>1</sup> working with single yeast-cells by the hanging-drop method, shewed that bios is contained in protein-free milk, in wheat germ, in lactose (as an impurity<sup>2</sup>) and in pancreas tissue; from these results, and from a study of its heat stability and behaviour towards reagents, he concludes that the substance now commonly referred to as "water soluble vitamine" is nothing but Wildiers' bios. Lachmann (loc. cit.) and Eddy and Stevenson<sup>3</sup> agree with this conclusion; Fulmer<sup>4</sup> does not.

In view of the work of Wildiers and his successors, it seems reasonable to ascribe the retardation of the rate of reproduction of yeast in solutions containing low percentages of wort to the exhaustion of the bios from the solution. That bios is removed from the solutions under like circumstances has already been proved by Wildiers and by Amand; the results of Fig. 1, which shew that almost up to the last moment the rate of reproduction follows the logarithmic formula, seem to require that its removal should be rapid and complete. To test this conclusion, 50 cc portions of pure wort and of 10% wort were shaken in the rocker each with 4 g twice washed yeast-cake, the count was thus about  $C = 2000$ ;<sup>5</sup> after shaking at 25° C for 30 minutes, and again after shaking for three hours, portions were pipetted out, freed from cells by filtration and from alcohol by distillation at low pressure, made up to the original volume with water, seeded to a count of 1.0, and put back in the rocker. After 24 hours the counts were:

<sup>1</sup> Jour. Biol. Chem., 38, 465 (1919).

<sup>2</sup> It is also contained in impure maltose, Kluyver: Biochem. Zeit., 52, 486 (1914); Kita: Zeit. Gärungsphysiol, 4, 321, Chem. Abs., 8, 3809 (1914).

<sup>3</sup> Jour. Biol. Chem., 43, 295 (1920).

<sup>4</sup> Jour. Am. Chem. Soc., 43, 186 (1921).

<sup>5</sup> The count remained constant; even after shaking for ten hours no budded cells could be found in the 10% wort, and but one or two in the 100% wort out of several thousand examined.

TABLE 8

100% wort	with yeast 30 minutes	Final count 950
100% wort	with yeast 3 hours	Final count 320
10% wort	with yeast 30 minutes	Final count 90
10% wort	with yeast 3 hours	Final count 16

Each portion of yeast cake was washed twice with 20 cc of water and centrifuged; the washings were used instead of water to make up an artificial medium (by addition of salts and sugar, see p. 48). This medium was seeded and rocked like the others; the count after 24 hours was about 25 or 50, the cells were badly bunched.

Estimating the bios as described in the following section, and calling the concentration of bios in pure wort 100, after shaking with the yeast for half an hour the concentration has fallen to 35, and after three hours to 5. The concentration in 10% wort will be 10, after half an hour with the yeast it has fallen to 1, and after three hours to zero. Practically no bios was contained in the yeast washings.

#### Estimation of Bios

Wildiers, Amand, and Devloo determined the maximum amount of carbon dioxide evolved per day when 1, 2, 3, etc. cubic centimeters of yeast-water were added to a standard solution of sugar and salts; by measuring the gas evolution when an unknown substance was added to the artificial medium, the number of "units of bios" it contained could be determined.

The "vitamine" contents of various extracts were compared qualitatively by Bachmann, who measured the gas evolved; by Williams, who counted the yeast crop from a single cell in a hanging drop; and by Eddy and Stevenson who sealed in a glass tube and incubated minute quantities of the "vitamine" solution and of a suspension of yeast in Naegeli's artificial medium. In no case was it attempted to reduce the comparisons to a quantitative basis, i. e., to express the results in units of bios.

The objections to the gas method have been pointed out by Eddy and Stevenson; the cell counting method can be put

on a quantitative basis by means of Fig. 4, which gives the yeast crop obtained in 24 hours under the conditions of my measurements. It is obvious that the first part of the curve (up to 5% or 10% wort) is the most suitable for the purpose, and that for final determinations the bios solution should be suitably diluted. Mr. Lucas has found this curve useful in enabling him to estimate the losses incurred at each step of an attempt to isolate bios from the naturally occurring substances which contain it.

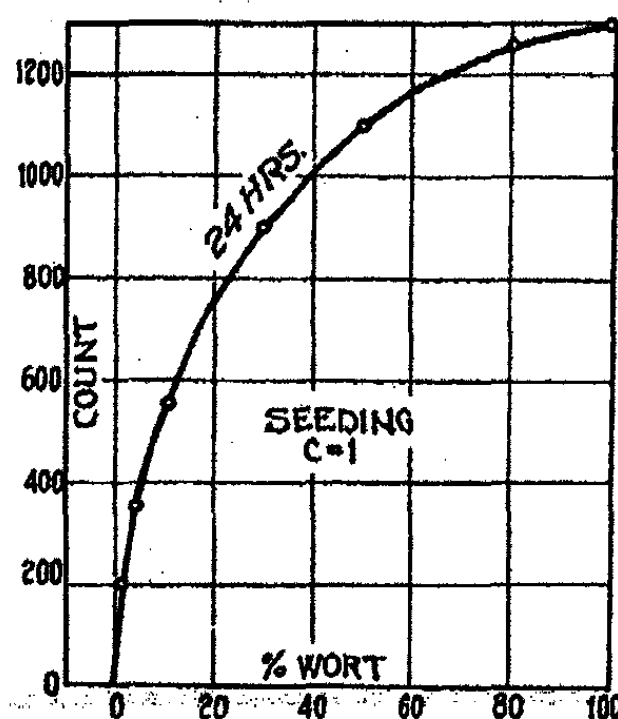


Fig. 4

Carlson's maximum yeast crops in wort diluted with water were much less affected by the dilution than in my experiments where artificial medium was used as diluent. From Fig. 4, it appears that when a constant volume of wort is diluted to 100 times its volume with artificial medium, the yeast crop is multiplied by 8; according to Carlson's results, if water be used as the diluent the factor is 2. I measured the rate of reproduction in 50% wort in which the dilution was effected by adding water, and found both rate and yield substantially the same as when artificial medium had been used; thus the smaller crops found by Carlson with high dilutions can only be ascribed to lack of sugar during the later stages of the fermentation.

Delbrueck<sup>1</sup> has affirmed that the crop of yeast in wort may increase with increase in the amount of yeast used as seed. Carlson denied this on the evidence of experiments in which the initial count "varied in the ratio of 1:10:100"—but never reached twenty percent of the final crop. In my own work,

<sup>1</sup> Wochenschr. Brauerei, 1884, 381, quoted by Carlson.

from initial counts of  $C = 1.0$  to  $C = 100$  and even higher I always found the same final yield of  $C = 1300$ . When the wort was seeded from a yeast cake to  $C = 2000$  no reproduction took place and only a very little budding; but when wort was seeded to a count of 1600 with "normal" yeast and incubated in the rocker, a final crop of  $C = 2700$  was obtained. In the presence of this large seeding, alcohol was rapidly formed; at the end of the first hour the concentration was 1.84% and at the end of the second hour 3.76%; but as during almost the whole of the first hour the alcohol was below the retarding concentration, and there was plenty of sugar bios and air, it is not surprising that the yeast should grow, and it did.

#### Crowding

Here and there in the literature may be found indications of the belief that the mere presence of a large number of cells in a small volume of nutrient liquid may have some direct effect in hindering reproduction apart altogether from the indirect effects due to lack of food circulation, formation of alcohol, removal of bios, etc. Carlson, for instance says "it may happen that for lack of space no cell division occurs" and quotes Hayduck<sup>1</sup> in support.

To study this, 50 cc of wort in a flask standing in the thermostat was seeded with active yeast to an initial count of  $C = 800$ ; throughout the experiment stirring and aeration were effected by a current of filtered air blown through the liquid, and a continuous stream of fresh wort (155 cc in all) ran in from a tap-funnel, while the volume of liquid in the flask was kept approximately constant by continually removing the excess through a filter. The filter consisted of a thistle funnel over the head of which was tied a piece of fine copper gauze, this was covered with a layer of fine linen, and outside of all a layer of hardened filter paper; joints were tightened by brushing with a solution of paraffin wax in ether. The stem of the funnel was connected to an air-pump by way of a pump bottle containing a little phenol to sterilize the filtrate. Very

<sup>1</sup> Wochenschr. Brauerei, 1911, 231.

few cells got through the filter, and after 5 hours the count in the fermentation flask had risen to 5000—the logarithmic formula calls for 5300. Considering that for part of the time the yeast was collected as a thick cake on the under side of the filter paper, it is obvious that if other circumstances are propitious, “crowding” has but little effect.

#### Summary

If wort be seeded with “normal” actively budding yeast cells (*Sacch. cerev.* race F), and the culture be properly shaken and aerated, at 25° C the rate of reproduction follows the “logarithmic formula”  $\log C/C_0 = 0.160 t$ , from the moment of seeding until the crop reaches one hundred million cells per cubic centimeter, whether the seeding be 5 cells or 8 million cells per cc or even more. At this point the solution contains 1.8 g alcohol per 100 cc.

When the concentration of alcohol exceeds 1.8%, the constant  $k$  of the logarithmic formula must be replaced by a function of the percentage of alcohol, viz:  $k = 0.2774 - 0.0806\% + 0.008543 (\%)^2$ , which holds from 1.8 to 5.0%.

The crop of yeast reaches its maximum, about 325 million cells per cc, in about 24 hours: this maximum is independent of the seeding up to 25 million cells per cc; but if the wort be seeded up to 400 million cells per cc, the crop may reach 675 million, this difference is to be ascribed to lower content of alcohol.

If wort be diluted with an artificial medium made up from sugar and salts, the rate of reproduction is the same as in pure wort; the maximum crop is also the same provided that the culture medium contains at least 10% of wort. In solutions containing less wort the rate is the same as usual, but the maximum crop is less; this must be ascribed to lack of bios in the culture liquid.

Quantitative measurements of the maximum crop can be used as a convenient means of determining bios.

Washed yeast cake rapidly absorbed bios from wort; if enough yeast is used the removal is practically complete, and the cells do not bud.



Under the conditions specified above, the rate of reproduction is independent of the concentration of sugar and of bios; it is independent of the concentration of alcohol until this reaches 1.8 grams per 100 cc. The assumptions underlying Carlson's formula for the rate of reproduction are thus without foundation.

---

This work was carried out in the chemical laboratory of the University of Toronto during the winters of 1918-1921, under the direction of Prof. W. Lash Miller.

*University of Toronto*  
*July, 1921*

**"THE WATER-PROOFING EFFICIENCY OF SOME BI-  
AND TRIVALENT SALTS OF HIGHER FATTY  
ACIDS" AND THEIR ADSORPTION BY THE  
FIBRES OF PAPER**

BY SHANTI SWARUPA BHATNAGAR

The investigation, part of which is described here, originated from the demands that persistently arose during the war for water-proofing materials suitable for manufacturing paper-made substitutes for basins and surgical limb baths. These substitutes for enamelled ware were very handy and light and could be produced quite cheaply. Various materials like copper-ammonium salts and cellulose solutions were tried and found useful. Certain bi- and trivalent salts of oleic, linoleic, palmitic and stearic acids were also tried and effectively used for the purpose. The knowledge about these salts is mainly restricted to patent literature, and as far as the author is aware their chemistry is not fully worked out. In this paper no attempt will be made to show that the bi- and trivalent soaps obtained by precipitation methods are not pure chemical compounds, but complex adsorption compounds, and only the results concerning the water-proofing efficiency of some of the more important bi- and trivalent soaps will be described.

**Experimental**

*Preparation of Soaps.*—In order to obtain the bi- and trivalent salts of oleic acid, a saturated solution of Kahlbaum's Sodium Oleate was prepared and solutions of bivalent and trivalent electrolytes were gradually added to precipitate the soap. With different strengths of the precipitating electrolyte the composition of the precipitate varied. The strength of electrolytic solutions in these cases was always one required for simple chemical action. In case of stearic, palmitic and linoleic acids the salts of these fatty acids were first prepared by the action of alcoholic potash and the soaps so obtained

were dried and purified in an evacuated desiccator, according to the method of McBain.<sup>1</sup> The bi- and trivalent salts of these acids were obtained by precipitation methods as described above.

There are two methods in which the bi- and trivalent salts of higher fatty acids can be conveniently utilized for water-proofing paper. First by giving a surface coating of the soaps by a brush or a like device. In order to do that a fairly thick paste of the soaps in suitable solvents is prepared in a glass mortar and this paste is painted on the surface of the paper by a moving roller or a painter's brush. The great disadvantage of this method is that after some time cracks appear on the surface of the coating. Some of these cracks are so fine that they cannot be detected by the naked eye and the water still leaks out through them. It is no doubt true that cracks do not appear quite so quickly in some cases, especially when the coating is very light and a suitable soap and solvent have been used. These special combinations of the soaps and the solvents are mentioned later on. In handling and transporting these basins made from cardboard or wood-pulp and so treated, cracks do invariably make their appearance on the surface of the paper, and their efficiency as utensils for containing water is completely destroyed.

The second method which entailed a considerable research on the question of solubilities of these soaps in various solvents was found to be more successful. The method consisted in dipping the paper vessel in a solution of the soap in an organic solvent. The solution penetrated the pores of the vessel and a slight amount of the soap was adsorbed at the surface of the pores, thus giving a thin uniform coating of the soap on the surface and making it water-proof.

As the point of view of cost was of special importance in the problem, cheap and easily available solvents like crude benzole, turpentine and methylated spirit alone were examined at that time.

---

<sup>1</sup> *Trans. Faraday Soc.*, 9, 99 (1913).

In order to investigate the water-proofing efficiency of the soaps they were first dissolved in various solvents and filter papers of equal weight were dipped in equal quantities of solution containing known and equal amounts of soap for equal times. The filter papers after being treated in this fashion were dried by passing hot air. When dry they were attached by means of a strong thread to the end of small funnels having long graduated stems. The funnels were then filled with distilled water at room temperatures (20°–21° C) up to a definite mark on the stem and the amount of water which passed out in 48 hours was read on the graduated stems. The paper which allowed the least amount of water to ooze out was considered to be the best water-proofed. Some of the results are shown in Tables I and II.

Some preliminary experiments with the barium and calcium salts of these fatty acids and some heavy metal soaps of stearic and palmitic acids showed very little water-proofing efficiency due to their solubility. For the same concentration of the solution irrespective of the solvent the order of

TABLE I  
Time for which the Papers were kept in Solution—65 Mins.

Soap	Quantities in gms, %	Solvent	Mark on which the water lay at the commencement	Mark at the end of 48 hours	Amount flowed
Aluminium Oleate	.198	Benzole	30	18	12
Zinc Oleate	.2	Benzole	32	30	2
Mg Oleate	.2	Benzole	32	30.4	1.6
Copper Oleate	.2	Benzole	32	31.89	0.1
Lead Oleate	.2	Benzole	32	18.6	13.4
Copper Linoleate	.201	Benzole	32	31.8	0.2
Mn Linoleate	.201	Benzole	32	28.4	3.6
Zinc Linoleate	.200	Benzole	32	29.0	3.0
Nickel Oleate	.2	Benzole	32	31	1
Nickel Linoleate	.2	Benzole	30	28.2	1.8
Mg Linoleate	.2	Benzole	30	28.0	2.0
Zinc Linoleate	.2	Benzole	32	28.0	4.0
Aluminium Linoleate	.2	Benzole	32	18.0	14.0

TABLE II

Soap	Quantities in gms, %	Solvent	Mark at com- mence- ment	Mark at the end of 48 hours	Amount flowed
Aluminium Oleate	.15	Turpentine	32	18	14
Aluminium Lino- leate	.15	Turpentine	32	14	18
Copper Oleate	.15	Turpentine	30	28.1	1.9
Copper Linoleate	.15	Turpentine	30	28	2.0
Zinc Oleate	.18	Turpentine	31	28	3.0
Zinc Linoleate	.18	Turpentine	30	26	4.0
Nickel Oleate	.18	Turpentine	32	30	2.0
Nickel Linoleate	.2	Turpentine	31	29	2.0
Mn Linoleate	—	Turpentine	30	21	9

efficiency was Copper Oleate, Mg Oleate, Copper Linoleate, Mg Linoleate, Nickel Oleate, Nickel Linoleate, Zn Oleate, Zn Linoleate, Al Oleate, Lead Oleate.

#### Effect of the Concentration of the Solution and the Time

On varying the concentration of the solution, it was found that the greater the concentration the greater the efficiency of the solution in making the paper water-proof. This was supposed to be due to the fact that the adsorption of the soap on the fibres of the paper had increased due to the increase in concentration, and some experiments were performed to find how this adsorption varied according to the concentration and time. In order to see if this supposition was correct solutions of different strengths were prepared and known quantities of them were put in wide-mouthed stoppered jars and fairly large sheets of thick filter paper (about 6 x 10) weighing 2 gms of similar texture were rolled and put in the jars. When noting the effect of time on the adsorption of the soap on the fibres of the paper, six jars containing equal volumes of a solution of known strength were selected and the sheets of filter paper were dipped in them as described above. From the first jar 150 cc of the solution were taken out and evaporated on a weighed crystallizing basin after half an hour, from the second after one hour, from the third after an hour and a half and so on. The decrease in the amount of

dissolved substances noted by weighing the crystallizing basins after evaporation gives a fair idea of the amount of soap taken up by the filter paper. A few check experiments were made by analyzing the solutions in different jars and the results obtained by the two methods were in satisfactory agreement. Some of these results are shown in Tables III, IV, and V.

TABLE III

Time	Amount adsorbed by the filter paper from Copper Oleate Solution in benzole
30 Minutes	0.09
60 Minutes	0.110
90 Minutes	0.118
120 Minutes	0.127
150 Minutes	0.130
180 Minutes	0.130

TABLE IV

Time	Amount of Al Linoleate adsorbed by the filter paper from solution in turpentine
30 Minutes	0.069
60 Minutes	0.079
90 Minutes	0.080
120 Minutes	0.082
150 Minutes	0.082
180 Minutes	0.082

TABLE V

Time	Amount adsorbed by the filter paper from Zinc Linoleate Solution in turpentine
30 Minutes	0.067
60 Minutes	0.070
90 Minutes	0.072
120 Minutes	0.078
150 Minutes	0.078
180 Minutes	0.079

It is easily seen from these results that the adsorption is greatest in the first hour, and reaches a state of equilibrium in 120 minutes. The rate of adsorption is different with different solutions; but a state of equilibrium is always reached before or soon after 120 minutes.

The effects of concentration with different soaps have been shown in Tables VI-IX.

The figures in the last column represent the amount of soap adsorbed by one gram of filter paper. The terminology of Freundlich has been preserved and unless otherwise mentioned,  $a$  represents the original total amount of the solute before adsorption, and therefore  $a/v$  the original concentration of the substance, and  $x$  amount adsorbed if  $m$  grams of the filter paper are employed. Then  $x/m$  is the amount adsorbed per gram.

Table VI represents the original concentration of the solution, the concentration after adsorption, the amount adsorbed by 2 gms of filter paper and the  $\frac{a-x}{v}$  and  $x/m$  calculated from these figures in case of Copper Oleate and the solvent being benzole (density 0.76).

TABLE VI  
Copper Oleate in Benzole

Original concentration Copper Oleate per 1000 cc of solvent	Concentration after adsorption per 1000 cc	Amount adsorbed by 2 gms from the solution	$\frac{a-x}{v}$ Concentration per cc after adsorption	$\frac{x}{m}$ Amount adsorbed per gm
6.338	6.2	0.138	0.0062	0.069
12.164	12.0	0.164	0.012	0.082
24.212	24.0	0.212	0.024	0.1064
38.258	38.0	0.258	0.038	0.1292
48.274	48	0.274	0.048	0.137
60.29	60	0.288	0.060	0.144

TABLE VII  
Copper Linoleate in Turpentine

11.180	11.000	0.18	0.011	0.087
12.485	12.310	0.185	0.0123	0.089
15.295	15.10	0.195	0.0151	0.095
17.498	17.30	0.198	0.0173	0.099
21.200	21.00	0.20	0.021	0.105
22.501	22.30	0.201	0.0223	0.107
24.210	24.00	0.21	0.024	0.109
26.22	26.00	0.221	0.026	0.112
29.23	29.00	0.239	0.029	0.126

TABLE VIII  
Nickel Oleate in Turpentine

Original concentration Nickel Oleate per 1000 cc of solution	Concentration after adsorption per 1000 cc	Amount adsorbed by 2 gms from the solution	$\frac{a-x}{v}$ Concentration per cc after adsorption	$\frac{x}{m}$ Amount adsorbed per gm
5.098	5.01	0.098	0.0051	0.049
10.136	10.01	0.126	0.011	0.063
15.168	15.03	0.138	0.0153	0.069
18.188	18.04	0.148	0.0184	0.074
20.540	20.01	0.153	0.020	0.076

TABLE IX  
Zinc Oleate in Benzole

Original concentration Zinc Oleate per 1000 cc of solution	Concentration after adsorption per 1000 cc	Amount adsorbed by 2 gms from the solution	$\frac{a-x}{v}$ Concentration per cc after adsorption	$\frac{x}{m}$ Amount adsorbed per gm
5.126	5.00	0.126	0.005	0.063
7.344	7.2	0.144	0.007	0.072
8.248	8.1	0.148	0.0081	0.074
9.658	9.5	0.158	0.0095	0.079

Somewhat similar results were obtained with the following salts in methylated spirit, though it was found that these solutions gave results which were not so satisfactory for efficiency of water-proofing as in case of benzole and turpentine: Al Oleate, Mg Oleate, Mg Linoleate, Copper Oleate, and Copper Linoleate; and with Zinc Oleate, Aluminium Oleate, Aluminium Linoleate, Mg Oleate, Mg Linoleate and Lead Oleate in benzole and turpentine. The figure for soaps used in actual practice alone have been given. A mixture of Zinc Oleate and Zinc Linoleate in equal proportion was used; the results are shown in Table X.

TABLE X

Concentration per cc	$\frac{x}{m}$
0.0068	0.0867
0.0075	0.090
0.0081	0.093
0.0099	0.098

**Methods of making the Paper Basins**

Before entering into the discussion of results described in this paper, a very brief reference will be made to the various



methods employed in making these basins. A considerable amount of time was spent in deciding as to which method was the most convenient and efficient and the details of investigation regarding this question will not be entered into in this paper. The following three methods were generally employed:

(1) Basins made from thick cardboard: The basins were quite handy and well shaped; but after some days, the water began to leak out from the corners.

(2) Basins made from moist paper-pulp: These basins were extremely well shaped and could be easily made of any shape on a potter's wheel, and the defects of leakage at the corners were thus minimised; but they required a lot of solution before the state of equilibrium was reached as the solution penetrated inside the rather thick walls of the vessel.

(3) In order to avoid this, thin-walled basins were so constructed as to allow the one to fit into the other rather loosely. The space between the two was padded by scraps of waste-paper. This strengthened the walls, and the outer and interior crests alone had to be water-proofed. The mouth of the vessel was plastered with paper-pulp and the edges were smoothed by painting a thick paste of the soaps in suitable solvents. It has been pointed out that a coating like this is liable to crack. It was found that pastes of most of the soaps in methylated spirit did invariably crack. The best soaps for this purpose were those which were gummy, and of a curd-like structure, and the best solvent was benzole. Copper Oleate and Linoleate and Ni and Al Oleate and Mn Linoleate were found very serviceable.

The reason for the appearance of cracks in case of pastes made in methylated spirit may be attributed to the fact that some of the soaps when evaporated from alcoholic solutions assume crystalline structure. To this fact may also be attributed the inferiority of alcoholic solutions of these soaps for water-proofing filter papers.

#### **Discussion of Results**

A large amount of data on adsorption questions obtained

by Freundlich,<sup>1</sup> Schmidt,<sup>2</sup> MacBain,<sup>3</sup> Davis, Walker and Appleyard, Briggs,<sup>4</sup> bears support to the well-known empirical equation put forward by Freundlich

$$\frac{x}{m} = Bc^n$$

where  $x$  and  $m$  have the same meanings as described above, and  $c$  denotes the final concentration and  $B$  and  $n$  are two constants.

A few of the results not described before, and the results of Table VI are plotted in curves in Figs. 1-3. The shape of

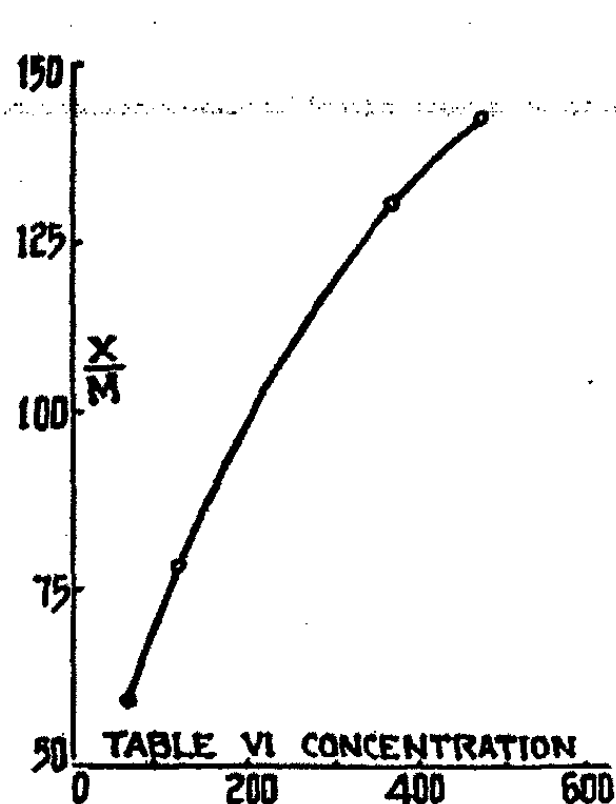


Fig. 1

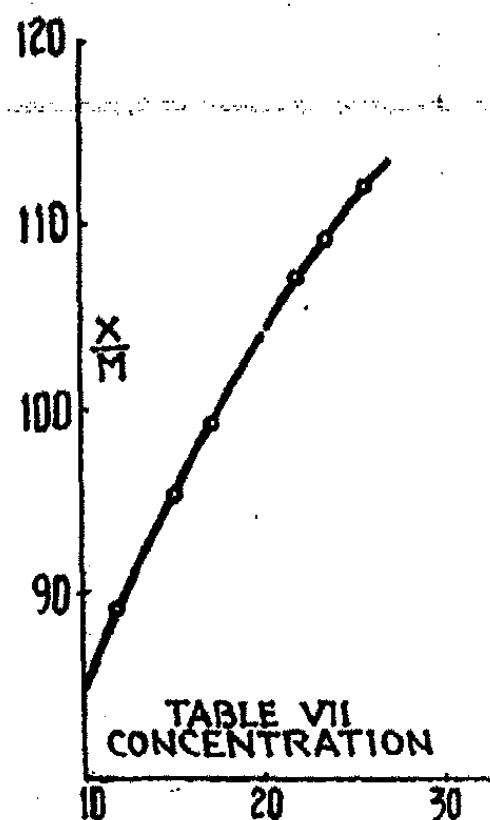


Fig. 2

the curves resembles the typical adsorption curves. The best test of the validity of the adsorption law is to plot the logs of the concentrations against the logs of  $x/m$ ; if the law holds these curves are straight lines. Figs. 4-5 show that this is very nearly the case in some of the experiments described here.

<sup>1</sup> "Kapillarchemie," 1909; Zeit. phys. Chem., 59, 284(1907); Kolloidchem. Beihefte, 6, 297 (1914), etc.

<sup>2</sup> Zeit. phys. Chem., 91, 103 (1916).

<sup>3</sup> Trans. Faraday Soc., 9, 99 (1913).

<sup>4</sup> Jour. Phys. Chem., 19, 210 (1915).

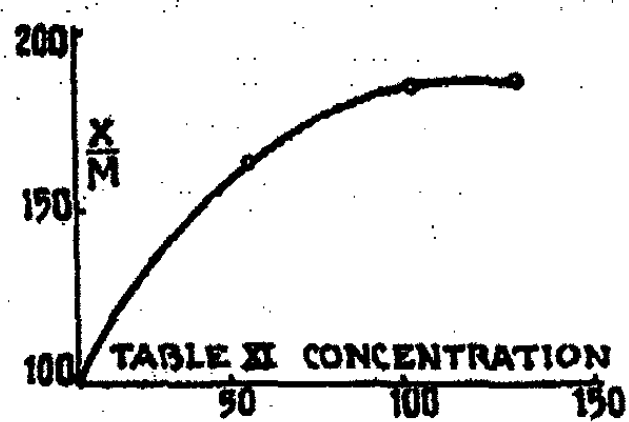


Fig. 3

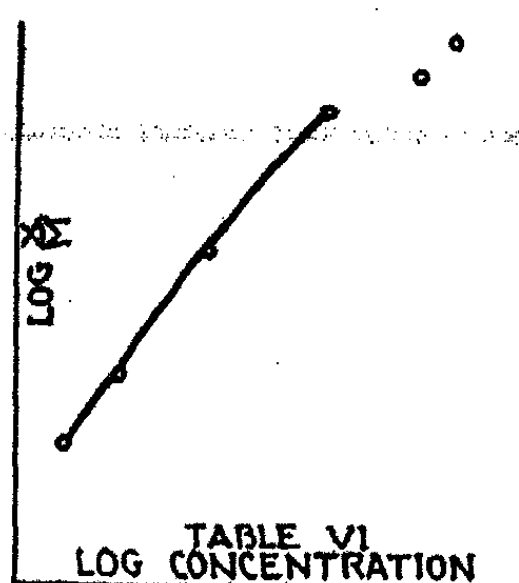


Fig. 4

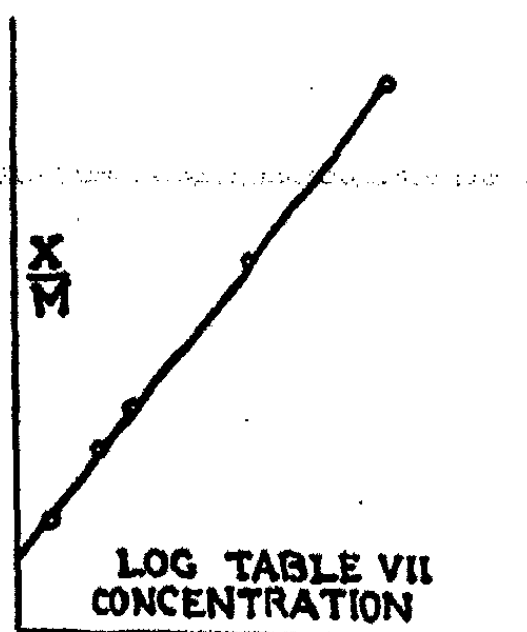


Fig. 5

For the sake of closer comparison some of these results are gathered together in Table XI.

TABLE XI

Concentration	Constant B	Constant n	$\frac{x}{m}$ found	$\frac{x}{m}$ calculated
0.0071	—	—	0.120	0.119
0.0092	0.4	4.1	0.129	0.127
0.012	0.4	—	0.137	0.136
0.015	0.4	—	0.142	0.143
0.005	—	—	0.049	0.047
0.01	0.34	2.7	0.073	0.076
0.015	—	—	0.077	0.079
0.018	—	—	0.077	0.079
0.02	—	—	0.080	0.087

These results seem to show that Freundlich's equation for the adsorption isothermal holds, and that besides the nature of the soap and the solvent, adsorption plays an important part in the process of water-proofing paper. If a proper soap solution and a suitable kind of paper-pulp are selected the rather expensive method of making the paper fibre water-proof by giving a thin coating of the water-proofing material by a brush can be replaced by the adsorption process described here. Considering the saving in material the results obtained are fairly efficient, and the defects of the crack-formation which are so ruinous to the efficiency of the basin as a water-proof utensil are also obviated in this process.

#### **Summary**

1. The water-proofing efficiency of a large number of bi- and trivalent soaps has been determined.
2. The adsorption of these soaps by the fibres of thick filter paper has been investigated.
3. It is shown that Freundlich's empirical rule holds good in several cases.
4. The methods of making water-proof basins have been briefly described.
5. The usefulness of adsorption process for water-proofing paper has been described.

## THE SCATTERING OF LIGHT: NOTE ON WOLSKI'S PAPER ON OPTICALLY EMPTY LIQUIDS

BY FRANK B. KENRICK

P. Wolski<sup>1</sup> has recently described experiments in which he filtered water and other liquids through collodion filters and in this way obtained liquids which showed no bright specks under the ultra-microscope. In expressing these results, however, he uses language which is capable of a very different interpretation from that which is justified by his experiments. He says "the water had become completely optically empty," and (in his final conclusions) "therefore the bright specks and scattering phenomena observed up to the present time result from the presence of a foreign substance."

In view of these statements it seems necessary once more to make clear that, as found by Martin,<sup>2</sup> the notes in a liquid may be removed by several different methods: distillation without ebullition, cataphoresis, and envelopment, but that there still remains a light-scattering which is constant in intensity irrespective of the method of purification. No doubt filtration through collodion is also an effective method for removing notes, and it seems likely that the liquids filtered in this manner would be similar in light-scattering property to the same liquids after treatment by distillation without ebullition, etc.

That the "bright specks" described by Wolski are the same as the "notes" referred to above, and must be carefully distinguished from the light-scattering of dust-free media is, I think, conclusively shown by the following experiments.

In the exhausted apparatus, Fig. 1, water can be distilled without ebullition from bulb *A* into bulbs *B* and *C*, and rinsed back repeatedly until it is dust-free. The long tube connecting *B* and *C* has a length of thin-walled, much flattened capillary tube sealed in at *D*, in such a position that its con-

<sup>1</sup> Kolloidchemische Beihefte, 13, 137 (1920).

<sup>2</sup> Chem. Abstracts, 8, 3739 (1914).

tents may be viewed in the ultra-microscope. A drop of cedar oil was placed between the tube *D* and the glass prism *E* used for indirect illumination. A converging beam of sunlight, directed by a heliostat and passing through a cell of water was used in all the experiments. The flow of water through *D* was produced and controlled by a slight tilting of a board on which the whole apparatus, including the microscope, was fixed. The approximate number of motes per cc of liquid was estimated from the number of light discs seen crossing a field of known size in a given time, the rate of flow of the liquid, and the depth of focus. The

dimensions of the field covered by a square etched on a glass plate in the 12x eyepiece were  $0.085 \times 0.075$  cm. The depth of focus, i. e., the distance the objective (16 mm focus) could be raised or lowered while an average sized light disc remained easily visible was 0.0066 cm. The rate of flow was estimated by the average of the times required for a

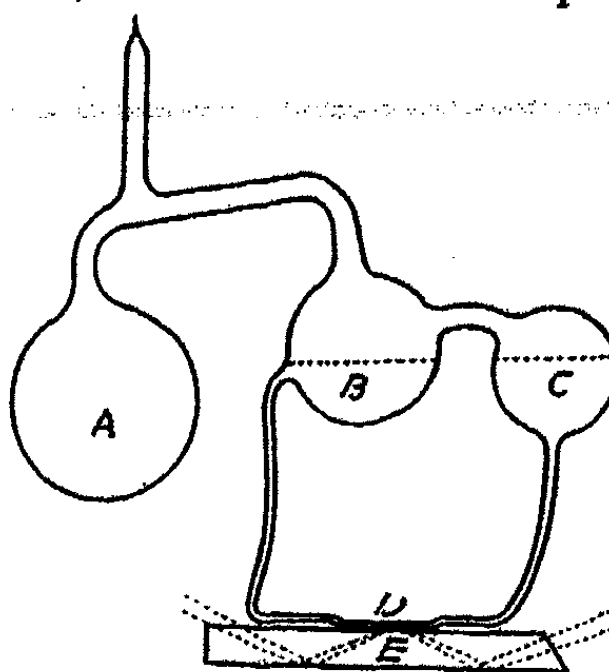


Fig. 1

light disc to cross the field at the beginning and at the end of the count. If no discs passed the rate was taken from other experiments in which the board was given the same tilt. The flow was adjusted so that the discs took from  $\frac{1}{2}$  to 5 seconds to cross the field and the counts ranged from about 50 to 0 per minute, in the different experiments.

*Results.*—Ordinary distilled water gave about  $2 \times 10^4$  light discs per cc. Wolski found 29,000 so it is evident that he and I are looking at the same thing. The relative light-scattering of this water was 0.7 (benzene=1);<sup>1</sup> after two distillations the number was  $1 \times 10^3$  and the scattering 0.12;

<sup>1</sup> Measured by Mr. Martin in his apparatus described in Jour. Phys. Chem., 24, 478 (1920).

after eight<sup>1</sup> distillations no more discs were seen, and the scattering was 0.07. The scattering is obviously not proportional to the number of motes; in fact the values are as would be expected on the assumption of a constant light-scattering by the mote-free liquid (0.07) with an additional scattering proportional to the number of motes (no. of motes per cc  $3 \times 10^{-5}$ ).

The distillation, therefore, removes the ultra-microscopic particles just as Wolski's filter does, but the liquid still scatters light, as was shown by Martin in 1913.

Experiments to determine the actual scattering of water filtered through collodion are in progress. Preliminary experiments in which the collodion film was formed on a fine brass gauze soldered into a copper funnel showed that a specimen of water filtered under a pressure of about one atmosphere at the rate of 50 cc per hour was optically empty in the sense that no motes were visible in Martin's light-scattering apparatus, but that it still showed the familiar blue haze seen in all dust-free liquids. It is hoped that Wolski's method of filtering will make it possible to extend the scope of the measurements of light-scattering to solutions of non-volatile substances to which the method of purification by distillation has not been applicable.

<sup>1</sup> It was harder to rinse out the motes from this apparatus than from Martin's plain bulbs.

*Chemical Laboratory  
University of Toronto  
May, 1921*

## THE SCATTERING OF LIGHT BY DUST-FREE LIQUIDS. II

BY W. H. MARTIN AND S. LEHRMAN

### 1. Modifications in the Method

Measurements of the light scattered by dust-free liquids were previously<sup>1</sup> made in round bulbs. Such bulbs had a considerable disadvantage in that they acted as lenses, the power of which varied with the contained liquid; so that the exciting beam of light was converged to a different degree by the various liquids. This difficulty was mentioned in the former paper, but it is only since then that a method has been found to overcome it.

Gibson and Argo<sup>2</sup> have described a method of sealing a flat glass plate into a round glass tube, with no distortion of the plate save at the edges. Following the directions given in their paper, it was possible after practice to seal a flat plate cut from a microscope slide into a lead glass tube. A cross-shaped container (Fig. 1) with arms about 1.5 cm diameter was thus constructed, which replaced the round bulb formerly used. Such a container had a small volume (about 20 cc) and when painted black on the outside permitted very little "parasite" light to reach the observer's eye.

The crosses were kept hot with a soft Bunsen flame till all four ends had been sealed in; then annealed for two

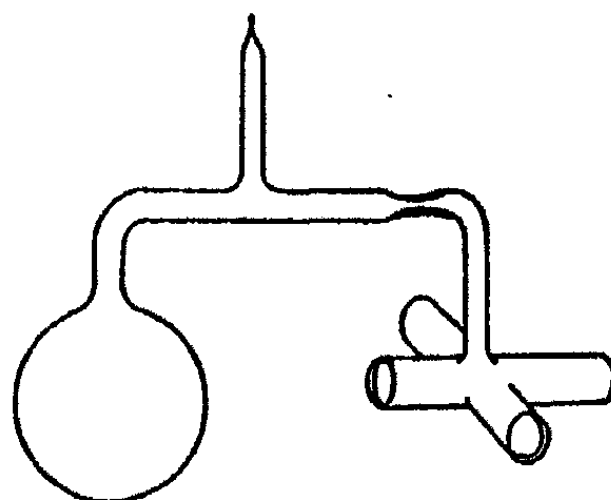


Fig. 1

<sup>1</sup> Jour. Phys. Chem., 24, 478 (1920).

<sup>2</sup> Jour. Am. Chem. Soc., 40, 1327 (1918). See also Jour. Opt. Soc. Amer., 4, 496 (1920), and Trans. Faraday Soc., 12, 305 (1916).



hours at 475° in an electric oven and cooled overnight to room temperature. Occasionally after completion and without apparent cause a plate would crack. Always sudden change of temperature, and often even gradual change of temperature cracked a plate. However a dozen or more such crosses have been successfully made and used.

It proved more difficult to make the crosses from soda-glass tubing. One soda-glass cross was successfully made, but one of its plates cracked after having been made for ten days. Evidently the glass of which the plates were made had a somewhat different coefficient of expansion from that of the tubing. Various annealing temperatures up to that at which the glass distorted did not overcome the difficulty.

Finally it was found that the crosses could be made quite easily from pyrex plates and tubing. The plates were made from the bottom of a pie-plate of pyrex oven-ware, ground to the required thickness of about 2 mm and polished by an optical company. It proved to be very easy to make the seals from such plates, even with no special annealing. The apparatus not only had great mechanical strength, but such sudden changes of temperature as plunging into liquid air or boiling water did no harm. The seals, when made with a dentist's blow-pipe burning gas with air, were quite vacuum-tight. The use of pyrex glass evidently solves all difficulties in the making of such a seal.

The liquids were rendered free of dust by the method of distillation described in the former paper (Fig. 1). Only slight modifications were made in the apparatus for measuring the light-scattering. A "Pointolite" tungsten-arc lamp proved to be a very satisfactory point source and replaced the troublesome carbon arc. The piece of paper which served as a comparison field for the scattered light was illuminated from behind by light from the same source reflected by a series of mirrors. The exciting beam of light passing through the cross was wider than before, and the scattered light was observed through a slit about 0.5 cm wide.

## 2. Measurement of the Relative Intensity and Polarization of the Scattered Light

The liquids used were Kahlbaum's and Baker's C. P. These were fractionated once and the boiling points of the fractions used are given. Benzene has been chosen as the standard for comparison. Kahlbaum's gold-label benzene for molecular weight determinations, and Baker's C. P. benzene showed, within the experimental error, the same intensity of scattered light. The result was also the same whether the distillation was carried out in lead or in soda-glass. This did not, however, prove to be true for all liquids. It was found that water, when distilled in lead glass, scattered about 50 percent more light, methyl alcohol about 100 percent more light, and ethyl alcohol 15 percent more light, than when distilled in soda-glass. Ether, propyl alcohol and benzene were unaffected by the glass, so it was taken for granted that this would also be true for the higher alcohols and the higher members of the benzene series.

Samples of water distilled in soda-glass and in pyrex glass—the solubility of which is much less than that of soda-glass, and indeed even less than that of Jena utensil glass<sup>1</sup>—showed the same amount of light-scattering. In the previous paper it has been shown that, whether the distillation be carried out in soda-glass or in fused quartz, the result is the same. The explanation of the surprising effect of lead-glass is no doubt to be found in the comparatively greater solubility of this glass (about 10 to 15 times greater than that of soda-glass<sup>2</sup>).

In Table I, Columns 1 and 3, are the results of the measurements of relative intensity and polarization of the scattered light for a few members of the benzene series, a few alcohols, and water. Similar measurements for some other pure liquids are given in the section on solutions.

The results do not differ markedly from those given in our previous paper. The averages of various sets of readings

<sup>1</sup> Jour. Ind. Eng. Chem., 9, 1092 (1917).

<sup>2</sup> Ber. deutsch. chem. Ges., 24, 3561 (1891).

TABLE I

Liquid	B. P.	Rel. int. sc. light (benzene = 1)	1	2	3
			$(\mu^2 - 1)^2 F$ $\rho$	$(\mu^2 - 1)^2 F$ $\rho$	Int. in plane of pol'n $\times 100$ Int. in plane at rt. angles
Benzene	80	1.00	1.00	1.00	48.4
Toluene	110	1.14	1.16	1.16	49.0
Xylene <sup>1</sup>	139.3	1.26	1.26	1.32	52.5
Chlorobenzene	132	1.46	1.29	1.29	53.9
Methyl alcohol	66	0.191	0.161	0.161	7.1 <sup>2</sup>
Ethyl alcohol	78	0.200	0.289	0.289	7.8
n-Propyl alcohol	97-98	0.260	0.429	0.429	8.5
Isobutyl alcohol	107	0.280	0.564	0.564	8.5
Isoamyl alcohol	129-130	0.298	0.696	0.696	9.0
Water	—	0.068	0.074	0.074	6.7 <sup>2</sup>

show greater uniformity than before, and seem to warrant a probable error of from 3% for those liquids scattering most light, to 5% for those scattering less. Nothing of any importance can be added to the summary of results made before. Various formulae have been tried to find one which would best fit the experimental results. The values of

$$\frac{(\mu - 1)^2 F}{\rho} ; \frac{(\mu^2 - 1)^2 F}{\rho} ; \frac{(\mu^2 - 1)^2 F}{(\mu^2 + 2)^2 \rho}$$

where  $\mu$  is the refractive index,  $F$  the formula weight, and  $\rho$  the density of the liquid, have been calculated. Of these  $\frac{(\mu^2 - 1)^2 F}{\rho}$  seems the best, and the calculated values of this

expression for the various liquids are listed in Table I, Column 2.

Cabannes<sup>3</sup> has proposed a modification of Rayleigh's formula. His equation contains a factor which is an expression of the extent of the polarization of the scattered light; but, although his formula fits the observed results for gases even better than the original Rayleigh formula, the same cannot be

<sup>1</sup> A mixture of xylenes for which the refractive index and density were determined.

<sup>2</sup> Taken from previously published results.

<sup>3</sup> Jour. Phys. Rad., (6) 1, 129 (1920). See also Ann. Phys., 15, 5 (1921).

said for liquids. His modified formula is evidently unsuitable for liquids, since the maximum value of our polarization factor (see Table I, Column 3) compatible with the theory on which his formula is based is 50, whereas measurements show for such liquids as carbon bisulphide and chloronaphthalene a value as great as 70.

### 8. Two-component Solutions

Using the apparatus shown in Fig. 2,<sup>1</sup> dust-free liquids were prepared in the cross A and the graduated tube B by the method of distillation. The two parts of the apparatus

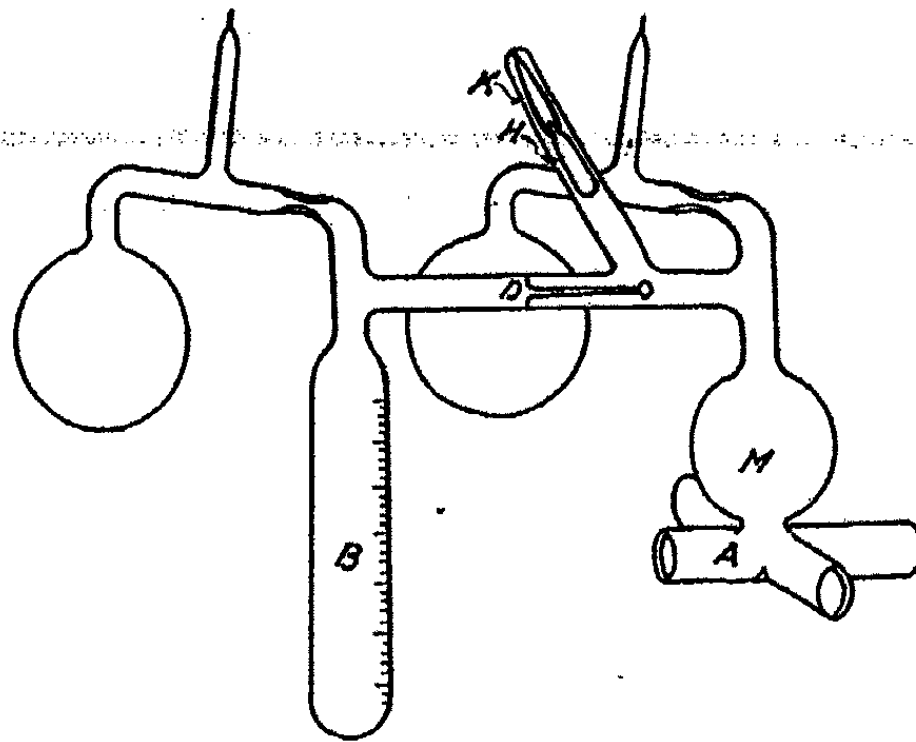


Fig. 2

are separated by a capillary seal-in at D. A ball of thin glass at the end of the capillary could be subsequently broken by a glass hammer, H, held in the side-arm K by a glass spring in the shape of a tuning-fork. On jarring the apparatus the spring released the hammer, which in turn broke the glass ball. A measured volume of the liquid in B could then be

<sup>1</sup> It is difficult to distill directly a liquid which has been previously made up to a known composition. The more volatile component goes over first, and unless the liquid be completely distilled over, the composition of the distillate in the cross is unknown. Separate distillations, moreover, must be made for each composition, whereas with the apparatus described above as many compositions as desired may be studied after one set of distillations.

distilled to A, the volume of which had previously been determined. The bulb M allowed space for thorough mixing. Thus readings could be taken on a series of solutions from 100% A to about 50% A. To complete the series a duplicate apparatus was made, with the liquids reversed in the containers. During the removal of the motes by distillation the whole of the side-tubes were washed carefully with the dust-free distillate. Generally four distillations sufficed to wash the dust from the walls of the tubes.

The results for three pairs of liquids are given in the following tables and graphs.

The results are given graphically in Fig. 3 with the exception of the results of the polarization for solutions of hexane and cyclohexane, the polarizations of which are so nearly equal, that any deviation from the straight line relation might be attributed to experimental error.

Components: Carbon Bisulphide and Ether

Percent by volume carbon bisulphide	Rel. int. sc. light (benzene = 1)	Int. in plane of pol'n × 100
		Int. in plane at rt. angles
100	4.55	71
71	4.30	39.5
47	3.43	30.5
46.5	3.60	31.5
44.5	3.17	32
21	1.84	31.5
11	1.25	30
0	0.355	10

Components: Benzene and Normal Hexane

Percent by volume benzene	Rel. int. sc. light (benzene = 1)	Int. in plane of pol'n × 100
		Int. in plane at rt. angles
100	1.00	48.5
92	1.06	39
80	1.19	33
61	1.10	27
44	1.02	28
24	0.77	27
10	0.59	18
0	0.40	10

Components: Normal Hexane and Cyclohexane

Percent by volume hexane	Rel. int. sc. light (benzene = 1)	Int. in plane of pol'n X100 / Int. in plane at rt. angles
100	0.40	10
77	0.46	9
53.5	0.48	9
43	0.455	10
33	0.41	9
16	0.37	8
0	0.31	8

The results show that the relative intensity of the scattered light for these solutions is always somewhat greater than that calculated on the assumption that the scattering is an additive property for the two liquids. This seems to be true even for pairs of liquids such as hexane and benzene, and also for hexane and cyclohexane, which when mixed form so-called ideal

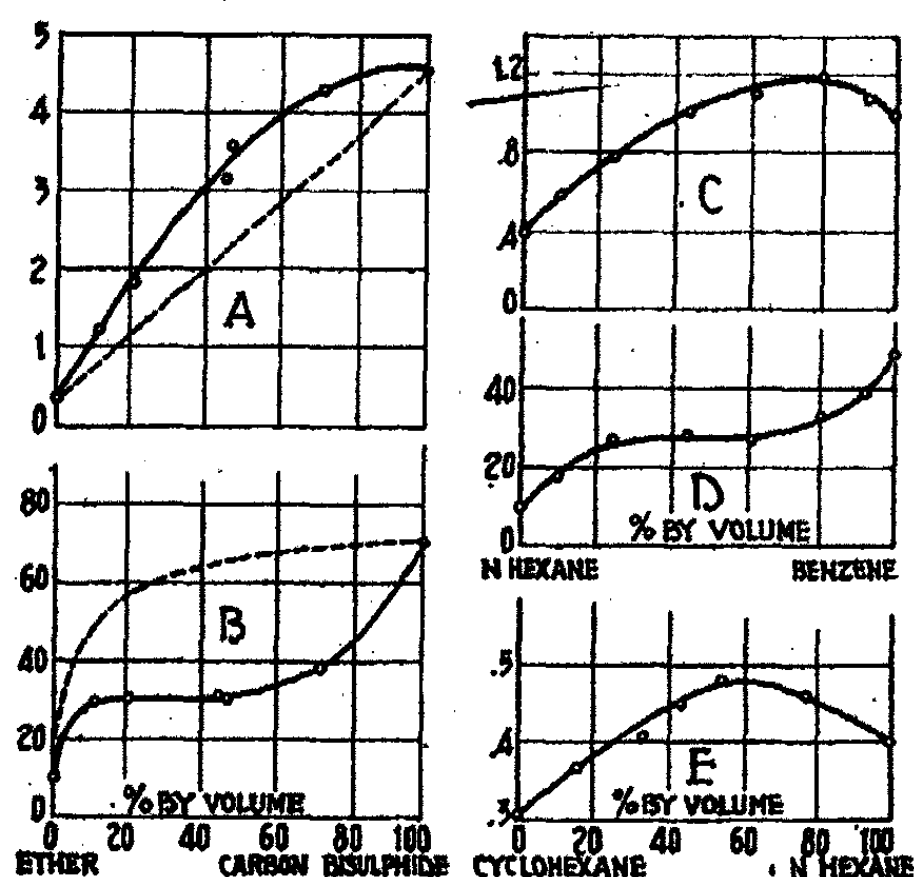


Fig. 3

Solutions of Carbon Bisulphide and Ether. A. Relative Scattering.  
 B. Percent Polarization.  
 Solutions of Benzene and Normal Hexane. C. Relative Scattering.  
 D. Percent Polarization.  
 Solutions of Normal Hexane and Cyclohexane. E. Relative Scattering.

solutions. This is surprising in view of the fact that the refractive index of such solutions is apparently an additive property.

Liquids which polarize the scattered light very far from completely show, on dilution, much more nearly complete polarization. In Fig. 3, A and B, the dotted lines are the intensity and polarization curves, calculated on the assumption that each of the components scatters light in exactly the same way as regards intensity and polarization as it does when pure.

If the two liquids in the solution are regarded as still possessing their own ability to scatter and polarize light, modified, however, by the dilution by the other liquid, it is interesting to note that the general type of the above curves could be accounted for by the assumption that, as the concentration of each liquid becomes less, its ability to scatter light and to polarize the scattered light increases. This assumption would help to collate the behavior of liquids with that of gases, for a comparison of our results for liquids with those of Strutt and Cabannes for gases shows that gases scatter more light, and also polarize the scattered light to a greater degree, than do the same substances in the liquid state.

#### 4. The Ratio of Incident to Scattered Light

Lord Rayleigh in 1899 formulated the relations for the light scattered by a nearly transparent medium consisting of particles much smaller than the wave-length of light and distributed at random. His theory leads to the following relation:

$$I r^2 / E V = \frac{\pi^2 (\mu^2 - 1)^2}{2 n \lambda^4}$$

where  $\lambda$  is the wave-length of the light,

$\mu$  the refractive index of the medium,

$n$  the number of scattering particles per unit volume,

$V$  the volume of substance under observation,

$I$  the intensity of the scattered light at a distance,  $r$ , in a

direction perpendicular to that of the exciting beam,  $E$  the intensity of the exciting beam itself.

Measurement of the ratio  $I/E$  for a given wave-length of light leads therefore to a value of  $n$ . This value Cabannes<sup>1</sup> has recently determined for argon gas to be  $3.08 \times 10^{19}$ , a value in excellent agreement with the values of  $n$  for a gas deduced from other experiments.

*Measurement of the Ratio  $Ir^2/EV$  for a Liquid.*—The difficulty of the measurement is that the ratio is extremely small. To overcome this difficulty the ratio  $I/E$  was first determined for a piece of milk-glass with a ground surface. This was done by means of the photometric arrangement shown in Figure 4.

The source of light  $S$  was a mercury vapour lamp at equal distances from  $A$  and  $B$ .  $A$ ,  $B$  and  $C$ , all similar pieces of ground milk-glass, are parallel to one another and at an angle of 45 degrees to  $SB$ . The glass  $B$  is illuminated directly by  $S$ , but the glass  $C$  is illuminated only by the light from a certain area of  $A$  outlined by a circular aperture,  $H$ .  $B$  and  $C$  are seen side by side through a circular aperture,  $D$ , and the brightness of  $B$  is made to match that of  $C$  by a photometric wedge,  $W$ , and a whirling disc,  $K$ , with a small measured sector cut out.  $C$

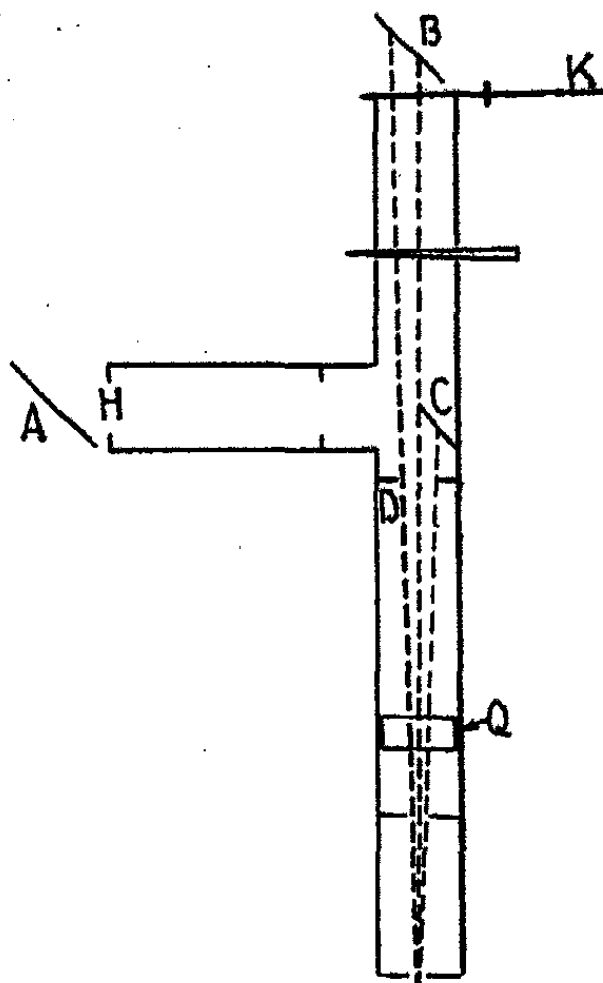


Fig. 4

and  $B$  were seen through two cells  $Q$ , one containing ammoniacal copper sulphate and the other quinine sulphate solution, so that together they were transparent only to the mercury line

<sup>1</sup> Jour. Phys. Rad., (6) 1, 129 (1920). See also Ann. Phys., 15, 5 (1921).



4358 Å. Since A and B are similar pieces of glass and equally illuminated, we have measured the ratio  $I/E$  for the glass A. The value  $I/E$  for the milk glass was found to be 0.00289, where  $r = 30.7$  cm. The aperture N was 28.6 cm from C and had an area of  $1.50^2\pi$ .

Some freshly distilled carbon bisulphide<sup>1</sup> (used because it scatters relatively so much light) was placed in a flat-walled cell and illuminated by a beam from a mercury vapour lamp. The intensity of the scattered light from a column of this liquid 2.80 cm in depth was measured and compared with that of the piece of milk-glass in place of the carbon bisulphide and at an angle of  $45^\circ$  to the exciting beam. When the glass plate was measured, the light which illuminated it traversed a parallel-sided glass cell filled with carbon bisulphide to compensate for the loss by reflection of the exciting light on entering and of the scattered light on leaving the glass cell containing the carbon bisulphide. The line 4358 Å was isolated as before by absorbing solutions.

The ratio  $\frac{\text{carbon bisulphide}}{\text{milk-glass}}$  was found to be 0.00113.

Next the light scattered by the same sample of carbon bisulphide in a cross was compared by the usual method with that scattered by a sample of dust-free ether in a cross.

The ratio  $\frac{\text{ether (dust-free)}}{\text{carbon bisulphide}} = 0.068$ .

Therefore  $Ir^2/EV$  for dust-free ether =

$$\frac{0.00289 \times 0.001133 \times 0.7^2 \times 0.068}{1.5^2\pi \times \frac{30.7^2}{28.6^2} \times 2.80} = 9.2 \times 10^{-6}$$

*Comparison with Cabannes' Measurement for Argon Gas.—*  
Cabannes' value for the same ratio  $Ir^2/EV$  for argon<sup>2</sup> gas

<sup>1</sup> Carbon bisulphide may seem a poor liquid to choose because it is acted upon by light. During the course of the experiments, however, the light-scattering was quite constant. Whether or not the carbon bisulphide contained impurities has no bearing on the conclusions drawn regarding ether and water.

<sup>2</sup> The gas used was really a mixture of 91% argon and 9% nitrogen, but it has seemed unnecessary to make a correction here for this fact. The correction would at any rate amount to only one percent.

at 27°, 760 mm is  $1.34 \times 10^{-8}$ .

Since Strutt's<sup>1</sup> and Cabannes' results show that, for gases which completely polarize the scattered light, the intensity of the scattered light varies as the square of the refractivity, therefore for gaseous ether<sup>2</sup> calculated at 27° and 760 mm

$$I_r^2/EV = \frac{0.00154^2}{0.000285^2} \times 1.34 \times 10^{-8}; \text{ and if liquid and gaseous}$$

ether scattered light in proportion to their densities, the value of  $I_r^2/EV$  for liquid ether at room temperature would be

$$\begin{aligned} & \frac{0.00154^2}{0.000285^2} \times 1.34 \times 10^{-8} \times 237 \\ & = 9.27 \times 10^{-6} \end{aligned}$$

The observed value is therefore about one-tenth<sup>3</sup> of the value calculated on the assumption that the light-scattering of gaseous and liquid ether are in proportion to their densities.

Strutt has compared with gaseous ether a sample of liquid ether freed of dust by shaking with water. He found that such ether scattered one-seventh as much light as did the same amount of ether in the gaseous state. We find that a sample of ether shaken up with water scatters about 1.7 times as much light as our best dust-free ether. This would make dust-free ether 11.9 times less than gaseous ether, a ratio in fairly good agreement with our ratio 10.

It is hoped shortly to increase the accuracy of the above measurements, and to make similar measurements for other wave-lengths of light. Such measurements would put to a strict test the inverse fourth power law for liquids.

*The Relation of the Above Result to Some Deductions Which have been made regarding the Value of n for Liquid Water.—* The above result has considerable importance in relation to

<sup>1</sup> Proc. Roy. Soc., 95A, 155 (1919).

<sup>2</sup> *Ibid.* 84A, 13 (1910); Wied. Ann., 11, 70 (1880).

<sup>3</sup> This ratio may now be easily obtained for any liquid for which we have given the relative light-scattering (Table I). For the various alcohols and aliphatic compounds the ratio is of the same order of magnitude as for ether. For benzene and its derivatives the ratio is about one-fifth, while for carbon bisulphide the ratio is about two-thirds.

some calculations made by Fowle,<sup>1</sup> based on certain measurements by Ewan and Aschkinass of the coefficients of absorption of light by liquid water.<sup>2</sup> To quote from Fowle: "For these wave-lengths (0.2 to 0.5  $\mu$ ) therefore liquid water scatters transmitted radiation just as would the same amount of water in gaseous state according to Rayleigh's theory."

Now the observed ratio of the scattered light for water (liquid)/ether (liquid) is 0.192.

Therefore  $I_r^2/EV$  for liquid water (observed) =  
 $0.192 \times 9.20 \times 10^{-6} = 1.77 \times 10^{-6}$

Now  $I_r^2/EV$  for water vapour calculated at 27° and 760 mm from Cabannes' and Strutt's results =

$$\frac{0.000253^2}{0.000285^2} \times 1.34 \times 10^{-8} = 1.06 \times 10^{-8}$$

Multiplying this value by the ratio of the density of liquid water to that of the vapour as would be required for the application of Rayleigh's theory to liquid water:

$$I_r^2/EV \text{ for liquid water (calculated)} = \\ 1370 \times 1.06 \times 10^{-8} = 1.44 \times 10^{-6}$$

It would appear then that a wrong interpretation has been placed on the results of Ewan and Aschkinass since our observed value is about ten times less than would be the case if the liquid and gas scattered light in proportion to their densities.<sup>3</sup>

The conclusions drawn by Fowle are placed in doubt also on other grounds. The water used by Ewan in his extinction-

<sup>1</sup> Smith. Mis. Coll., 69, No. 3 (1918).

<sup>2</sup> Proc. Roy. Soc., 57, 117 (1894); Wied. Ann., 55, 401 (1895).

<sup>3</sup> It seems worth while to quote here from Lord Rayleigh (Phil Mag., 47, 375(1899)) on the application of his formula to the light-scattering by liquids: "It is more than doubtful whether the calculations are applicable to such a case (the case of a liquid or a solid), where the fundamental supposition, that the phases are entirely at random, is violated. When the volume occupied by the molecules is no longer very small compared to the whole volume, the fact that two molecules cannot occupy the same space detracts from the random character of the distribution. And when, as in liquids and solids, there is some approach to a regular spacing, the scattered light must be much less than upon a theory of random distribution."

coefficient measurements was prepared by distillation in a block tin condenser in the presence of air and must have contained a good deal of dust. Fowle's reason for assuming that all the absorption was due to scattering was that the absorption-coefficients for the various wave-lengths considered followed the inverse fourth power law. But this would also be true for scattering by fine dust particles. There is, moreover, no good reason to assume that the light of the shorter visible wave-lengths has no heating effect. It is indeed true that there are no absorption bands in this region of the spectrum; but there may easily be some slight heating effect general throughout the spectrum and increasing for the shorter wave-lengths so as to make no great deviation of the extinction-coefficients from the inverse fourth power law.

It would be very interesting to study the light-scattering of some gases near the critical conditions. R. J. Strutt gives results for carbon dioxide at high pressures which indicate that for the pressures and temperatures at which he worked the scattering was proportional to the density of the gas. If this be true some rather sudden departure from this relationship must occur at or near the critical point.

The authors have in prospect the measurement of some extinction-coefficients for dust-free water and other liquids to obtain further evidence on this disputed question.

#### Summary

1. The relative intensity and the polarization of the light scattered by various liquids have been measured with an accuracy greater than that attained in our previously published papers. This increased accuracy was made possible by the use of cross-shaped containers with sealed-in, flat, glass end-plates in place of the bulbs used heretofore.

2. Measurements of the light scattered by two-component liquid solutions show that the relative intensity of the scattered light is always somewhat greater than that calculated on the assumption that the scattered light is an additive property for the two liquids.

Liquids which polarize the scattered light very far from completely show, on dilution, much more nearly complete polarization.

3. Measurements of the ratio of the intensity of incident light to that of scattered light have been made for liquids. The results show that ether and water scatter about one-tenth as much light as do the same weights of these liquids in the gaseous state. For benzene and its homologues the ratio is about one-fifth.

The authors wish to express their thanks to Professor F. B. Kenrick for the great interest he has taken in the work, and especially for his help in overcoming the experimental difficulties which have been encountered.

[Note received December 14. Since the manuscript of this article was sent forward the ratios of exciting to scattered light have been measured also for mercury green and sodium yellow lines. The same method was used as is described above for  $\lambda$  4358Å. A comparison of these ratios for the three wave-lengths shows that the intensity of the scattered light varies inversely as the fourth power of the wave-length.]

*Chemical Laboratory  
University of Toronto  
June, 1921*

## NEW BOOKS

**Chemical Warfare.** By Amos A. Fries and Clarence J. West. 20 × 15 cm; pp. XI + 445. New York and London: McGraw-Hill Book Company, 1921. Price: \$3.50.—In the preface the authors say that "shortly after the signing of the Armistice, it was realized that the story of Chemical Warfare should be written, partly because of its historical value and partly because of the future needs of a text-book covering the fundamental facts of the service for the Army, the Reserve Officer, the National Guard, and even the Civilian Chemist. The present work was undertaken by both authors as a labor of patriotism and because of their interest in the Service. . . . Those familiar with the work of the Chemical Warfare Service will discover that the following pages contain many statements which were zealously-guarded secrets two years ago. This enlarged program of publicity on the part of the Chief of the Service is being justified every day by the ever-increasing interest in this branch of warfare. Where five men were discussing Chemical Warfare two-years ago, fifty men are talking about the work and the possibilities of the Service today. It is hoped that the facts here presented may further increase the interest in Chemical Warfare, for there is no question but that it must be recognized as a permanent and very vital branch of the Army of every country. Reasons for this will be found scattered through the pages of this book."

No two men are better qualified than the authors to write such a book, General Fries because of his first-hand knowledge of the use of gas in actual warfare, and Major West because of his unequalled knowledge of the reports issued by the Allies and the United States. The result is what might have been expected, an admirably written, well-balanced book which covers the ground thoroughly and in an interesting manner. The reviewer has been interested to note that the book strikes army officers who are not chemists just as favorably as it does those who know chemistry at first hand and war only from books. It is to be hoped that this book will get the wide circulation that it deserves.

The headings of the chapters are: the history of poison gases; modern development of gas warfare; development of the Chemical Warfare Service; the Chemical Warfare Service in France; chlorine; phosgene; lachrymators; chloropicrin; "mustard gas;" arsenic derivatives; carbon monoxide; development of the gas mask; absorbents; testing absorbents and gas masks; other defensive measures; screening smokes; toxic smokes; smoke filters; signal smokes; incendiary materials; the pharmacology of war gases; chemical warfare in relation to strategy and tactics; the offensive use of gas; defense against gas; peace time uses of gas; the future of chemical warfare.

Dundonald's proposal to use sulphur dioxide in the Crimean War is given and also an account of Shenstone's mask, p. 7. Lewisite comes in for a mention pp. 23, 188. The account of the development of the gas mask is excellent and so is the story of the development of Edgewood Arsenal. It was a pleasure to see the recognition given to the foresight and energy of Manning, p. 32. Many will enjoy the account of the Chemical Warfare Service in France, p. 72, and all will read the chapter on strategy, p. 363. The use of phosphorus against ma-

chine gun nests, p. 393, was one of the distinctly interesting developments of the war. The illustrations are excellent and the reviewer was glad to see the two cartoons, pp. 66, 223.

As a sample of the book we can take the remarks, p. 334, on signal smokes. Screening smokes were developed for protection and for cutting off the view of observers in aeroplanes and balloons. This use of smoke, coupled with the deadly fire of machine guns and high explosives, forced men to take shelter in deep shell holes, in deep trenches and other places that were safe, but which made it nearly impossible to see signals along the front of battle.

"Every man can readily be taught to read a few signals when clearly indicated by definite, sharply-defined, colored smokes. At first these were designed for use on the ground and will be used to a certain extent in the future for that purpose, particularly when it is desired to attract the attention of observers in aeroplanes or balloons. In such cases a considerable volume of smoke is desired. For the man in the trench or shell hole some means of getting the signal above the dust and smoke of the battlefield is needed. It is there that signal smokes carried by small parachutes, contained in rockets or bombs, have proven their worth. These signals floating high above the battlefield for a minute or more, giving off brilliantly colored smokes, afford a means of sending signals to soldiers in the dust and smoke of battle not afforded by any other method so far invented. As before stated, every man can be taught these simple signals, where but very few men can be taught to handle even the simplest of wireless telephones.

"Thus smoke has already begun to complicate, and in the future will complicate still more, every phase of fighting. It will be used for deception, for concealment, for obscuring vision, for signaling and to hide deadly gases. The signal rocket will be used to start battles, change fronts, order up reserves, and finally to stop fighting.

"The signal smokes by day will be displaced at night by brilliantly colored lights which will have the same meaning as similarly colored smokes during the day. Thus, literally, smoke in the future will be the cloud by day and the pillar of fire by night to guide the bewildered soldier on the field of battle with all its terrors and amidst the confusion, gas, smoke and dust that will never be absent while battles last."

There is a foot-note on p. 285 which might well be changed in the next edition. The authors say that "while it is a well-known fact that black smoke is not as efficient as white smoke for screening purposes, the reason for this fact is not clear." With white smoke we get a certain amount of diffuse reflection from the front of the cloud which serves to blur the image behind the cloud. This disturbing factor is absent with black smoke. The phenomenon is quite familiar to the aviator who wishes to photograph through haze. Since the light scattered by the haze consists largely of the shorter wave-lengths, the aviator puts a red screen over the lens of his camera, thereby cutting off the disturbing light and thereby making it possible to take photographs in a way that he could not possibly do without the red screen. Tyndall has shown that the light scattered by haze is mostly polarized and that a mountain which is invisible to the naked eye can be seen by looking through a Nicol prism. It is probable that the



difference in the screening powers of white and black smokes would disappear if one used a Nicol prism.

There was one lesson which the war taught the Chemical Warfare Service and which should have been emphasized more strongly in the book. That was the need for more adequate co-operation between the home and the foreign services. Things cannot be handled adequately by cable or by letter. There should have been a constant stream of good officers going from the United States to France and staying there for a month or six weeks. In that way the various divisions could have been kept in touch with affairs at the front. That would have made life much easier for General Fries in France and would have made a world of difference at home. Until Col. Lewis returned, there had been no chemists coming back who knew anything about gas warfare. There was obviously nothing of any value to be got out of young engineer officers no matter how capable they were. From the beginning to the end of the war, there was a painful lack of adequate contact between the two branches of the Chemical Warfare Service. The War Department never appreciated that written communications are always inadequate and that one officer differs from another in what he knows or can tell.

*Wilder D. Bancroft*

*Contemporary Science.* By Benjamin Harrow. 17 X 11 cm; pp. 253. New York: Boni and Liveright, 1921. Price: \$1.00.—In the preface the author says that "the men who have been good enough to co-operate with me in the preparation of this volume are masters of their respective subjects: what they say represents, in summary form, some of the latest achievements in science. The book does not pretend to be an exhaustive treatise, but it does claim to review some of the more recent and more suggestive work."

The subdivisions are: Introduction, by Benjamin Harrow; Modern Physics, by R. A. Millikan; The Structure of Atoms and its Bearing on Chemical Valence, by Irving Langmuir; Engineering before and after the War, by Sir Charles Parsons; Methods of Gas Warfare, by S. J. M. Auld; What are Enzymes? by Benjamin Harrow; Natural Death and Duration of Life, by Jacques Loeb; The Physiology of the Aviator, by Yandell Henderson; Twenty-five Years of Bacteriology, by Simon Flexner; Before and after Lister, by W. W. Keen; The Measurement and Utilization of Brain Power in the Army, by R. M. Yerkes; Conceptions and Misconceptions in Psychoanalysis, by Trigant Burrow; Einstein's Law of Gravitation, by J. S. Ames.

Millikan cites the following ten discoveries as the ten most important advances in physics of the last twenty years: the verification of the atomic and kinetic theories; the divisibility of the atom; radio-activity; the atomicity of electricity; the electrical origin of mass; the nucleus atom; the nature of X-rays; crystal structure; the atomic numbers; the quantum relations.

Sir Charles Parsons states, p. 56, that before the war, the estimated cost of sinking a shaft to a depth of twelve miles was five million pounds and the time required about eighty-five years. When we consider that the estimated cost at present-day prices is not much more than the cost of one day of the war to Great Britain alone, the expense seems trivial as compared with the possible knowledge that might be gained by an investigation into this unexplored re-



gion of the earth. In Italy, at Lardarello, bore holes have been sunk, which discharge large volumes of high-pressure steam, which is being utilized to generate about 10,000 horse-power by turbines.

Under enzymes, p. 83, we read that Bertrand has adopted a dual conception of the enzyme, also shared by Armstrong. "One of the constituents is capable of producing to a slight degree on its own account the chemical reaction associated with the particular enzyme in question; but requires its activity to be augmented by the presence of another substance—inactive in itself—before its action becomes appreciable. The former may consist of acid, alkali, calcium or magnesium salt, etc. The latter component is more complex, usually protein-like (egg-white, for example), and colloidal." Falk considers that the inactivation of lipases is due to an internal rearrangement of certain of the atoms in the molecule of the enzymes.

Jacques Loeb says, p. 90, that "the effect of temperature on the length of life of the fruit fly is the same as the influence of temperature on the velocity of a chemical reaction, inasmuch as a lowering of the temperature by ten degrees results in an increase in the duration of life by two or three hundred percent, and the same figure would be obtained if we investigated the effect of temperature upon the time required to complete a chemical reaction. At 30° the flies live on an average 21.15 days, at 20° they will live on an average 54.3 days or a little over twice as long. At 25° they live 38.5 days and at 15° 123.9 days or about three times as long. The fruit fly is a tropical organism and 30° is not far from the optimal temperature. By lowering their temperature twenty degrees we prolong the duration of their life by nine hundred percent. We cannot lower the temperature below 10° since the flies suffer in the chrysalid stage when the temperature becomes 10° or less. While these are thus far the only experiments on the duration of life of higher organisms carried out with the necessary scientific precaution, there are many casual observations mentioned in the literature which suggest that lowering the temperature prolongs the duration of life of lower animals in general.

"The body temperature of a normal human being is constant, namely about 37.5° and this temperature remains the same in the tropics and in the arctic regions. Human beings and most mammals differ in this respect from insects whose temperature is as a rule practically that of their surroundings. If it were possible to reduce the temperature of human beings and if the influence of temperature on the duration of life were the same as that in the fruit fly, a reduction of our temperature from 37.5° to about 16° would lengthen the duration of our life to that of Methusaleh; and if we could keep the temperature of our blood permanently at 7.5° our average life would (on the same assumption) be lengthened from three score and ten to about 27 times that length, *i. e.*, to about nineteen hundred years. Unfortunately our body does not tolerate any considerable lowering of its temperature and if it did, life at so low a temperature would probably become very monotonous and uninteresting since in all probability sensations of pleasure as well as pain, of joy and of sadness, would be at a very low level.

"The experiments on aseptic flies therefore lend support to the idea that the duration of our life is the time required for the completion of a chemical reaction or a series of chemical reactions. If these reactions consist in the grad-

ual accumulation of harmful products in our body, or in the gradual destruction of substances required for a youthful condition, we understand why a senile decay and death are the natural result of life."

When discussing the physiology of the aviator, Yandell Henderson says, p. 100, that the "influence of low barometric pressure is not mechanical but chemical. Life is often compared to a flame; but there are marked differences, depending upon the peculiar affinity of the blood for oxygen. A man may breathe quite comfortably in an atmosphere in which a candle is extinguished. The candle will burn with only slightly diminished brightness at an altitude at which a man collapses. The candle is affected by the proportions of oxygen and nitrogen. The living organism depends solely upon the absolute amount of oxygen—its so-called partial pressure."

On p. 112 he says that "it is particularly interesting to note that when the breathing test is pushed beyond the limit that the man can endure, be it the equivalent of only 10,000 or 25,000 feet, two different physiological types with all gradations between them are revealed. The fainting type collapses from circulatory failure and requires an hour or two to recover. Often the heart appears distinctly dilated. The other and better type, on the contrary, goes to the equivalent of a tremendous altitude on the rebreathing apparatus and loses consciousness, becoming glassy-eyed and more or less rigid, but without fainting. When normal air is administered such men quickly recover."

On p. 126 Flexner says that "time has taught the distinction between the two varieties of infectious disease and their corresponding immune states, according as their main effects and symptoms arise from the toxalbumins or poisons we have been considering, or the intimate presence within the organs of the microbes themselves. The former variety chances indeed to be in the minority, and hence it has come about that the diseases to be successfully combated by antitoxins are few in number, while those in which the microbes penetrate deeply into the body and which poison its tissues by means of so-called endotoxin, are far more numerous. The latter class includes such important diseases as tuberculosis, typhoid fever, meningitis, plague, cholera, the septicemias, and still others. And yet the failures have been only partial and success has been and is still being won against odds which were once considered insuperable."

On p. 133 Flexner says: "Hypersensitiveness may exist independently of purposive artificial sensitization, and some of the most important examples of that condition have been observed in man. Because of their size, perhaps for other reasons, human beings even when sensitive react to parenteral injection of native proteins less severely than the smaller animal species. And yet lamentable instances, if very few in number, of serious and even fatal anaphylactic effects have been observed in man. These have occurred especially in connection with the therapeutic employment of curative serums derived from the horse. The greatest danger from this source is at the time of the first injection, for while severe effects do sometimes follow upon a second or subsequent injection, they have never been attended by fatal consequences. Luckily, means are known for anticipating these even in frequent accidents, and of guarding against their dangers without at the same time depriving those in need of the benefits of serum protection of therapy.

"Besides the active state of sensitization another is known which may be termed negative. Thus it has been found that when a sensitive animal is given an injection of a protein which produces a certain degree of anaphylactic effect but not a fatal outburst, the treated animal can for a time be rendered insensitive. And thus human beings who are sensitive, say to horse serum, may be desensitized by means of successive small inoculations of the diluted serum, and, while in the refractory state thus induced, receive without risk larger injections of the serum.

"On the other hand, lesser states of anaphylaxis in man are by no means infrequent. To them belong the rashes of "serum sickness" following the injection of curative serums which while annoying are not dangerous, and the very disagreeable manifestations of hay fever and its allied conditions, now attributed to the action of vegetable materials, pollens chiefly, upon the sensitized mucous membranes of the nose and throat. Recent studies by Auer have shown that animals sensitized with harmless proteins, such as horse serum, develop severe local inflammations when from any local cause an extrusion of the antigen-containing fluid of the blood is enabled to penetrate the extravascular tissues; and on the basis of this observed fact he has suggested that functional disturbances of many organs of the body in sensitive human subjects may be brought about in a similar manner."

Dr. Keen gives some awful figures, p. 162, as to infections after amputations of arm, forearm, thigh, and leg before the time of Lister. Of 2089 such amputations in hospitals, 855 died or 41 percent. Of 2098 in country practice, 222 died or 10.8 percent. The difference is due to the crowding and lack of sanitation in the hospitals of that day. In the large Parisian hospitals 62 percent died after these amputations and 11 percent after amputations in isolated rooms in country practice.

*Wilder D. Bancroft*

*A Textbook of Inorganic Chemistry for Colleges. By James F. Norris. 20 X 15 cm; pp. VIII + 677. New York: McGraw-Hill Book Company, 1921. Price: \$3.50.*—In the preface the author says: "For a number of years the author of this textbook had the opportunity to teach students who were beginning the study of chemistry. His experience, acquired in the recitation room and in the laboratory, led him to the view that the average student finds it difficult to understand many of the apparently simple concepts of the science. It appears, therefore, to be an interesting task to attempt to present the material commonly treated in elementary books on chemistry in a form which could be reasonably well followed by the student through private study and with the smallest amount of explanation on the part of the teacher. Since this book has been written from this point of view, the subject has been developed slowly, and the consideration of the more abstruse material has been deferred until the student has gained some familiarity with chemical phenomena and with the language of the science. No attempt has been made at conciseness in the discussion of important principles. Analogies have been repeatedly pointed out in an endeavor to indicate to the student the way in which he should classify the facts brought to his attention.

"The aim of the author has been to present the general principles underlying the science; as a consequence, chemical phenomena have been discussed from the standpoints of both matter and energy. The law of mobile equilibrium

in its broadest sense has been used repeatedly in interpreting many important acts. The more elementary parts of thermochemistry and electrochemistry have also been emphasized. In fact, physical chemistry has been drawn on frequently, but an endeavor has been made to limit its use to the elucidation of the more important facts of inorganic chemistry."

This is praiseworthy and the book is interesting reading to the chemist. It brings up the old question as to the proper order of treatment. Should the atomic theory, chemical equations, and the measurement of gases, come in the first eighty pages with nitrogen and the atmosphere on p. 284, or should it be the other way round? The reviewer's temperament inclines him always to a deductive rather than to an inductive presentation of any subject; but that is a question of the science and not of the student. It is by no means certain that a systematic and logical presentation of a subject is the best for a beginner. That is the goal towards which the advanced man is striving. It seems to the reviewer that a book on introductory chemistry should begin with air and water, and that the quantitative gas laws should be put as late in the book as possible. There are few things which disgust the student more than the gas laws and the balancing of equations, the two things which are fetishes to the instructing staff. Perhaps the student is wrong in this and perhaps it is really good for him to get the worst things at the start; but one would feel more certain of this if somebody had tried the other method intelligently and had failed. We do know that the teaching in the schools and the colleges is wrong in one respect, that it knocks out of the boy the heaven-sent gift of asking why. Perhaps the inductive, or so-called scientific method is the best for the beginner, though it is admittedly not the quickest way of getting a knowledge of the subject. There is a story that Louis Agassiz was once asked whether he began his lectures with a statement of the fundamental laws and he answered that he began with a bushel of clams. Agassiz was one of the greatest teachers we have ever had and perhaps even the chemist could learn something from him.

Whatever we may decide as to the merits of the type, Mr. Norris has done the work he planned in an admirable way. There are one or two slips but they are of relatively little importance. The explanation that nature abhors a vacuum was not put forward to account for the fact that water cannot be raised more than thirty-four feet by a suction pump, p. 284. The Castner cell is a cell with a mercury diaphragm and not with a mercury cathode as drawn, p. 519. While it is true, p. 545, that metallic gold in the colloidal condition gives a ruby glass, it would have been helpful to the student to have told him that most ruby glass contains copper and not gold. The reviewer doubts whether the hardness of glass is the most important factor in keeping it from crystallizing, p. 544. There seems to be a surplusage of ciphers in the statement, p. 647, that gratings have been made by ruling 200,000 lines to the inch.

The reviewer learned something from the statement about long flames, p. 207. The statement in regard to rusting, pp. 462, 618, is the best that the reviewer recalls.

"The metals down to and including copper are more or less affected by contact with the air; either an oxide is formed or, in certain cases, the presence in the air of carbon dioxide leads to the production of insoluble basic carbonates. Whether or not the metal is appreciably corroded is determined by the physical

properties of the rust formed. In the case of aluminum, for example, the superficial coating of hydrated oxide adheres firmly and as it is very thin it scarcely alters the appearance of the metal; with magnesium, however, another active metal, the result is different, for the basic carbonate formed is light and does not adhere so firmly, and as a consequence, the metal is slowly disintegrated. Nickel, cobalt, and tin are affected to only a slight degree if at all; zinc becomes covered with a thin coating of basic carbonate, which resists further action and is, therefore, permanent in the air. Lead becomes coated with a very thin adhering layer of basic carbonate and resists further corrosion. A clean surface of copper oxidizes rapidly in the air, but the coating of the oxide formed is so thin it only slightly deepens the color of the metal; it is very permanent in ordinary air.

"The behavior of iron is quite different; in this case the oxide formed is a powder the density of which is less than that of iron; when it is formed it occupies more space than the metal from which it was produced, and, therefore, falls away from the surface, leaving freshly exposed metal to be acted on farther and the rusting continues more or less rapidly."

"The presence of 'mill scale,' which is the oxide formed on the surface of the hot metal when it is worked, markedly increases the rate at which iron rusts. The scale is brittle and when it cracks and leaves a surface of iron exposed, a couple is set up and the metal is corroded. Rust itself forms a couple with pure iron and when it is once formed the corrosion proceeds more rapidly. It has been shown that the rate of rusting during the second year is about twice as fast as during the first year. Unused railroad rails rust more rapidly than those from which the rust is removed by the jarring produced by the passage of cars over them. When iron is strained in any way it assumes a different potential from that of the unstrained metal, and, as a result corrosion is greater in the neighborhood of punched holes than around holes drilled in the metal. Corrosion takes place where the metal has been scratched by a file or struck with a heavy tool.

"Since oxygen is involved in the corrosion of iron, the metal rusts very slowly when it is immersed in deep water, which contains but a little of the gas. Rain water, which is saturated with oxygen and carbon dioxide affects iron very rapidly."

*Wilder D. Bancroft*

*Organic Compounds of Mercury.* By Frank C. Whitmore. 23 X 15 cm; pp. 397. New York: The Chemical Catalog Company, 1921. Price: \$4.50.—This is another one of the American Chemical Society monographs. In the preface the author says: "Originally the writer hoped to include in the present monograph all of the organic compounds which contain mercury in any form. It soon became evident that the work could not be all-inclusive. Attention will therefore be confined entirely to the true organic mercury compounds in which mercury is attached directly to carbon. These substances have practically none of the properties of mercuric salts. The O—Hg compounds such as the salts of the organic acids, the N—Hg compounds such as the mercury acid amide compounds, and the S—Hg compounds such as the mercuric mercaptides will be touched on very lightly as most of their properties are the properties of inorganic mercury salts. The great mass of biological and pharmacological studies which have been made on organic mercurials will not be included both because of lack of space and because of the unsatisfactory condition of the literature of this phase of the

subject. Another subject of considerable interest which cannot be discussed is the host of 'double compounds' of mercury compounds and organic substances. These subjects which are not discussed are made available for further study by the supplementary bibliographical lists in the Appendix. In this way the writer has attempted to include in one form or another all of the material which has been gathered in the preparation of the work."

The subject is treated under the general heads: historical outline; general methods of preparing organic mercury compounds; general properties and reactions of organic mercury compounds, alkyl mercury compounds; mercury compounds obtained from olefines and acetylenes; mercury compounds from saturated and unsaturated alcohols; mercury derivatives of fatty acids and related compounds; mercury derivatives of aldehydes, ketones, amides, and related compounds; mercury derivatives of aromatic amines; mercury derivatives of phenols, naphthols, and related compounds; mercury derivatives of aromatic acids; mercury derivatives of aromatic ketones, terpenes, and related compounds; mercury derivatives of heterocyclic compounds, azo compounds, and aromatic arsenicals.

From this outline it appears that the field is enormously larger than most of us realized. It might be thought that there would be little in a volume like this to appeal to the physical chemist; but a glance through the pages will dispel that belief very promptly.

The formation of methyl mercuric iodide in sunlight, p. 26, seems to be a clear case of dissociation of the methyl iodide prior to reacting with the mercury and somebody ought to determine the exact wave lengths which bring about the reaction. On p. 24 we read that L. W. Jones "advanced evidence to show that the two benzyl groups in mercury dibenzyl are of opposite charge, because they are removed by hydrolysis in the form of toluene and benzyl alcohol, respectively.

This would indicate that the mercury atom is  $\overset{+}{\text{Hg}}\overset{-}{\text{I}}$ , at least at the instant splitting takes place. This is in harmony with the fact that the mercury appears as the free metal at the end of the reaction."

On p. 88 is the very interesting statement that "methyl mercuric halides electrolyzed in liquid ammonia solution give a fine black deposit on the cathode. This deposit is a good conductor of electricity but does not amalgamate with mercury. When allowed to come to room temperature, it decomposes suddenly with the evolution of heat, forming mercury and mercury dimethyl. The free methyl mercury group can also be obtained as fine black flakes by electrolyzing a water or alcohol solution of methyl mercuric chloride."

The reviewer was also much interested in the following paragraphs, pp. 118, 137, 155:

"Acetylene reacts with solutions of mercuric salts giving extremely insoluble amorphous precipitates. When these precipitates are treated with mineral acids, acetaldehyde is produced. This reaction, first discovered by Kutscheroff, has become very important as a means of producing ethyl alcohol and acetic acid from acetylene. The nature of the organic mercury compounds first formed is by no means settled although many chemists have proposed formulas for them. The problem is of theoretical rather than immediate practical interest as the mercurated products are not isolated but are continuously changed to



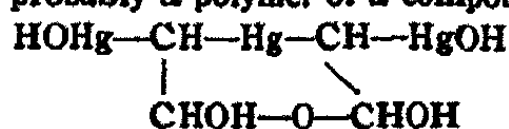
acetaldehyde by the acid present during this formation. The rôle of the mercury salts thus becomes that of catalysts. Among the formulas which have been suggested for the intermediate mercury compounds obtained from acetylene and mercuric chloride are  $\text{Cl}-\text{CH}=\text{CH}-\text{HgCl}$  and  $(\text{ClHg})_2:\text{C}-\text{CHO}$ . Monochloroacetylene reacts with mercuric chloride giving a product which is believed to be trichloromercuri-acetic acid. Acetylene reacting with a slightly acid solution of mercuric nitrate gives a substance believed to have the formula  $\text{Hg}:\text{C}(-\text{CHO})-\text{HgNO}_3$ .

"Other investigators interpret these products from acetylene as "double compounds" of acetylene or mercury acetylides with various amounts of mercuric salts, mercuric or mercurous oxide, and water. Complicated formulas are arrived at which agree with the analytical results. The chief difficulty in the study of these compounds is their extreme insolubility which prevents their purification. Moreover the composition of the precipitates obtained undoubtedly varies considerably with changing conditions.

"The hydration of acetylene to form acetaldehyde does not necessarily mean that the intermediate mercury compounds have an aldehyde structure. The hydration of the triple bond may merely be catalyzed by the mercuric ions in acid solution. Cases are known in which this hydration takes place under the influence of dilute acid alone. Such a case is that of piperonyl acetylene which gives the corresponding ketone on warming with dilute hydrochloric acid."

"Mercuric salts in alcohol add carbon monoxide in much the same way that they add to ethylene compounds. As in the case of all such reactions the products may be formulated as true structure compounds or as molecular addition compounds,  $\text{O}:\text{C}(-\text{HgX})-\text{OR}$  or  $\text{CO.Hg}(\text{OR})\text{X}$ . Neither formula explains all of the reactions. Acids and alkyl halides liberate carbon monoxide, a fact which throws doubt on the first formula. Various reactions give formic acid derivatives, a fact which is hard to explain by the second formula."

"Acetaldehyde reacts with mercuric oxide and alkali giving a substance  $(\text{C}_4\text{H}_6\text{O}_4\text{Hg})_x$  which is probably a polymer of a compound,



The same reagents give another product which is formulated as a mercury compound of vinyl alcohol,  $(\text{CH}_2=\text{CH}-)_2\text{Hg.HgO}$ ."

In an appendix, p. 365, the author gives what he considers the best method for determining mercury in organic compounds. He places the mercury compound in an iron crucible, covers it with a mixture of barium and sodium carbonates, and heats very gently. The volatilized mercury amalgamates with an inverted, superposed, gold crucible.

*Wilder D. Bancroft*

**Concentration by Flotation.** By T. A. Rickard. 23 X 15 cm; pp. XI + 692. New York: John Wiley and Sons, 1921. Price: \$7.00.—The book contains forty articles on flotation, five of which were published in book form in 1916, and seventeen in 1917, while the remaining eighteen have appeared only as journal articles. The titles of the articles are: the history of flotation; principles of flotation; the flotation of gold and silver mineral; flotation litigation (2); testing ores for flotation (2); flotation in a Mexican mill; flotation at the



### *New Books*

Central Mine, Broken Hill; cyanide treatment of flotation concentrate; disposal of flotation residue; flotation principles; the theory of flotation; the flotation of minerals; principles underlying flotation; molecular forces and flotation; the armor in flotation; theory of ore flotation; colloids; differential flotation; flotation at the Calaveras Copper; the disposal of flotation products; mechanical development in flotation; the flotation of oxidized ores; flotation at Cobalt, Ontario; cascade method of froth flotation; flotation of semi-oxidized silver ore; the development of flotation at the Broken Hill Proprietary Mine, Australia; the Bradford process at Broken Hill; the flotation of galena at the Central Mine, Broken Hill; recovery of copper from flotation by leaching; the Horwood process as applied to the copper-zinc ore of the Aftersight Mine; a modification of Horwood's process for the treatment of copper-zinc ores; flotation practice of the Utah Copper Company; the smelting of flotation concentrate at Garfield; preferential flotation; froth flotation at Broken Hill; a résumé of the literature on the theory of flotation, with critical notes.

It would have been much better for the reader and would have saved much duplication if Mr. Rickard had worked this same material into a critical account of flotation; but that would have meant a great deal of work for him and one cannot blame him for dodging it. Mr. Rickard believes, pp. 31, 133, that the so-called bubbles process of the Minerals Separation Co., really grew out of the Froment process. That is the conclusion that most scientific men will reach, though it apparently cannot be proved legally. The reviewer does not agree with the author that a lowering of the surface tension is an essential to the production of bubbles, pp. 2, 52. What is needed is a sufficiently viscous, probably plastic, surface film. It happens to be easier to secure this with substances which lower the surface tension of water; but that does not affect the general theory.

The need for critical discussion appears on most of the pages. Mr. Durell says, p. 254, that "it is not the air that is held dissolved, but it is the air that comes out, which is available for mineral attachment. A hypothesis based on nascent and occluded gas explains all kinds of flotation as well as flotation machines." This may be true; but the reviewer would like to have it explained just why nascent gas is necessary. In the same article, p. 262, Mr. Durell says "that an acid or any electrolyte creates osmotic pressure, by trying to enter the solid particles, of which their surfaces act as septums. If this pressure be sufficient to drive most of the gas out from the gangue particles, the metallic particles can be floated, for the reason that there is still left sufficient gas in them to become nuclei for bubble formation by the nascent gas of the liquid . . . Everyone who has experimented with flotation has seen how too much acid will 'kill' the float. That is, the greater osmotic pressure drives the air from the metallic particles as well as from the gangue particles. . . . In maintaining that osmotic pressure of an electrolyte is the cause of selective flotation, it is well to look into the motive power of osmosis. . . . However, all theories of flotation, be they electrical or otherwise, must come to osmosis for their solution."

The reviewer finds it very difficult to understand how electrolytes can diffuse into metallic copper, for instance, or why the surface of metallic copper should act as a septum under these circumstances. There seems to be no good reason to suppose that an electrolyte, as such, has anything to do with flotation.



The addition of an electrolyte may modify the flotation and make it more or less selective; but that is quite a different matter. Even, then, it is not clear what important part is played by osmosis.

Corliss and Perkins are undoubtedly right in saying, p. 347, that the reason why lime is less beneficial than caustic soda in the Callow process is because of the coagulating effect of the calcium ion. The effect of the cation has been overlooked by Free, p. 369, who points out that caustic potash in low concentrations deflocculates kaolin suspensions and flocculates it in higher concentrations. He is dealing with the antagonistic action of the hydroxyl ion which deflocculates the kaolin and of the potassium ion which flocculates. The first predominates at low concentrations because the hydroxyl ion is adsorbed more strongly at low concentrations than the potassium ion. After the adsorption of the hydroxyl ion becomes practically constant, the adsorption of the potassium ion goes on increasing thereby causing flocculation.

On p. 135 it is stated that Minerals Separation has brought suit against the Nevada Consolidated Copper Company and the Magma Copper Company on the bubbles patent, No. 835,120, and the soluble frothing agent patent, No. 982,678. Mr. Rickard says that "it is interesting to note that in these Nevada cases the plaintiff is claiming that pine-oil has certain soluble fractions, and that the use of pine-oil constitutes an infringement of both patents, 835,120 and 982,678. It remains to be seen how Minerals Separation will square its present position with the testimony in the Miami case, wherein its expert, Dr. Leibmann, said that pine-oil, for all practical purposes, was insoluble. . . . The legal definition of solubility will be awaited with interest, likewise the juridical effort to distinguish between the use of the term in chemistry and in metallurgy, respectively." Mr. Rickard also states his belief that "the validity of the patent for a soluble frothing agent should be fought to a finish and it should be ascertained what is a 'soluble frothing agent' and whether it is covered by the description of the oil in the first patent." While this point is essentially a legal one and not a scientific one, the trial is sure to help clear up the whole problem of ore flotation.

*Wilder D. Bancroft*

*An Introduction to General Chemistry.* By H. N. McCoy and Ethel M. Terry. Second edition. 24 X 16 cm; pp. X + 648. New York: McGraw-Hill Book Co., 1920. Price: \$3.00.—The first edition was reviewed just over two years ago (23, 659). The only changes in this edition are the correction of a few misprints and the addition of a chapter on metallurgy. The authors still spell cation wrongly, p. 234. On p. 587 the atomic number of sodium is given as ten instead of eleven. The slips pointed out previously by the reviewer were not misprints and consequently still stand.

The chapter on metallurgy takes up iron and steel, copper, lead, zinc, aluminum, gold, and silver. One does not see why the lead storage battery should come in under metallurgy. The reviewer doubts the statement, p. 626 that "Hall found that the electrolysis of the fused double fluoride of sodium and aluminum,  $3\text{NaF} \cdot \text{AlF}_3$ , which is found in Greenland as the mineral cryolite, gave melted metallic aluminum." Cryolite is a complex salt and not a double salt. It is the sodium salt of aluminofluoric acid and gives sodium when electrolyzed.

*Wilder D. Bancroft*

PHYSICO-CHEMICAL STUDIES OF STRONG AND  
WEAK FLOURS. II. THE IMBIBITIONAL  
PROPERTIES OF THE GLUTENS FROM  
STRONG AND WEAK FLOURS\*

BY PAUL FRANCIS SHARP AND ROSS AIKEN GORTNER\*\*

Introduction

In the first paper of this series Gortner and Doherty<sup>1</sup> undertook a study of certain physico-chemical properties of the glutens from strong and weak flours, inasmuch as the purely chemical method of attack by numerous other workers had not led to any consistent results. To be sure, Upson and Calvin<sup>2,3</sup> had previously investigated the colloidal swelling of gluten and had concluded that strong and weak glutens were determined by the effect of salts and acids upon the gluten colloids. Their reasoning was from analogy, however, rather than from actual experimentation with the two types of glutens. As a result of their own investigations Gortner and Doherty concluded that the postulations of Upson and Calvin did not hold, that acids and salts, while they influence the gluten markedly, are not the primary cause of weakness or strength but that there is an inherent difference in the colloidal properties of the gluten gel as laid down in the endosperm of the wheat berry, and that the colloidal properties of the glutens

\* Published with the approval of the Director as Paper No. 270 of the Journal Series, Minn. Agr. Exp. Sta. Presented before the Division of Biological Chemistry of the American Chemical Society at the Fall Meeting, Chicago, Ill., Sept. 9, 1920.

\*\* From the Division of Agricultural Biochemistry, Minnesota Agricultural Experiment Station, St. Paul.

<sup>1</sup> Gortner, R. A., and Doherty, E. H.: Hydration capacity of gluten from "strong" and "weak" flours. Jour. Agr. Res., 13, 389-418, Fig. 17, May 20 (1918).

<sup>2</sup> Upson, F. W., and Calvin, J. W.: On the colloidal swelling of wheat gluten. Jour. Am. Chem. Soc., 37, 1295-1304, Fig. 3, pl. 2 (1915).

<sup>3</sup> Upson, F. W., and Calvin, J. W.: The colloidal swelling of wheat gluten in relation to milling and baking. Nebr. Agr. Exp. Sta. Res. Bul., No. 8, Fig. 5, June (1916).

from strong and weak flours are not identical, even at the isoelectric point, and would not be identical even if the flours had originally had the same acid and salt content.

The problem therefore is a deeper one than merely a study of the action of salts or acids on the physical properties of a colloid. It is a theorem in colloid chemistry that a colloidal system has a "memory," that the colloidal behavior of an emulsoid sol or an emulsoid gel is dependent not alone upon its present environment but upon its past history, and it would seem that the past history of the gluten while it is being deposited in the endosperm of the wheat berry is the determining factor of a strong or of a weak flour.<sup>4</sup>

The historical treatment of the strong and weak flour question was considered in the first paper of this series and it is unnecessary to repeat it here. Such papers as bear upon the subject under consideration will be considered from time to time as later papers are prepared for publication.

Since the appearance of the paper by Gortner and Doherty, Ostwald<sup>5</sup> and Lüers<sup>6</sup> and Lüers and Ostwald<sup>7,8,9</sup> have published a series of papers on the colloid chemistry of bread. It is not our intention to discuss their data in the present paper,

<sup>4</sup> In our work on strong and weak flours we are coming to recognize at least three classes of weak flours, i. e., (1) weakness due to an adequate quantity of gluten but an inferior quality; (2) weakness due to an inadequate quantity of a good quality of gluten and (3) weakness due to factors influencing yeast activity, such as inadequate diastatic activity, acidity and amount of proteolytic enzyme, etc. The present paper and the definition above refer only to flours whose weakness is of the first type.

<sup>5</sup> Ostwald, W. O.: Beiträge zur Kolloidchemie des Brotes I. Über kolloidchemische Probleme bei der Brotbereitung. Koll Zeit., 25, 26-45, Fig. 1 (1919).

<sup>6</sup> Lüers, H.: Beiträge zur Kolloidchemie des Brotes III. Kolloidchemische Studien am Roggen- und Weizen-gliadin mit besonderer Berücksichtigung des Kleber- und Backfähigkeitsproblems. Ibid., 25, 177-196; 230-240, Fig. 5 (1919).

<sup>7</sup> Lüers and Ostwald, W. O.: Beiträge zur Kolloidchemie des Brotes II. Zur Viskosimetrie der Mehle. Ibid., 25, 82-90; and 116-136, Fig. 16 (1919).

<sup>8</sup> Lüers, H., and Ostwald, W. O.: Beiträge zur Kolloidchemie des Brotes IV. Zur Kenntnis von Mehlen schlechter Backfähigkeit. Ibid., 26, 66-67 (1920).

<sup>9</sup> Lüers, H., and Ostwald, W. O.: Beiträge zur Kolloidchemie des Brotes V. Die Kolloide Quellung des Weizenklebers. Ibid., 27, 34-37 (1920).

inasmuch as such a discussion properly belongs in the third paper of this series and will shortly be presented there.

Lüers and Ostwald<sup>9</sup> in a fifth paper call attention to the work of Upson and Calvin and state that their own results are in substantial agreement. They add that there may be a difference in the quality of the gluten from different flours, but that the quality is profoundly influenced by salts and acids present in the flour. These workers make no mention of the work by Gortner and Doherty and they, like Upson and Calvin, reason from analogy rather than from actual experiments made upon both strong and weak flours. While in many instances it is possible to reach valid conclusions by such a method, it is a rather dangerous procedure when the material in question is an emulsoid gel. The same criticism applies to certain of the conclusions of Henderson and his co-workers<sup>10,11,12,13,14</sup> in so far as their statements deal with flours of different baking strength where the *quality* of the gluten is the determining factor. For example, Cohn and Henderson<sup>10</sup> state, "The 'body' of the dough is supplied by the wheat gluten alone. The degree to which the dough can be distended therefore depends upon the amount and the hydration of the gluten." Whether or not this statement is intended to apply to flours of different baking strength or only to war breads where wheat flour is diluted with other cereal flours cannot be determined from the context.

It is impossible to determine from the data given in the papers of Henderson, et al. exactly what type of flours they

---

<sup>9</sup> Cohn, E. J., and Henderson, L. J.: The physical chemistry of bread making. *Science*, 48, 501-505 (1918).

<sup>10</sup> Cohn, E. J., Wolbach, S. B., Henderson L. J., and Cathcart, P. H.: On the control of rope in bread. *Jour. Gen. Physiol.*, 1, 221-230 (1918).

<sup>11</sup> Cohn, E. J., Cathcart, P. H., and Henderson, L. J.: The measurement of the acidity of bread. *Jour. Biol. Chem.*, 36, 581-586, Fig. 1 (1918).

<sup>12</sup> Henderson, L. J., Fenn, W. O., and Cohn, E. J.: Influence of electrolytes upon the viscosity of dough. *Jour. Gen. Physiol.*, 1, 387-397, Fig. 5 (1919).

<sup>13</sup> Henderson, L. J., Cohn, E. J., Cathcart, P. H., Wachman, J. D., and Fenn, W. O.: A study of the action of acid and alkali on gluten. *Jour. Gen. Physiol.*, 1, 459-472, Fig. 1 (1919).

worked with, for baking tests and flour analyses are lacking. However, from the form of the viscosity curves (13, Fig. 2, p. 391) it appears probable that flour "A" is markedly superior in gluten quality to the other three flours. At any rate their curves show that while viscosity may be *altered* by a change in hydrogen ion concentration, the initial viscosity of the dough is not determined *solely* by this factor. Of course it is possible that all of the flours possessed approximately the same *quality* of gluten, but that flour "A" had a greater *quantity*, in which case a higher initial viscosity would result. Unfortunately no nitrogen determinations are available, nor is the source or grade of the samples noted.

Martin<sup>15</sup> has recently carried out an investigation of some of the properties of wheat flour which he thought might be correlated with strength. He finds for the flours which he investigated that "flours with high gas-retaining capacities and high bakers' marks have been shown to be those in which the 'amended gliadin' figure is high." "For flours having a satisfactory gas-producing capacity, bakers' marks, gas-retaining capacity, and 'amended gliadin' content are closely related, and it is considered that the estimation of either of the latter together with the determination of the gas-producing capacity will indicate the 'strength' of the flour."

The amended gliadin figures as used by Martin were determined by subtracting from the percent of protein ( $N \times 5.7$ ) extracted from a sample of flour in a Soxhlet extractor by means of 50% alcohol, the percent of protein ( $N \times 5.7$ ) extracted from 25 grams of flour by 250 cc of water at 24-25°, the time of extraction being three hours.

It would be interesting to know whether or not the proteolytic enzyme activity *varied* with the different flours which Martin used. In one of the flours which he worked with he showed that there was appreciable proteolytic activity. He also pointed out that the diastatic activity varied with the

<sup>15</sup> Martin, F. J.: Properties affecting strength in wheaten flour. Jour. Soc. Chem. Ind., 39, 246-251 (1920).

flours used. If proteolytic activity varied this would influence the amount of water-soluble nitrogen and accordingly his "amended gliadin" values.

#### Experimental

*The Problem.*—Gortner and Doherty (p. 417) sum up their investigation on the hydration capacity of gluten as follows: "The difference between a strong and weak gluten is apparently that between a nearly perfect colloidal gel with highly pronounced physico-chemical properties, such as pertain to emulsoids, and that of a colloidal gel in which these properties are much less marked. It is suggested that such differences may be due to the size of the gluten particles and that at least a part of the particles comprising the weak gluten may lie nearer the boundary between the colloidal and crystalloidal states of matter than is the case with the stronger glutes."

The investigations reported in this paper and those which will follow were undertaken in order to put the above hypothesis to a test, and to see if other physico-chemical properties of the glutes from strong and weak flours could be correlated with flour strength.

Unfortunately none of the flours with which Gortner and Doherty worked were available for the present series of investigations. Consequently it became necessary to repeat at least a part of their work using gluten from new samples of flours in order that the comparative data for the present set of flours would be complete. The present paper is devoted to a consideration of the hydration or imbibitional properties of the new samples of flours. The following physico-chemical properties of the glutes are considered:

1. Imbibition in the presence of different strengths of lactic and hydrochloric acids.
2. Imbibition in the presence of different strengths of the following alkalies: potassium hydroxide, sodium hydroxide, calcium hydroxide, barium hydroxide and ammonium hydroxide.
3. The effect of M/200 sodium sulfate on the rate of imbibition in solutions of potassium and calcium hydroxide.

4. The optimum hydrogen ion concentration for the swelling of discs in the following acids: lactic, acetic, ortho-phosphoric, hydrochloric, and oxalic.

*The Material used.*—The strong flour used, B-780, was milled from northern spring wheat and was an especially high grade patent flour prepared for a select trade. B-781 is a first clear flour made in the same mill as B-780. The weak flours used were B-782, a patent milled from a soft western wheat grown around Waitsburg, Washington, and B-783, a patent milled from soft club wheat grown at Genessee, Idaho.

*Flour Analyses and Baking Tests.*—Table I shows certain of the analytical values usually determined on flours and also records the conventional baking test values.

TABLE I  
Flour Analyses and Baking Tests

Lab. no. of flour	Ash content of flour, %	Crude protein in flour (N × 5.7) dry basis, %	Dry matter in wet gluten; ave. of 5 determinations, %	Water added per 100 g of flour to make dough, cc	Vol. of fermented dough given by 150 g of flour, cc	Volume of loaf, cc	Color score of loaf B-780 as 100	Texture of loaf B-780 as 100
B-780	0.44	12.13	32.51	57.9	733	1639	100	100
B-781	0.90	14.25	37.55	59.7	820	1580	98	101
B-782	0.49	9.58	36.63	59.7	900	1430	100	101
B-783	0.53	12.03	35.25	57.4	715	1530	100	98

The baking values given for B-780 are the average of three bakings, and those for B-783 are the average of two independent bakings.

It was thought advisable to repeat the bakings with flours B-780 and B-783 and also inasmuch as a low volume might be due to deficiency of soluble carbohydrates to investigate the effect of diastase. Jessen-Hansen<sup>16</sup> has pointed out that the optimum hydrogen ion concentration for baking is around pH value of 5.0 and that the volume of the loaf may be in-

<sup>16</sup> Jessen-Hansen, H.: *Études sur la farine de froment. I. Influence de la concentration en ions hydrogène sur la valeur boulangère de la farine. Comptes-rendus des Travaux Lab. de Carlsberg, 10, p. 170-206, Fig. 4 (1911).*



creased by the addition of acid if the pH without acid would be greater than pH 5.0. In order to partially test this conclusion and to see what effect the addition of acid would have on the relative volume of the loaves produced with the two flours, 2 cc of normal lactic acid per 475 grams of flour were added to one set. It is regretted that the supply of flours did not permit further tests along this line, but the tests tend to show the superiority of flour B-780. The baker noted that flour B-780 indicated its superiority in the handling of the dough; it was more firm and elastic and did not break in the kneading process. The method and baking formula as described by Bailey<sup>17</sup> was used. The amount of an especially active diastase preparation necessary to bolster up flours low in diastase had been previously determined. The hydrogen ion concentration of the baked loaf was determined by the potentiometric method 12 hours after baking. For this determination 8 grams from the center of the loaf were mixed with 20 cc of water and 15 cc of the mixture placed in a large Bailey<sup>18</sup> electrode which handles such mixtures easily. The results are given in Table II. The pH values were checked by duplicate determinations which agreed within 1 millivolt.

TABLE II

Baking Test of Flours B-780 and B-783 giving the Volume of Loaf and the Hydrogen Ion Concentration of the Baked Bread on Normal Doughs, Doughs to Which Lactic Acid has been added, and Doughs to which Diastase has been added

	B-780		B-783	
	Volume of loaf, cc.	pH of baked bread	Volume of loaf, cc.	pH of baked bread
Normal control loaf	1630	5.47	1520	5.49
Loaf to which lactic acid has been added	1570	5.22	1360	5.36
Loaf to which diastase has been added	1690	5.40	1220	5.52

<sup>17</sup> Bailey, C. H: A method for the determination of the strength and baking qualities of wheat flour. *Jour. Ind. Eng. Chem.*, 8, p. 53-57, Fig. 1 (1916).

<sup>18</sup> Bailey, C. H: A simple hydrogen electrode. *Jour. Am. Chem. Soc.*, 42, 45-48, Fig. 2 (1920).



In order to ascertain whether or not the amended gliadin figure of Martin<sup>16</sup> differed in the two flours worked with, the protein fractions were determined by several methods. The first and third determinations were carried out essentially as described by the Association of Official Agricultural Chemists.<sup>19</sup>

*Potassium Sulfate-Soluble Protein.*—12 grams of the flour were weighed into a 500 cc flask and exactly 200 cc of a 5% potassium sulfate solution, measured at 25° and then cooled to 8–10°, were added; the mixture was shaken at 30 minute intervals for 3 hours and filtered. All of this process was carried out at a temperature of from 8–10°. The filtrate was brought to the temperature of 25° and two 50 cc aliquots taken with a pipette calibrated at 25°. Nitrogen in these aliquots was determined by the Kjeldahl method. The protein was calculated from the amount of nitrogen by the use of the factor 5.7.

*Water-Soluble Protein.*—20 grams of flour were treated with exactly 200 cc of water and shaken at frequent intervals for 40 minutes and then filtered, the whole process taking place at from 8–10° C. Two 50 cc aliquots were taken and protein determined as above.

*Alcohol-Soluble Protein.*—4 grams of flour were treated with exactly 200 cc of 70% alcohol by volume, and shaken at convenient intervals during 24 hours. The material was filtered and the protein content determined as above.

*Water-Soluble Protein at the End of 3 Hours at 25°.*—For this determination 20 grams of flour were treated with exactly 200 cc of distilled water and allowed to stand for 3 hours with frequent shaking in a water bath at 25° ± 0.01°. At the end of this time the material was filtered and nitrogen determined on aliquots of the filtrate.

*Potassium Sulfate-Soluble Protein by Centrifuge Method.*—About 42 cc of a 5% potassium sulfate solution were shaken with 3 grams of flour; the suspension was then centrifuged

<sup>19</sup> "Methods of Analysis." Association of Official Agricultural Chemists, Washington, 1920, pp. 167–168.

and the clear supernatant liquid decanted into a Kjeldahl flask. The residue remaining was then treated with a fresh portion of potassium sulfate solution and the process repeated. This extraction was continued until six separate portions of potassium sulfate solution had been used or a total of about 250 cc. Nitrogen was determined on the material in the Kjeldahl flask and from this the protein content was calculated by the factor 5.7.

*Alcohol-Soluble Protein in the Residue after Extraction with Potassium Sulfate.*—The residue from the potassium sulfate extraction above was treated with 250 cc of 70% alcohol in six separate portions, the procedure being the same as for the above potassium sulfate extraction. Protein was determined on the total alcohol extract by the Kjeldahl method as described above.

*Residue from the Potassium Sulfate and Alcohol Extractions.*—The residue remaining after extraction first by the six portions of potassium sulfate and subsequently by six portions of 70% alcohol was placed in a Kjeldahl flask and protein determined as described above.

*Total Protein of Flour.*—The total protein of the flour was determined on 1 gram samples and calculated on the basis of  $N \times 5.7$ .

These determinations were all carried out in duplicate. The average of the different determinations is given in Table III.

These results show by whatever method the amended gliadin figure is calculated that flour B-783 has the higher figure and should according to Martin have the higher baking strength. The reverse is actually the case.

*The Moist Gluten.*—The gluten was easily obtained from sample B-780 and was a firm elastic mass that could be separated from the starch very rapidly. More difficulty was evidenced in collecting the gluten from B-781; it was rather intermediate between B-780 and B-782 and B-783. The glutens from these last two flours could be collected only with extreme difficulty. They were whiter, it was harder

TABLE III

The Various Protein Fractions of Flours B-780 and B-783 (All Results calculated on the Dry Basis). Protein obtained by  $N \times 5.7$  in Each Case

	Flour B-780, %	Flour B-783, %
Potassium sulfate-soluble proteins, A. O. A. C. method (modified)	1.63	1.67
Water-soluble protein at the end of 40 minutes at 10° C.	1.59	1.24
Alcohol-soluble protein, A. O. A. C. method	6.60	7.31
Water-soluble protein at the end of 3 hours at 25° C.	1.85	1.67
Potassium sulfate-soluble protein by the centrifuge method	3.09	2.94
Alcohol-soluble protein in residue after extraction with potassium sulfate by the centrifuge method	5.73	6.41
Residue from the above potassium sulfate and alcohol extraction	3.32	2.80
Total protein from the sum of the last three determinations	12.14	12.03
Total protein as determined on the original flour	12.13	12.15

to separate them from the starch, and they were not firm or elastic. It is particularly interesting to compare the data for B-780 and B-783, the "strongest" and the "weakest" samples studied. The ash values are not widely different and are indicative of a "patent" and a "straight" flour. The crude protein values are almost identical so that, in this instance at least, the "weakness" of B-783 does not lie in a lower gluten content. The marked contrast in the baking tests shows that in these contrasting samples we have excellent material for testing as to whether or not the differences observed in the baking tests are paralleled by differences in the physico-chemical behavior of the gluteins.

*The Preparation of Dried Gluteins.*—It is obvious that if the gluten could be washed from a large quantity of flour and then dried, this dried material would be a much more satisfactory type of material to use in physico-chemical work than would the moist gluten because each day's material would then be exactly comparable. Using dried material

would also save a considerable amount of time. Therefore the attempt was made to prepare considerable quantities of the dried glutes washed from the four flours.

Wheat gluten is an emulsoid colloid and it is well known that emulsoid colloids will not withstand the effect of high temperature. Consequently the drying must necessarily be carried out at a temperature that would not be at all unfavorable to bacterial and enzyme action. The first attempts to dry the gluten were made in a vacuum oven at a temperature of about 30° but the moist gluten retains the water rather tenaciously and the drying could not be completed at this temperature before the gluten began to decompose. It was finally found necessary to dry at a temperature of 45-50°. The method finally adopted for preparing the dried gluten was as follows:

About 3 kilos of flour were made into a stiff dough with distilled water and allowed to stand under distilled water for an hour. The material was then placed in an electrically driven dough-mixing machine. Distilled water under considerable pressure was run continuously into the mixer at a rather rapid rate. At the end of about 7 minutes all of the starch appeared to have been removed, the liquid from then on remaining only slightly turbid; the treatment was continued for 13 minutes longer, the water by this time had begun to froth slightly. The moist gluten was then pressed out between glass plates into sheets approximately 3 mm thick and was cut into small squares of about 1 sq cm area weighing less than 0.5 gram. Glass plates were used for shelves in the vacuum oven and these little squares were placed on the glass plates at least 1 centimeter apart. The material was then placed in the vacuum oven and dried at a temperature of 45-50° under a pressure of 30-40 mm. It was possible to dry the material to a crisp in less than 18 hours by this method, the drying was, however, continued for a total of 48 hours. This material showed no evidence of decomposition that could be detected by odor. The dried material was then placed in a ball mill and ground to a fine powder. The powder so ob-

tained was quite hygroscopic and was triboelectric. The dried material was preserved in tightly stoppered glass bottles. Inasmuch as opportunity for the absorption of moisture was afforded during the standing, etc., moisture determinations were made on the dried ground material by heating 18 hours in vacuo at 100°. The percentage of crude protein was likewise determined by multiplying the total nitrogen by the factor 5.70. The percentages of moisture and crude protein are recorded in Table IV. The values given are averages of closely agreeing duplicate determinations.

TABLE IV  
Moisture and Crude Protein in the Dried Glutens

Lab. no.	Moisture, %	Crude protein in dried gluten, %
B-780	6.29	79.42
B-781	5.89	75.28
B-782	7.30	56.27
B-783	7.13	65.86

#### 1. Imbibition in the Presence of Different Strengths of Hydrochloric and Lactic Acids

(a) *Relative Imbibitional Capacity of the Glutens before Drying.*—Gortner and Doherty<sup>1</sup> studied the effect of lactic, acetic, boric, phosphoric, hydrochloric and oxalic acids in various concentrations on the imbibition of glutens. From their data it is evident that two types of results may be expected, i. e., a strong acid will produce marked imbibition at the lower acid concentration followed by marked dehydration effects at higher acid concentrations. On the other hand, a weak acid produces marked imbibition throughout the entire range of concentration tested or from N/500 to N/2 concentration.

We have felt that it would not be profitable to repeat all of the work of Gortner and Doherty using the new flours, and have accordingly selected hydrochloric acid as typifying one type of imbibition phenomena and lactic acid as typifying the other. The *modus operandi* was the same as in the earlier paper (Gortner and Doherty I). The discs of gluten were al-

lowed to remain in the acid solution for exactly 50 minutes, then drained for 7 minutes and weighed.

In all of the work the value reported is the average of 5 individual determinations. An example of the determination on the basis of the gain in weight of the individual discs per gram of moist gluten is given in Table V. The gluten used was B-780. The temperature of all swelling experiments was  $20^{\circ} \pm 2^{\circ}$ . It will be noted that while some of the individual determinations vary, as a whole the agreement is good, and we believe that the average value is a reliable evidence of the degree of hydration, under the conditions of the experiment.

TABLE V  
Quantity of Water imbibed (Grams of Water per Gram of Moist Gluten) from Individual Discs of Gluten B-780 in Different Concentrations of Hydrochloric Acid. Imbibition Period 50 Minutes

Acid concentration	N/2	N/5	N/10	N/25	N/50	N/100	N/200	N/500
Water imbibed per g of moist gluten	-0.024	0.055	0.230	0.696	1.050	0.863	0.846	0.747
	-0.058	0.066	0.170	0.730	0.665	0.895	0.855	0.642
	-0.031	0.075	0.250	0.635	1.017	0.808	0.812	0.850
	-0.028	0.050	0.200	0.650	0.960	1.085	0.774	0.574
	-0.032	0.026	0.275	0.720	0.921	1.040	0.577	0.822
Average	-0.035	0.054	0.225	0.686	0.923	0.938	0.773	0.727

TABLE VI  
The Quantity of Water imbibed (Grams Water per Gram Moist Gluten) for the Various Glutens (before drying) in Different Concentrations of Hydrochloric Acid. Imbibition Period 50 Minutes. (Average of 5 Determinations)

Concentration of acid	B-780	B-781	B-782	B-783
N/2	-0.035	-0.024	0.028	-0.035
N/5	0.054	0.061	0.061	0.033
N/10	0.225	0.150	0.155	0.151
N/25	0.686	0.400	0.374	0.367
N/50	0.923	0.553	0.514	0.453
N/100	0.938	0.633	0.422	0.477
N/200	0.773	0.517	0.459	0.478
N/500	0.727	0.296	0.428	0.412

Table VI shows average imbibitional values for all four glutes. The data of Table VI are shown in the form of curves in Fig. 1.

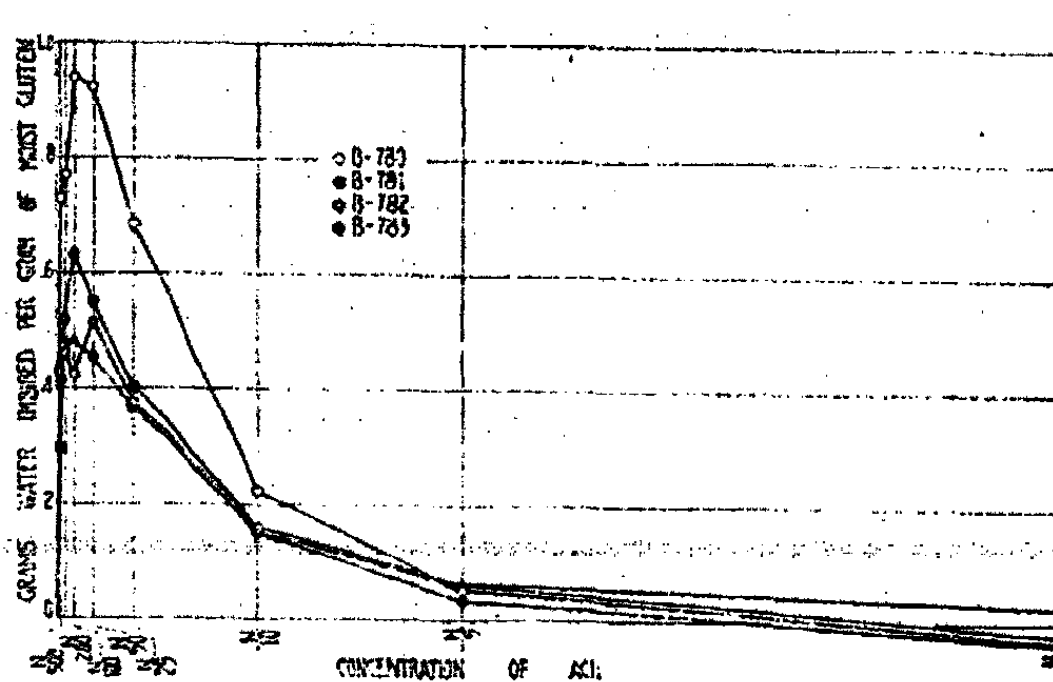


Fig. 1

The imbibition curves for the various glutes in different concentrations of hydrochloric acid (before drying, imbibition period 50 minutes).

There is a distinct difference in the swelling capacity in hydrochloric acid between the strong gluten, B-780, and the other three.

TABLE VII

The Quantity of Water imbibed (Grams Water per Gram Moist Gluten) for the Various Glutes (before Drying) in Different Concentrations of Lactic Acid. Imbibition Period 50 Minutes. (Average of 5 Determinations)

Concentration of acid	B-780	B-781	B-782	B-783
N/2	1.328	0.669	0.546	0.406
N/5	1.395	0.701	0.687	0.476
N/10	1.518	0.816	0.627	0.528
N/25	1.552	0.603	0.580	0.572
N/50	1.417	0.642	0.611	0.598
N/100	1.080	0.367	0.487	0.521
N/200	1.231	0.421	0.457	0.460
N/500	0.787	0.232	0.467	0.497

Table VII and Fig. 2 show the average imbibitional values for the four glutes (before drying) in different concentrations of lactic acid.

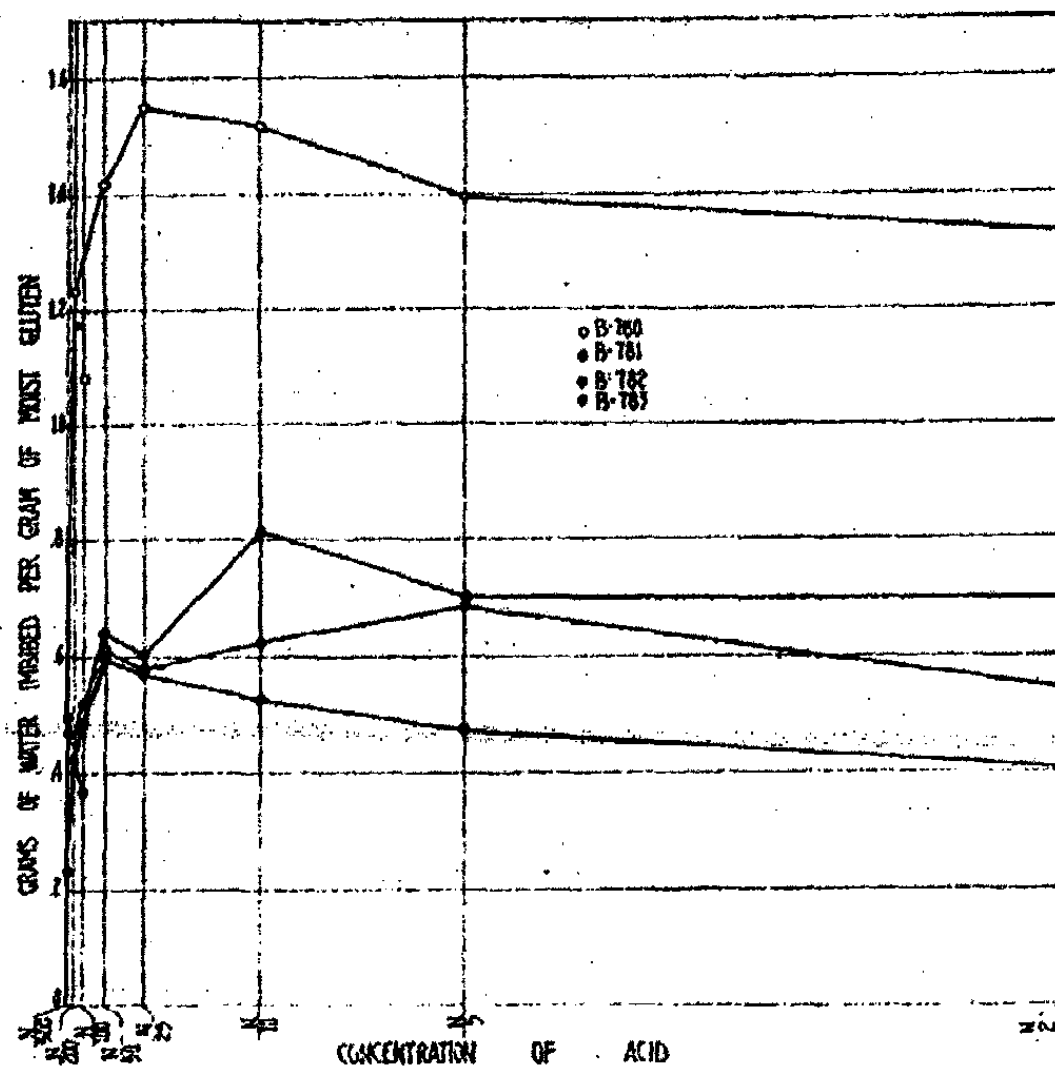


Fig. 2

The imbibition curves for the various glutes in different concentrations of lactic acid (before drying, imbibition period 50 minutes).

It will be observed that there is a wide difference in the imbibitional capacity of glutes B-780 and B-781 and there is also a marked difference between glutes B-781, B-782 and B-783. The difference between these glutes is more marked than that found by Gortner and Doherty to exist between their "strong" and "weak" glutes, the "strong" flour B-780 being stronger than the one worked with by them, and the "weak" flours being weaker, as shown by imbibitional experiments.

(b) *Relative Imbibitional Capacities of the Glutes after drying.*—The dried gluten, prepared as noted above, was converted into moist gluten discs in order that the imbibitional values might be comparable with those determined on the freshly washed out gluten. Twenty grams of the dried gluten



were mixed with just enough water to make a rather dry dough. This dough was allowed to stand under distilled water for one hour. The gluten so obtained was much more tough and rubberlike than the original gluten before drying. In order to obtain sheets of uniform thickness it was necessary to press it out between the glass plates as thin as possible and weights had to be placed on the glass plates in order to keep the gluten from springing back into a mass. After remaining under pressure for some time additional pressure was applied and the sheet could then be pressed a little thinner. This process was repeated until sheets about 3 mm thick were obtained. Discs were then cut which were not placed in water for a preliminary period but were placed directly into the various solutions. Two sets of experiments were made. The first set is directly comparable with the moist gluten imbibitional experiments noted above where an imbibitional period of 50 minutes was used. In the second set the imbibitional period was reduced to 25 minutes inasmuch, as will appear later, it was desirable to compare imbibition in alkali with imbibition in acid and a fifty minute imbibitional period could not be used in the alkaline solutions. In addition the dilutions of the 25 minute set are not identical with the preceding acid sets, but correspond with the dilutions which are used later in this paper for the various alkalis.

*Fifty Minute Imbibitional Experiments.*—In view of the fact that hydrochloric acid did not appear to differentiate the glutens nearly so well as did lactic acid, no experiments were made in which the imbibitional capacity of the various dried glutens were tested in the various concentrations of hydrochloric acid. Table VIII and Fig. 3 show the imbibitional data for the different dried glutens, prepared as noted above, in different concentrations of lactic acid.

*Twenty-Five Minute Imbibitional Experiments.*—In order to directly compare the action of acids and alkalis as noted above the swelling in acids was carried out for 25 minute periods in the same concentrations that were used for the al-

TABLE VIII

The Quantity of Water imbibed (Grams Water per Gram Moist Gluten) for the Various Glutens (after drying and milling the Gluten) in Different Concentrations of Lactic Acid. Imbibition Period 50 Minutes. (Average of 5 Determinations)

Concentration of acid	B-780	B-781	B-782	B-783
N/2	0.801	0.731	0.469	0.690
N/5	0.972	0.625	0.508	0.690
N/10	1.015	0.628	0.501	0.764
N/25	0.887	0.625	0.407	0.684
N/50	0.920	0.558	0.409	0.592
N/100	0.791	0.435	0.383	0.536
N/200	0.647	0.365	0.381	0.486
N/500	0.520	0.453	0.424	0.354
Water	0.039	0.063	0.026	0.042

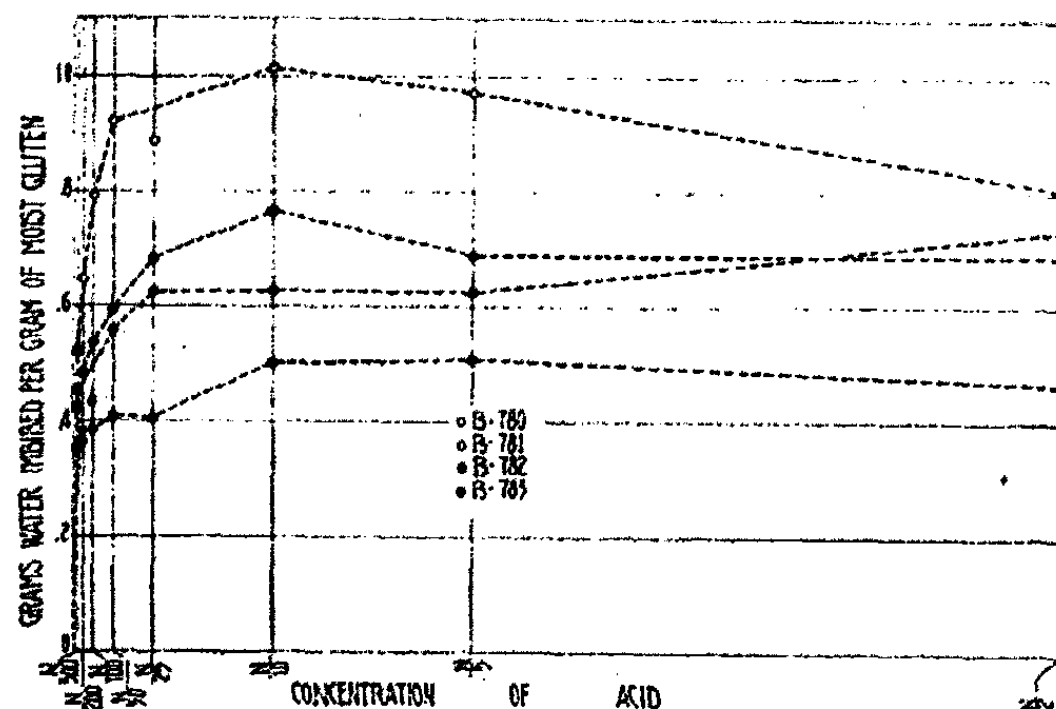


Fig. 3

The imbibition curves for the various glutens in different concentrations of lactic acid (after drying, imbibition period). The top curve is B-780, the second B-783, the third B-781, and the lowest B-782.

kalies as noted later in this paper. The data obtained with lactic acid are given in Table IX and graphically in Fig. 4 and those obtained with hydrochloric acid are given in Table X and are also expressed graphically in Fig. 4.

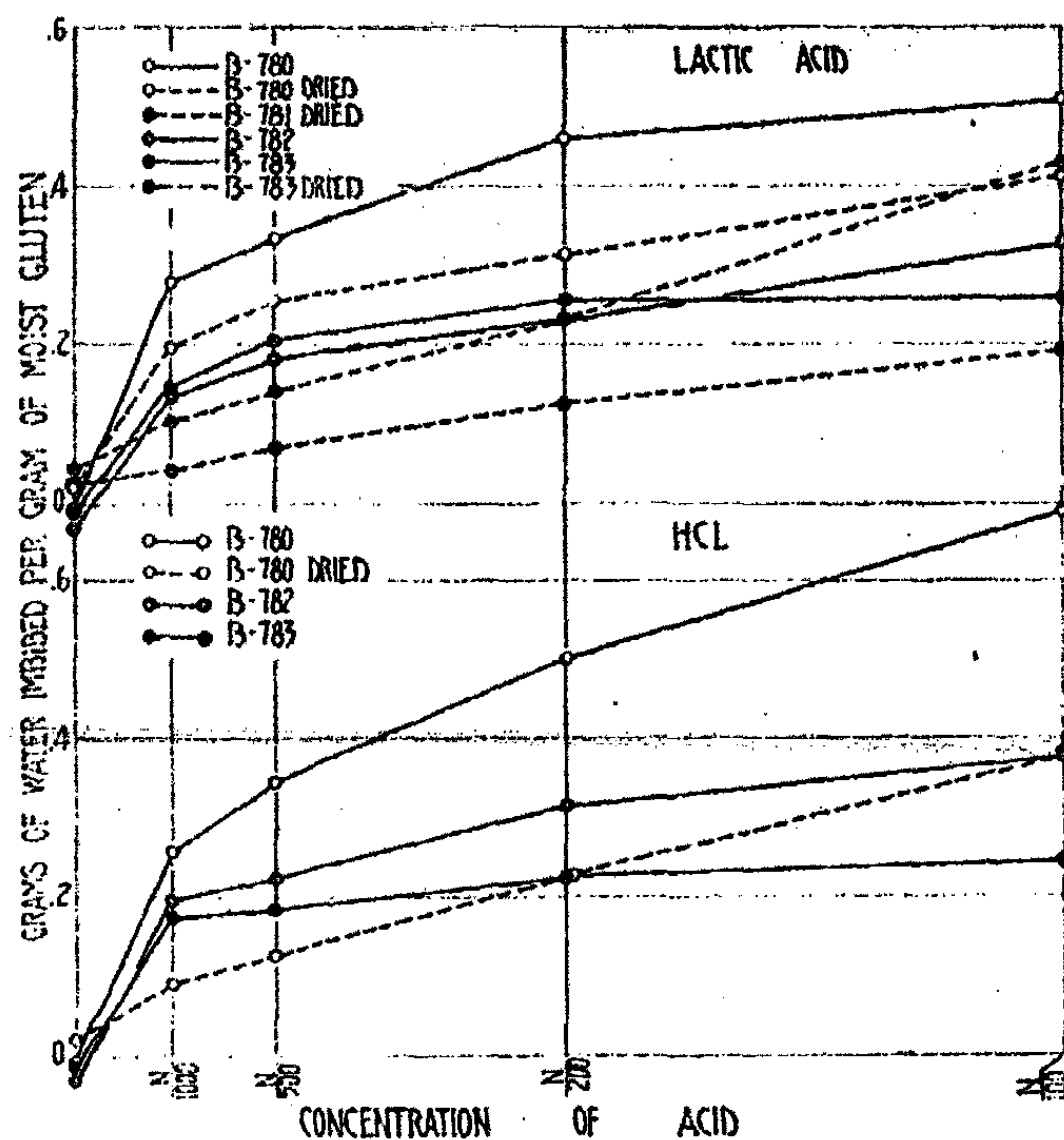


Fig. 4

The imbibition curves for the various glutes in the same concentrations of hydrochloric and lactic acids as used in the case of imbibition in alkalies (before and after drying, imbibition period 25 minutes).

TABLE IX

The Quantity of Water imbibed (Grams Water per Gram Moist Gluten) for the Various Glutes (before and after drying) in Different Concentrations of Lactic Acid. Imbibition Period 25 Minutes. (Average of 5 Determinations)

Concentration of acid	B-780		B-781	B-782	B-783	
	Before drying	After drying	After drying	Before drying	Before drying	After drying
N/100	0.509	0.411	0.195	0.329	0.259	0.427
N/200	0.458	0.311	0.127	0.234	0.255	0.231
N/500	0.332	0.253	0.071	0.184	0.207	0.142
N/1000	0.277	0.196	0.043	0.135	0.149	0.103
Water	-0.007	0.020	0.024	-0.031	-0.014	0.044

TABLE X

The Quantity of Water imbibed (Grams Water per Gram Moist Gluten) for the Various Glutens (before and after drying) in Different Concentrations of Hydrochloric Acid Imbibition Period 25 Minutes. (Average of 5 Determinations)

Concentration of acid	B-780		B-782	B-783
	Before drying	After drying	Before drying	Before drying
N/100	0.687	0.378	0.375	0.247
N/200	0.501	0.227	0.317	0.222
N/500	0.346	0.129	0.223	0.185
N/1000	0.259	0.091	0.198	0.176
Water	-0.007	0.020	-0.031	-0.014

It is of interest to note that in the 50 minute experiments B-780 has decreased in its imbibing capacity in lactic acid to a very appreciable extent, that B-781 has decreased somewhat but the other two glutens have not changed to so marked a degree. This appears to indicate that the glutens are tending to become alike. The change is if anything even more marked in the 25 minute sets where an enormous decrease in imbibing capacity is noted for the dried gluten of B-780. In all of the glutens the concentration of acid necessary to produce maximum imbibition has likewise increased. Thus with B-780 maximum imbibition is attained in the undried gluten in N/25 lactic acid while in the dried gluten the corresponding point is in N/10 acid. Similarly for B-783 the values are N/50 and N/10, respectively. It has been our experience that weak glutens reach their point of maximum imbibition only in a higher concentration of acids than do strong glutens, and in the present instance the drying process appears to have produced a "weak" gluten as measured by rate and extent of imbibition. We know that alternate hydration and dehydration, or freezing and thawing, are some of the more common methods for coagulating or deflocculating colloids, and the present observation is a direct confirmation of the hypothesis set forth by Gortner and Doherty that a strong gluten is strong because of more marked col-

loidal properties, a part of which colloidal properties are lost when the gluten gel is dried, remilled and again made into a gel.

**2. Imbibition in the Presence of Different Strengths of the Following Alkalies: Potassium Hydroxide, Sodium Hydroxide, Calcium Hydroxide, Barium Hydroxide, and Ammonium Hydroxide**

(a) *Relative Imbibitional Capacities of the Glutens before drying.*—It is well known that when animal proteins are treated with different concentrations of alkali imbibitional effects similar to those in acid are obtained. It was thought desirable, therefore, to see if the glutens from the strong and weak flours showed the marked imbibitional differences noted in acids when the glutens were treated with alkalies of different concentrations.

A series of sodium hydroxide solutions was prepared of the same normalities as those employed in the study of the acids. The experiment was first tried with gluten from B-780 during an imbibition period of 50 minutes. The discs which were placed in N/2 solution became colored a light yellow; they did not swell but seemed to grow smaller, the rough edges becoming rounded off. It was impossible to remove the discs at the end of the imbibitional period, all coherence having been destroyed. The discs which were placed in the concentrations ranging from N/5 to N/25 did not have such a yellow color and the swelling was at first perceptible, but the discs were not coherent enough to be removed for weighing. In the case of the more dilute alkaline solutions the discs were coherent enough to be removed for weighing. Increases in weight were noted for those discs in N/200 and N/500 alkali while decreases were recorded for N/100 and N/50 solutions. The time in alkali was the same as was used for the acids, i. e., 50 minutes. In all solutions but N/500 there was a perceptible cloudiness and a ring of white solid material (probably starch) settled around the discs. This ring was not present in the N/500 solution. In order to ascertain whether or not this was a case of complete

dispersion or solution of the protein, or whether the alkali was merely causing loss of coherence, the solutions of alkali used in the imbibitional experiments were neutralized. A curdy precipitate appeared in each solution excepting N/500, the quantity being roughly proportional to the concentration of the alkali. This showed conclusively that the gluten was in reality being dispersed and by the amount of precipitate one would conclude that the process was going on rather rapidly.

It would seem that the action of alkalies on gluten is somewhat different from the action of the acids. In the case of acids the first step is the swelling of the gluten with no apparent dispersion. This is easily shown by bringing the solution after the removal of the gluten discs at the end of the 50 minute period to the isoelectric point of the gluten. In no instance was there more than a slight turbidity produced. In the case of acid there is marked imbibition as shown by appearance and by the increase in weight. In the case of alkali however the two steps, imbibition and dispersion, follow one another almost immediately so that in some concentrations they compensate each other. In the more dilute solutions the imbibitional factor is the more prominent, in the more concentrated solutions the dispersion factor is the most apparent.

As the imbibition in the case of alkali appeared to be greater in the more dilute solutions, concentrations of sodium hydroxide were tried ranging from N/1000 to N/10,000. No appreciable imbibition was noted however.

In an attempt to make the imbibition factor more prominent the time for the swelling determination in the presence of alkalies was shortened from 50 minutes to 25 minutes. A comparison of the results obtained in these two time intervals is shown in Table XI.

It was concluded from Table XI and the swelling size as shown by appearance that 25 minutes would indicate the imbibition factor more accurately.

The imbibition of the different glutes was studied in solutions of the following alkalies: potassium, sodium, barium,

TABLE XI

The Quantity of Water imbibed (Grams Water per Gram Moist Gluten) by Gluten B-780 (before drying) in Different Concentrations of Sodium Hydroxide. Comparison of Imbibitional Periods of 50 and 25 Minutes. (Average of 10 Determinations)

Concentration of alkali	50 minutes	25 minutes
N/100	-0.025	0.088
N/200	0.099	0.242
N/500	0.090	0.033
N/1000	0.010	0.007

calcium and ammonium hydroxides. The data are shown in Table XII and graphically in Fig. 5.

TABLE XII

The Quantity of Water imbibed (Grams Water per Gram Moist Gluten) for the Various Glutens (before drying) in Different Concentrations of the Various Alkalies. Imbibition period 25 Minutes. (Average of 5 Determinations)

Concentration of alkali	B-780	B-781	B-782	B-783
Potassium Hydroxide				
N/100	0.138	0.208	-0.084	-0.109
N/200	0.328	0.072	0.008	-0.011
N/500	0.042	0.000	0.018	0.017
N/1000	0.001	-0.023	-0.012	-0.029
Sodium Hydroxide				
N/100	0.088	0.237	-0.039	-0.092
N/200	0.242	0.061	0.059	0.025
N/500	0.033	-0.001	-0.002	0.000
N/1000	0.007	-0.005	-0.014	-0.019
Barium Hydroxide				
N/100	0.065	0.142	0.001	-0.055
N/200	0.114	0.021	0.045	0.023
N/500	0.023	-0.021	-0.022	-0.018
N/1000	0.016	-0.011	-0.022	-0.009
Calcium Hydroxide				
N/100	0.125	0.070	0.025	-0.057
N/200	0.108	0.046	0.041	0.018
N/500	-0.003	0.008	-0.011	-0.013
N/1000	-0.015	0.002	-0.021	-0.016

TABLE XII (continued)  
Ammonium Hydroxide

N/100	0.158	0.070	0.067	0.053
N/200	0.080	0.021	0.012	0.013
N/500	0.016	-0.002	-0.015	-0.020
N/1000	-0.011	-0.014	-0.020	-0.012

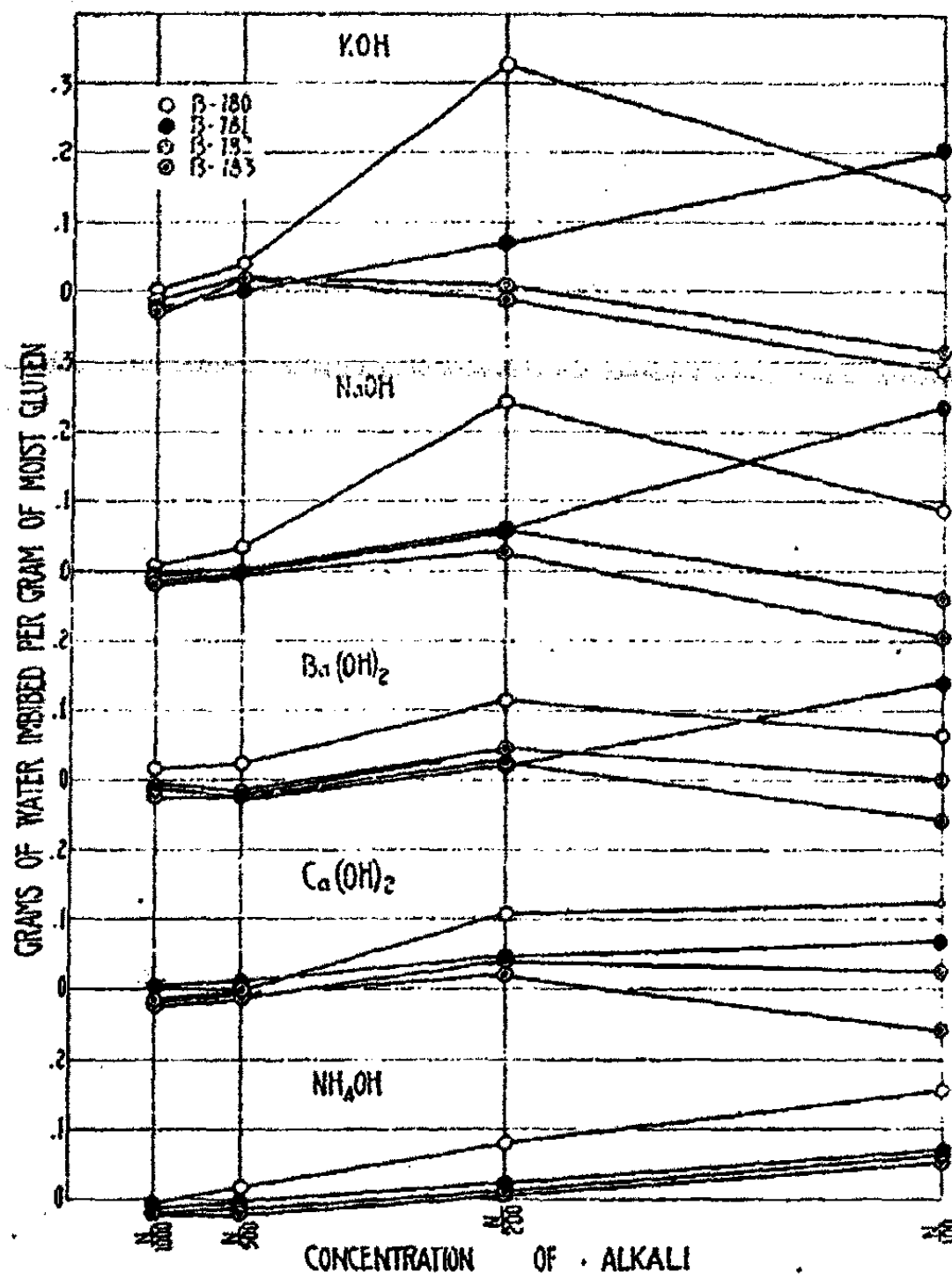


Fig. 5  
The imbibition curves for the various glutes in different concentrations of potassium, sodium, barium, calcium and ammonium hydroxides (before drying, imbibition period 25 minutes).

In all experiments the strong flour gluten, B-780, showed a distinctly greater imbibition in the alkalies than did the gluten from the weak flours, B-782 and B-783. This is par-



ticularly noticeable in the potassium hydroxide series. The differences are more apparent in the N/200 concentrations. In the higher concentrations the dispersion factor is more prominent as shown by the fall in the curve. The clear flour, B-781, does not behave like the others in this respect. The discs from gluten B-780 that were placed in the N/100 alkalies dispersed more than those placed in the lower concentrations. The discs placed in N/200 dispersed somewhat, those in the other two concentrations hardly at all. B-782 and B-783 behaved in all respects like gluten B-780 with the exception that the dispersion was more marked in the case of B-782 and B-783. The clear B-781 did not disperse as readily as did the other three glutes. This would be indicated by the above tables and is shown very clearly in Fig. 5 where the curve for B-781 rises above the others in the N/100 concentration.

(b) *Imbibition of the Dried Glutes in Alkali.*—In the first attempt to prepare moist gluten from the dried material the dried gluten was treated in the same way that the original flour was treated, that is, enough water was added to the dried material to form a stiff dough. This dough was allowed to stand under distilled water for one hour and was then washed in a stream of distilled water. As soon as the washing was begun, however, the gluten began to disperse. This was tried repeatedly with the dried glutes from the different flours. It was found, however, that if a very small amount of sodium chloride was added to the wash water the gluten immediately came together in a coherent mass which showed greater elasticity than the gluten before drying. If the coherent mass obtained by washing in sodium chloride solution was washed in distilled water it began to disperse but was easily brought to a coherent mass by again washing in the salt solution. This process was repeated several times with the same sample and probably could be repeated indefinitely. The method finally adopted was to add enough water to make a dough and let this dough stand under distilled water for one hour. The material was then pressed into sheets without working.

It was found that discs cut from gluten prepared in this manner varied in their behavior to alkali according to the length of time the cut discs stood in water before placing them in the alkali solutions. The following conditions were tested:

A. Discs stood in water overnight before placing in the alkali, B-780.

B. Discs stood in water one hour before placing in the alkali, B-780.

C. Discs stood in water 10-35 minutes before placing in the alkali, B-780.

D. Discs were not placed in water at all, B-780.

E. Added sodium chloride to wash water after trying to wash in distilled water, B-780.

F. Added sodium chloride to wash water after trying to wash in distilled water; the cut discs were allowed to stand in distilled water three hours before placing in the alkali, B-780.

G. Washed with sodium chloride solution; the cut discs were allowed to stand in distilled water overnight. Considerable swelling took place in these discs on standing in water overnight, B-783.

H. Discs stood in water one hour before placing in alkali, B-783.

The gain in weight per gram of moist gluten is given in Table XIII.

TABLE XIII  
The Quantity of Water imbibed (Grams per Gram Moist Gluten) for the Glutens B-780 and B-783 (after drying) in Different Concentrations of Potassium Hydroxide, showing the Effect of Different Treatments of Discs of Moist Gluten prepared from Dried Gluten. Imbibitional Period 25 Minutes. (Average of 5 Determinations)

Concentration of alkali	B-780						B-783	
	A	B	C	D	E	F	G	H
N/100	—	0.052	0.158	0.120	0.193	0.207	0.188	0.163
N/200	-0.111	-0.056	0.007	0.033	0.119	0.112	0.072	0.088
N/500	—	-0.087	-0.045	0.026	0.007	0.036	-0.001	-0.010
N/1000	—	-0.054	-0.019	0.051	-0.019	0.025	0.008	-0.021
Water	—	0.103	0.160	0.124	0.077	0.137	-0.003	0.025

The effect of the different treatments on imbibitional rate is shown very clearly in the N/200 concentration where variations from  $-0.111$  to  $+0.119$  are recorded, depending on previous treatment.

The method finally adopted for the study of imbibition of the dried glutens was the same as that employed in the work with dried glutens and acids, i. e., not to place the discs in water at all before placing them in the solutions to be tested. The losses in all cases with alkalis are not attributed to the dehydration of the gluten but rather to its dispersion. After the discs had been removed for weighing the alkali was neutralized and a precipitate was formed which appeared to be approximately proportional to the concentration of the alkali and therefore more or less proportional to the loss in weight of the discs. Although a rather extensive series of experiments was carried out it was found that no method could be devised whereby imbibitional values could be obtained with the dried glutens which were free from large errors due to dispersion. Consequently it is not thought worth while to record the tabular data. The experiments, however, emphasize rather strongly the marked changes in colloidal condition which occur in drying the glutens and confirm the conclusions arrived at in the earlier sections where imbibition of dried and undried glutens in acid solutions is considered.

### **3. The Effect of Calcium and Potassium Hydroxides containing M/200 Sodium Sulfate on Imbibition**

It is well known that neutral salts markedly decrease imbibition of proteins in acid or alkaline media. Gortner and Doherty (I) have already presented data showing that wheat gluten is no exception to this general rule, at least in so far as acids are concerned. In order to ascertain whether or not the same relative effect held true with imbibition in alkali in the presence of salts, experiments were carried out with glutens B-780 and B-783 in the presence of M-200 sodium sulfate in potassium and calcium hydroxides. The results obtained are found in Tables XIV and XV and are expressed graphically in Fig. 6.

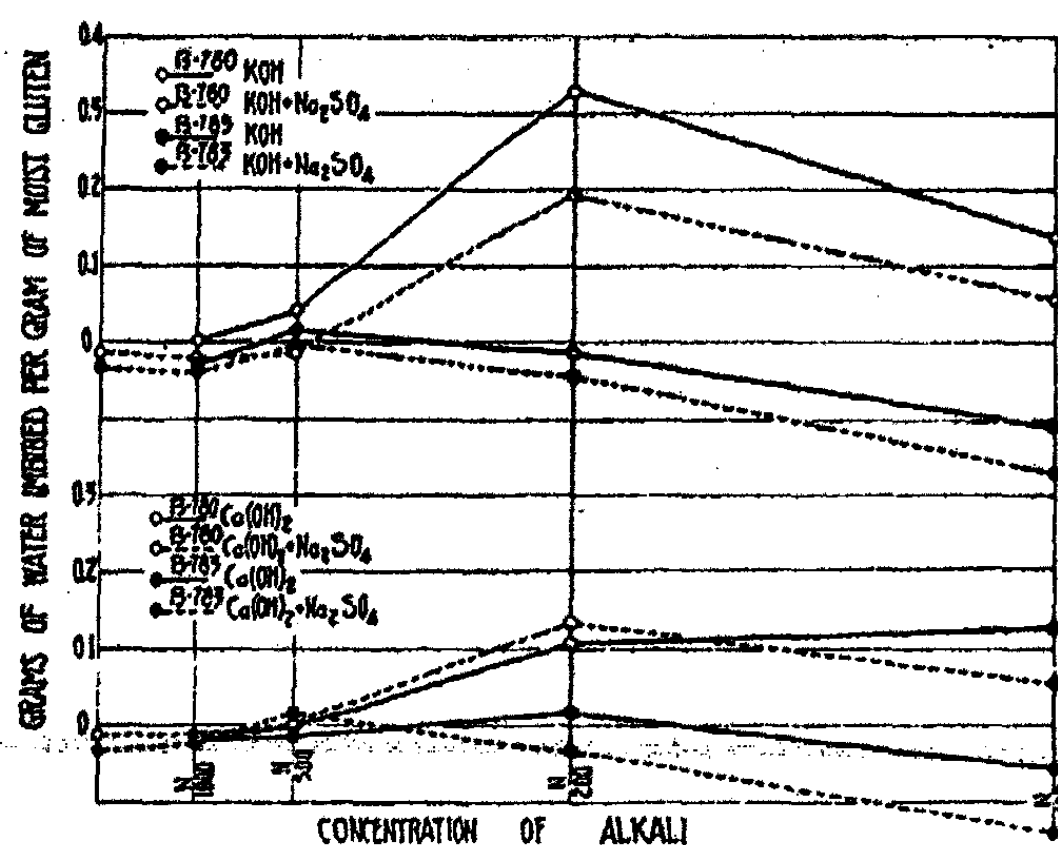


Fig. 6

The imbibition curves for the glutens B-780 and B-783 in potassium and calcium hydroxides alone and in potassium and calcium hydroxides plus M/200 sodium sulfate (before drying, imbibition period 25 minutes).

TABLE XIV

The Quantity of Water imbibed (Grams Water per Gram Moist Gluten) for the Glutens B-780 and B-783 (before drying) in Various Concentrations of Potassium Hydroxide, and Potassium Hydroxide plus M/200 Sodium Sulfate. Imbibition Period 25 Minutes. (Average of 5 Determinations)

Concentration of alkali	B-780		B-783	
	KOH	KOH + Na <sub>2</sub> SO <sub>4</sub>	KOH	KOH + Na <sub>2</sub> SO <sub>4</sub>
N/100	0.138	0.059	-0.109	-0.170
N/200	0.328	0.196	-0.011	-0.043
N/500	0.042	-0.013	0.017	-0.005
N/1000	0.001	-0.020	-0.029	-0.039
Water	—	-0.011	—	-0.031

The results are in good accord with the depressing effect of salts upon imbibition in acids and it was not thought worth while to conduct any further experiments to show the effect of salts inasmuch as their effect has been shown on so many proteins by many different workers. The present series of experi-

ments, however, points to the fact that the difference between a strong and a weak gluten is not merely a question of the presence of more inorganic salts in the weaker gluten.

TABLE XV

The Quantity of Water imbibed (Grams Water per Gram Moist Gluten) for the Glutens B-780 and B-783 (before drying) in Various Concentrations of Calcium Hydroxide, and Calcium Hydroxide plus M/200 Sodium Sulfate. Imbibition Period 25 Minutes. (Average of 5 Determinations)

Concentration of alkali	B-780		B-783	
	Ca(OH) <sub>2</sub>	Ca(OH) <sub>2</sub> + Na <sub>2</sub> SO <sub>4</sub>	Ca(OH) <sub>2</sub>	Ca(OH) <sub>2</sub> + Na <sub>2</sub> SO <sub>4</sub>
N/100	0.125	0.055	-0.057	-0.140
N/200	0.108	0.131	0.018	-0.033
N/500	-0.003	0.002	-0.013	0.017
N/1000	-0.015	-0.011	-0.016	-0.022
Water	—	-0.011	—	-0.031

#### 4. Relation of Hydrogen Ion Concentration of Various Acids to Imbibition as Measured by Increase in Weight of Discs

Thus far investigators of imbibition, as shown by the increase in weight of discs placed in different concentrations of various acids, have plotted their results against normality (titratable acidity) of the acid solutions. By the use of this method curves are obtained of radically different shapes with the different acids used of which hydrochloric represents the one extreme and acetic acid perhaps the other, as shown in Figures 1 to 5 in the article of Gortner and Doherty<sup>1</sup> and in Figures 1 and 2 of this paper.

Loeb<sup>20,21,22,23</sup> has recently presented evidence tending to show that the highest osmotic pressure of gelatin and albumin, the highest viscosity of gelatin, the greatest swelling

<sup>20</sup> Loeb, J.: Ion series and the physical properties of proteins. I. Jour. Gen. Physiol., 3, 85-106, Fig. 14 (1920).

<sup>21</sup> Loeb, J.: The proteins and colloid chemistry. Science, 52, 449-456, Fig. 2 (1920).

<sup>22</sup> Loeb, J.: Ion series and the physical properties of proteins. II. Jour. Gen. Physiol., 3, 247-269, Fig. 9 (1920).

<sup>23</sup> Loeb, J.: Chemical and physical behavior of casein solutions. Ibid., 3, 547-555, Fig. 6 (1921).

of gelatin, as measured by increase in volume, and the highest viscosity and osmotic pressure of casein solutions is reached at the same hydrogen ion concentrations with the various acids, and furthermore with a given protein the same high point is reached with the various acids, with the exception of sulfuric acid.

The questions as to the relationships existing between imbibition and hydrogen ion concentration were recognized at the time the experimental work by Gortner and Doherty was in progress, but at that time no apparatus for the direct determination of hydrogen ion concentration was available and it was not thought advisable to draw conclusions from hydrogen ion data which had been calculated from the existing tables of physical constants.

We have, therefore, determined by the potentiometric method the hydrogen ion concentration of the various solutions of lactic, acetic, orthophosphoric, hydrochloric and oxalic acids in the dilutions used by Gortner and Doherty. The various solutions were prepared by diluting N/1 solutions of the various acids as determined by titration with NaOH (using phenolphthalein as indicator) with the required amount of distilled water. A Leeds and Northrup potentiometer was used for the measurement of the voltage. A Type R high sensitivity galvanometer was used as a current detector, and the hydrogen electrodes were of the Bailey<sup>18</sup> type. All determinations were made in a constant temperature room kept at 25°. A normal KCl calomel electrode and a flowing junction of sat. KCl were used. The millivolt readings were changed to pH by means of the tables of Schmidt and Hoagland.<sup>24</sup>

The imbibitional data given by Gortner and Doherty for the "P" (a "strong" patent flour), and the "W<sub>2</sub>" (a "weak" flour) were used. The results are given in Table XVI and Fig. 7.

---

<sup>24</sup> Schmidt, C. I. A., and Hoagland, D. R: Table of pH, H<sup>+</sup> and OH<sup>-</sup> values corresponding to electromotive forces determined in hydrogen electrode measurements with a bibliography. University of California Publications in Physiology, 5, No. 4, p. 23-69, March 29 (1919).

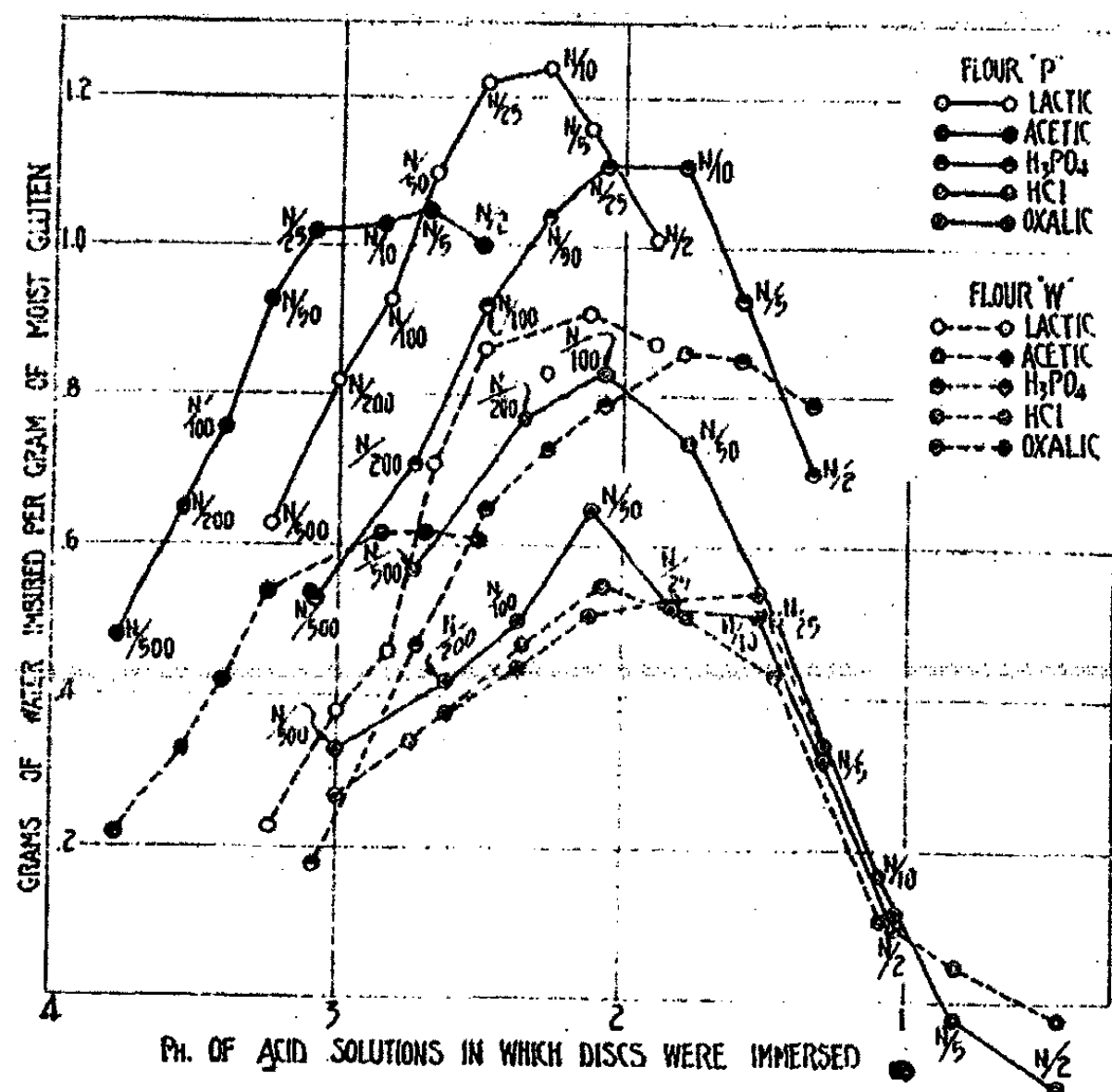


Fig. 7

The imbibition curves for a "strong flour," gluten "P" and a "weak flour," gluten "W," in various concentrations of lactic, acetic, ortho phosphoric, hydrochloric, and oxalic acids, plotted with the actual hydrogen-ion concentrations of the solutions in which the discs were immersed as abscissa (before drying, imbibition period 50 minutes).

If we compare the imbibition curves given with the two different flours by a single acid, we find that in each instance the curve for the flour "P" rises higher than the curve for the flour "W." The shape of the curves is very similar, each rising rather rapidly as the acid concentration increases, reaching a flat crest, and then falling. The pH of maximum imbibition as indicated on the abscissa does not appear to be the same for the various acids, the maximum points extending over a range of pH from 3.25 to 2.25. The reason for this difference is probably due to the fact that the

TABLE XVI

Relative Imbibition of Glutens "P" and "W<sub>2</sub>," from the Data of Gortner and Doherty, at Various Hydrogen Ion Concentrations of Lactic, Acetic, Ortho-Phosphoric, Hydrochloric and Oxalic Acids

Normality of acid solution	pH of acid solution at 25° C	Grams of water imbibed per gram of moist gluten	
		"P"	"W <sub>2</sub> "
Lactic Acid			
N/2	1.89	1.01	0.87
N/5	2.11	1.16	0.91
N/10	2.27	1.24	0.83
N/25	2.49	1.22	0.86
N/50	2.67	1.10	0.71
N/100	2.82	0.93	0.46
N/200	3.00	0.82	0.38
N/500	3.23	0.63	0.23
Acetic Acid			
N/2	2.50	1.00	0.61
N/5	2.69	1.05	0.62
N/10	2.85	1.03	0.62
N/25	3.08	1.02	0.54
N/50	3.24	0.93	0.54
N/100	3.39	0.76	0.42
N/200	3.54	0.65	0.33
N/500	3.76	0.48	0.22
Ortho-Phosphoric Acid			
N/2	1.33	0.70	0.79
N/5	1.59	0.93	0.85
N/10	1.79	1.11	0.86
N/25	2.05	1.11	0.79
N/50	2.26	1.04	0.73
N/100	2.49	0.92	0.65
N/200	2.73	0.71	0.47
N/500	3.08	0.53	0.18
Hydrochloric Acid			
N/2	0.46	-0.11	-0.02
N/5	0.81	-0.02	0.05
N/10	1.09	0.17	0.21
N/25	1.46	0.51	0.43
N/50	1.77	0.74	0.51
N/100	2.06	0.83	0.55
N/200	2.35	0.77	0.47
N/500	2.73	0.57	0.34



TABLE XVI (continued)

Normality of acid solution	pH of acid solution at 25° C	Grams of water imbibed per gram of moist gluten	
		"P"	"W <sub>1</sub> "
Oxalic Acid			
N/2	1.03	0.10	0.13
N/5	1.29	0.32	0.34
N/10	1.52	0.51	0.54
N/25	1.82	0.52	0.53
N/50	2.10	0.65	0.51
N/100	2.36	0.50	0.44
N/200	2.62	0.42	0.38
N/500	3.00	0.33	0.27

hydrogen ion concentration was measured on the pure solutions and does not necessarily indicate accurately the hydrogen ion concentration in that layer of liquid in actual contact with the disc during the whole of the imbibitional period. In the case of the strong acids while giving a relatively high concentration of hydrogen ions at the point of greatest imbibition the titratable acidity is relatively low. For this reason the layer of solution in immediate contact with the disc is soon depleted of hydrogen ions and the actual hydrogen ion concentration of the solution in contact with the disc is therefore much lower than is indicated by a determination in the upper parts of the solution. In order to increase the hydrogen ions in the immediate vicinity of the disc it is necessary that diffusion should act over a relatively great distance. In the case of the weaker acids the high point of the imbibition curve occurs at a normality of acid, as measured by titration, that is, much greater than is the case with the stronger acids. The weak acids by their buffer action tend to replenish the solution with hydrogen ions as fast as depleted by the disc. For this reason the maximum point of imbibition for the weak acids seems in general to occur at a lower hydrogen ion concentration than is the case with the strong acids. We think for this reason that these results tend to show that the point of maximum imbibition of gluten as measured by the increase in weight of discs occurs at practically the same hydrogen

ion concentration for the different acids. This conclusion has been clearly verified by an entirely different method where the errors mentioned above were eliminated. Further data on this part will be included in a later paper.

#### Discussion

The results on the rate of imbibition of the different glutes in the presence of hydrochloric and lactic acids confirm the findings of Gortner and Doherty. The differences for hydrochloric acids compare very favorably with the results they obtained with this acid. The present values show a somewhat greater variation between the glutes of the strong and weak flours than the differences found by Gortner and Doherty. In the case of lactic acid, the differences between the glutes are much more marked than any found by Gortner and Doherty, the gluten B-780 having almost three times the rate of imbibition of the weakest gluten, B-783, indicating that the "strong" flour is stronger and the "weak" flour weaker than the samples with which Gortner and Doherty worked.

The imbibitional rates of the various glutes in alkalis likewise show marked differences. The behavior of the glutes to alkalis is somewhat different from the behavior in the presence of acids, dispersion beginning almost coincident with hydration in the case of the alkalis. If we compare the results given with potassium and sodium hydroxide in the N/200 concentrations, we find differences greater than any found in the case of the acids. When we compare the reaction of the glutes to the various alkalis, we find that they follow the lyotropic series, potassium > sodium > barium and calcium > ammonium.

The imbibitional rate of the strong gluten, B-780, is markedly reduced by the addition of M/200 sodium sulfate to the potassium hydroxide solution as compared with potassium hydroxide alone. B-783 is also affected but to a less extent, probably due to the low imbibition in the alkali without sodium sulfate. In the case of calcium hydroxide plus M/200 sodium sulfate, the effect with both glutes is less marked.

The effect of the sodium sulfate on the swelling of gluten in potassium and calcium hydroxides is in agreement with the findings of others for the effect of salts on the swelling of animal proteins in alkalies.

In order to more directly compare the effect of acids and alkalies on the imbibitional rate, imbibitional experiments were carried out for 25 minute intervals in solutions of lactic and hydrochloric acids. These results indicate that under the same conditions the effect of the acids is somewhat greater than is the effect of alkalies. Here also the difference between hydrochloric and lactic acids is not so marked as it is in the higher concentrations and the longer intervals of time.

The studies with the dried glutens indicate that a marked change of the colloidal state has taken place in the process of drying. This was also shown by the appearance and texture of the wet gluten prepared from the dried material. The results obtained for the rate of imbibition of the dried material with lactic acid show very clearly that the colloidal structure has been profoundly altered by the drying process, the most pronounced change being in the case of the strong flour gluten B-780. It is of interest to note that drying causes the various glutens to become more alike in so far as all colloidal properties are concerned. The strong gluten in particular shows a lowered imbibitional capacity. This is what might be expected if the imbibitional capacity is due to marked colloidal properties, for we know that alternate freezing and thawing or subjection to alternate moist and dry conditions tends to break up the colloid complexes of a soil, and approximately the same factors are operating in the present instance.

The experiments show that results obtained for the dried material may not be compared to those obtained on the original moist gluten. The object of this investigation was not to investigate differences between glutens before and after drying but to study the glutens from the strong and weak flours, which explains why the drying experiments were not carried farther.

The determination of the hydrogen ion concentration of the solutions of acid used for the imbibitional experiments of Gortner and Doherty tends to show that the optimum hydrogen ion concentration for the swelling of discs occurs at a pH of 3.25 to 2.25. Because the hydrogen ion concentration of the solution is not necessarily the hydrogen concentration of the swelling layer of the disc, and because of the difference in behavior of strong and weak acids the true optimum probably is at a slightly lower hydrogen ion concentration. This indicates that the optimum hydrogen ion concentration of the solution of different acids in actual contact with the swelling discs of gluten lies at practically the same value for both strong and weak glutes and argues for little or no difference in the isoelectric points of the two glutes.

#### Summary

Certain physico-chemical studies were made on the glutes from four flours, one a high grade patent made from northern spring wheat (B-780), one a clear made from northern spring wheat (B-781), and two flours milled from soft western wheats (B-782 and B-783). The baking tests show that these flours are distinctly different. B-780 is what is known as a strong flour and B-782 and B-783 as weak flours.

The data presented seem to warrant the following conclusions:

(1) The rate of imbibition determined in hydrochloric and lactic acids is in agreement with the findings recorded in the first paper of this series, i. e., the "strong" flour gluten has a much higher rate of imbibition than has a "weak" flour gluten.

(2) There is a marked difference in the rate of imbibition of the different glutes in potassium and sodium hydroxides; the difference while not so apparent is noticeable also in the case of barium, calcium, and ammonium hydroxides. Here again in the case of alkalies the "strong" flour gluten has a higher rate of imbibition than has the "weak" flour gluten.

(3) The reaction of glutes to alkalies appears to be somewhat different from the reaction of the glutes to acids,

dispersion taking place much more rapidly and at lower concentrations in the case of alkalies. Indeed dispersion and imbibition are here almost coincident.

(4) The addition of sodium sulfate to the alkalies of potassium and calcium markedly lowered the imbibitional rate. It does not appear, however, from the shape of the curves that a low imbibitional rate in a weak flour is dependent on or determined by a higher salt content.

(5) Drying the glutes washed from the different flours in a vacuum oven at 45–50° C markedly altered the physico-chemical properties of the glutes, the properties of the different glutes studied becoming more nearly alike. This observation is in complete accord with the theory that the strong gluten is strong because of more pronounced colloidal properties inasmuch as it is well known that alternate wetting and drying a colloidal gel breaks down the gel structure.

(6) All of the data in the present paper confirm the postulation of Gortner and Doherty that a weak flour which owes its inferior strength to the *quality* of its gluten is weak because of the fact that its gluten possesses markedly inferior colloidal properties and is not so perfect a colloidal gel as is the gluten of a strong flour.

(7) Evidence is presented tending to show that the optimum hydrogen ion concentration for the imbibition of discs of gluten is the same for the various acids.

182  
318

## ELECTROLYTIC PRODUCTION OF SODIUM PERBORATE

BY PEDER CHR. ALSGAARD

The perborates, and principally the sodium perborate, have been used extensively for a long time in the industry, chiefly as a bleaching agent for all kinds of more delicate articles such as silk, feathers, ivory, animal fibers, wool, etc. They are also applied very much in connection with washing powders thereby producing a bleaching effect in addition to the cleansing one, due to the presence of soap powders, soda ash, etc. As a disinfectant and antiseptic they find use in medicine.

The properties of the solutions of the perborates correspond exactly to those of hydrogen peroxide, oxygen being split off readily in both cases. Thus sodium perborate gives off one atom of oxygen forming sodium metaborate:



just in the same way as hydrogen peroxide gives off oxygen forming water



This analogy is shown further by the fact that each is converted very readily into the other. When sodium perborate is treated with a dilute acid, hydrogen peroxide results. If the latter is added to a solution of metaborate—as borax and sodium hydroxide—the reverse reaction takes place, and the perborate is regenerated. Because of these properties, the sodium perborate may always replace the hydrogen peroxide chemically. Since it crystallizes readily, and is then very stable and can be kept indefinitely at the ordinary temperature, it affords a very convenient substitute for hydrogen peroxide. The content of active oxygen in sodium perborate is 10.4 percent, according to the formula  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ , while the common 3 percent hydrogen peroxide contains only 1.4 percent of active oxygen and is very unstable.

In the previous processes for the manufacture of sodium perborate, hydrogen peroxide was usually used as the oxidizing agent and was simply poured into a solution of borax and sodium hydroxide or soda ash, whereupon the perborate crystallizes out in large crystals. Instead of hydrogen peroxide other oxidizing agents may be used, such as percarbonates or sodium peroxide. From the last, it is also possible to obtain a compound called "Perborax,"  $\text{Na}_2\text{B}_4\text{O}_8$ , having practically the same properties as sodium peroxide. All these processes, however, are rather complicated, as they imply the intermediate preparation of an oxidizing agent, for example, hydrogen peroxide, the production of which is rather difficult and expensive. Much work has therefore been done by several investigators, to find a more direct and economic process for the manufacture of sodium perborate by means of electrolysis from borax solutions. The difficulties, however, involved in the solution of this problem, seemed for a long time to be as great as those involved in the electrolytic production of hydrogen peroxide.

On the request of "Die chem. Fabrik Grünau," Berlin, Professor Kurt Arndt started some research work on the problem, and in 1912 he happened to observe that sodium perborate was formed when electrolyzing a solution of borax containing sodium carbonate. A condensed report on this work may be found in the *Zeitschrift für Elektrochemie*, 22, 63 (1916).

By the electrolysis of a solution containing sodium carbonate and borax, sodium percarbonate is probably formed as an intermediate, which reacts instantaneously with borax forming perborate. By this process it is possible to produce sodium perborate directly, doing away with peroxides of hydrogen and sodium. The importance of this invention is obvious.

Some years ago Trygve Valeur did some research work at the Institute of Technology of Norway, in connection with the electrolytic production of sodium perborate. At that time he did not know anything of the work of Kurt Arndt, and the



results obtained were absolutely negative. In spite of variation of working conditions, and use of different electrolytes the quantities of sodium perborate obtained were very small. What made the problem look rather hopeless was the fact that that on electrolyzing a solution containing some sodium perborate, this was decomposed, no matter whether a diaphragm was used or not. It thus appeared that on electrolyzing a solution of sodium perborate, this is decomposed anodically as well as cathodically. After becoming aware of the patents taken out by Kurt Arndt, Valeur resumed his research work, and as his results were of great value for the subsequent development of a technical process for the electrolytic production of sodium perborate, they are first dealt with at some length.<sup>1</sup>

As the sodium perborate is more unstable at higher temperature, it is most likely that the current efficiency will be better the lower the temperature. On the other hand, the solubility of borax is very small in cold water, and as it may be assumed that the current efficiency increases with increasing concentration of borax in the electrolyte, the first experiments were carried out with a solution of borax and sodium hydroxide. On account of the greater solubility of the metaborate, such a solution can be made rather concentrated, even at a low temperature.

In order to increase the current efficiency a diaphragm was first used. As this causes the alkalinity of the anodic solution to decrease, the borax has a tendency to crystallize if no precautions are taken. For this reason, from the beginning of the electrolysis, there was added an excess of sodium hydroxide and the electrolysis was run until the borax began to crystallize out. From the results thus obtained, we gain an idea of the influence of the alkalinity on the formation of the sodium perborate. It now appeared that the concentration of the sodium perborate always increased during the electrolysis, until the point where the crystallization of the borax sets in. From that moment it begins to decrease, although very slowly.

---

<sup>1</sup> Cf. *Tidsskrift for kemi Farmaci og Terapi, Kristiania, 1916, Nos. 17, 18.*



Further it was found that this maximum concentration of sodium perborate, within a wide range, was nearly independent of the quantity of sodium hydroxide originally added, and hence, independent of the time from the start of the experiment until the beginning of the crystallization of the borax. This indicates that under the prevailing conditions the maximum concentration found is the largest obtainable at all. Since the sodium perborate is not only produced, but also decomposed at the anode, it seems very probable that there must be a concentration, at which the formation and the decomposition of the perborate counterbalance each other.

At first some experiments were carried out to determine the influence of the sodium carbonate on the production of the sodium perborate. The diaphragm used was a porous cylindrical clay cell, containing 85 cc of the anodic solution. The cell was placed in a beaker containing N/1 NaOH as cathodic solution. The anode was a platinum sheet with a total surface of 6.4 cm<sup>2</sup>. The current was 1.6 amperes and the anodic current density thus 25 amp/dm<sup>2</sup>. The cathode consisted of an iron plate surrounding the diaphragm cell. In order to keep down the temperature, the beaker was placed in ice water. The reagents used in these experiments were very pure, as impurities proved harmful. The sodium perborate produced was titrated in the usual way with N/10 KMnO<sub>4</sub> in an acid solution (Table I). The figures for the maximum concentra-

TABLE I

Ex. No.	Contents per 100 cc of electrolyte	Voltage on cell	Temperature	Maximum concentration
1	4 grs Na <sub>2</sub> CO <sub>3</sub> + 8 grs NaOH + 17 grs Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	6.0-7.9	9°-13° C	2.3
2	8 grs Na <sub>2</sub> CO <sub>3</sub> + 8 grs NaOH + 17 grs Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	6.2-7.7	9°-16° C	3.9
3	12 grs Na <sub>2</sub> CO <sub>3</sub> + 8 grs NaOH + 17 grs Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	6.4-7.4	9°-14° C	5.0
4	16 grs Na <sub>2</sub> CO <sub>3</sub> + 8 grs NaOH + 17 grs Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	6.5-7.7	9°-14° C	5.7

tion refer to the amount of N/10  $\text{KMnO}_4$  in cc used for the titration of 1 cc of electrolyte. The maximum concentration was reached after 6-8 hours of electrolysis. It appears that the production of sodium perborate is increased essentially by increasing the concentration of sodium carbonate in the electrolyte, which is only what might have been expected beforehand. In experiment No. 4 the solution is decidedly supersaturated with respect to the sodium carbonate; but no salt crystallizes during the electrolysis, nor was there any precipitation of sodium perborate in any of the experiments. If, instead of sodium carbonate alone, a mixture of sodium and potassium carbonates is used in the electrolyte a still higher maximum concentration of sodium perborate may be obtained. Some experiments were then carried out with electrolytes corresponding to those in Table I, with an addition of small amounts of different substances. Thus sodium fluoride was tried, which raises the overvoltage; also sodium phosphate, which is stated to stabilize perborate solutions, and many others. In most cases the addition had practically no effect upon the formation of the perborate, and in some they were detrimental. Sodium silicate—water-glass—however, proved to be favorable, as is shown by the following three experiments.

TABLE II

Ex. No.	Contents per 100 cc of electrolyte	Voltage on cell	Temperature	Maximum concentration
5	8 grs $\text{Na}_2\text{CO}_3$ + 8 grs NaOH + 17 grs Borax + 3 cc water-glass	7.4-8.1	9°-14°	5.25
6	12 grs $\text{Na}_2\text{CO}_3$ + 8 grs NaOH + 17 grs Borax + 3 cc water-glass	6.6-7.8	9°-14°	6.65
7	As in experiment 6	7.1-7.5	9°-14°	7.05

Except for the content of water-glass, the working conditions of these experiments were the same as in the experiments Nos. 2 and 3. (Table I.)

In all these experiments a layer of silica was formed on the anode. This layer, however, became visible only at the end of the experiment. When electrolyzing a solution con-

taining only water-glass, practically no sodium perborate was formed. There is therefore a marked difference between sodium carbonate and water-glass, as to their effect upon the formation of perborate. This difference is also shown by the fact that the effect of the water-glass as contrasted with the sodium carbonate is independent of the quantity added within a wide range. In all these experiments platinum has been used as an anode. It would, however, be of great interest, if the platinum could be replaced by a cheaper material.

Experiments were therefore carried out with lead, nickel, iron and graphite; but these metals all proved unsuitable. In some cases—lead and nickel—some perborate was formed, but the amounts were too small to make them available. By the use of an anode of nickel, the maximum concentration obtained corresponded to the amount of 0.5 cc of N/10  $\text{KMnO}_4$  used per 1 cc of the electrolyte.

The next problem was to determine the effect of the current density upon the maximum concentration of sodium perborate. From the previous experiments it follows that the concentration of the sodium carbonate should be as high as possible, and for that reason, the electrolyte in all cases was practically saturated with sodium carbonate. The working conditions were exactly as in the previous experiments. The current was always 1.6 amperes and consequently the size of the anode had to be varied in order to get a variation in the current density. The results of these experiments are tabulated in Table III. From this it will be seen that the most favorable current density varies from 25–35 amp/dm<sup>2</sup>. When the electrolyte contains water-glass, the favorable current density is apparently somewhat higher than in the cases where no water-glass is used. These experiments also show the favorable influence of the water-glass on the maximum concentration of the sodium perborate.

Besides the current density, there is another factor that might be of importance to the current efficiency, namely the temperature. When determining the temperature most favorable to the electrolysis, it must be borne in mind that the

TABLE III

Ex. No.	Contents per 100 cc of electrolyte	Current density	Voltage on cell	Temperature	Maximum concentration
8	12 grs sodium carbonate+ 8 grs NaOH +17 grs Borax	16 amps/dm <sup>2</sup>	6.0-6.7	8°-12°	3.0
3	12 grs sodium carbonate+ 8 grs NaOH +17 grs Borax	25 amps/dm <sup>2</sup>	6.4-7.4	9°-14°	5.0
9	12 grs sodium carbonate+ 8 grs NaOH +17 grs Borax	35 amps/dm <sup>2</sup>	7.4-8.0	10°-14°	4.0
10	12 grs sodium carbonate+ 8 grs NaOH +17 grs Borax	50 amps/dm <sup>2</sup>	7.2-8.6	9°-16°	3.8
11	12 grs Na <sub>2</sub> CO <sub>3</sub> +8 grs NaOH+ 17 grs Borax+ 3 cc water- glass	16 amps/dm <sup>2</sup>	7.0-7.5	10°-14°	5.4
12	12 grs Na <sub>2</sub> CO <sub>3</sub> +8 grs NaOH+ 17 grs Borax+ 3 cc water- glass	25 amps/dm <sup>2</sup>	6.4-8.0	9°-15°	6.5
13	12 grs Na <sub>2</sub> CO <sub>3</sub> +8 grs NaOH+ 17 grs Borax+ 3 cc water- glass	35 amps/dm <sup>2</sup>	7.5-8.5	10°-14°	6.6
14	12 grs Na <sub>2</sub> CO <sub>3</sub> +8 grs NaOH+ 17 grs Borax+ 3 cc water- glass	50 amps/dm <sup>2</sup>	8.2-9.2	9°-16°	6.1

solubility of the sodium carbonate, will vary at the different temperatures. When varying the temperature, it is therefore necessary also to vary the composition of the electrolyte, and to take care that the electrolyte is always practically saturated with sodium carbonate. In this way the most favorable temperature was found to be about  $10^{\circ}$ – $12^{\circ}$  C, which is shown by the following three experiments, Table IV.

TABLE IV

Ex. No.	Contents per 100 cc of electrolyte	Voltage on cell	Temperature	Maximum concentration
15	8 grs $\text{Na}_2\text{CO}_3$ + 8 grs NaOH + 17 grs Borax + 3 cc of water-glass	ca 10.0	$5^{\circ}$ – $10^{\circ}$	4.7
16	12 grs $\text{Na}_2\text{CO}_3$ + 8 grs NaOH + 17 grs Borax + 3 cc of water-glass	6.4–7.8	$10^{\circ}$ – $14^{\circ}$	5.45
17	16 grs $\text{Na}_2\text{CO}_3$ + 8 grs NaOH + 17 grs Borax + 3 cc of water-glass	6.9–7.5	$16^{\circ}$ – $22^{\circ}$	4.5

The experimental conditions were as before—current density  $25 \text{ amp/dm}^2$ , the only difference being the borax which had not been re-crystallized, and therefore caused a decrease in the current efficiency.

In spite of the fact that the concentration of the sodium perborate in many of the solutions was rather high, it never crystallized even when the solution was cooled down to  $0^{\circ}$  C. This is rather peculiar, as the solubility of sodium perborate in water is rather low. In order to get a more general idea as to the conditions of solubility, some experiments were made with very strong solutions of sodium perborate, prepared by means of hydrogen peroxide. The solutions were inoculated with crystals of sodium perborate and allowed to stand at  $0^{\circ}$  C for crystallization. By means of continuous analysis of the solution, the rate of crystallization could be followed, and the solubility determined in the different cases. First it proved that the sodium perborate has a very marked tendency to form supersaturated solutions. Usually crystalliza-

tion does not take place unless the solution is inoculated, and, in most cases, several days were required to bring the crystallization to an end, and to get a constant amount of sodium perborate in solution. Then it proved that sodium metaborate and sodium hydroxide increase the solubility of sodium perborate, while an addition of sodium carbonate causes some decrease in the solubility. It may be noted that it proved impossible to induce the sodium perborate to crystallize at 0° C from a solution containing per 100 cc 33 grs of borax, 12 grs of NaOH, and 20 cc of about 10 percent H<sub>2</sub>O<sub>2</sub>, although the amount of N/10 KMnO<sub>4</sub> used per cc of the solution was 12–13 cc. In pure water, however, the solubility was much less, the amount of N/10 KMnO<sub>4</sub> used per cc being only 1.2 cc. The reason for these solubility relations is most probably the formation of some complex or double salt. These changes in solubility are very important when making sodium perborate on a technical scale. The only thing to do in this case seems to be to use solutions containing less metaborate. In order to illustrate the state of things, when decreasing amounts of metaborate are in solution, the results of some experiments are given in Table V. The working conditions were as described before and the current density was 35 amps/dm<sup>2</sup>.

As mentioned before, it was impossible to induce crystallization of the sodium perborate in the experiments 9 and 13. In experiments 18 and 19, however, after cooling down to 0° C and filtering off the sodium carbonate which crystallized out, small quantities of sodium perborate were induced to crystallize by inoculation with sodium perborate crystals, and in the experiments 20 and 21, after inoculation of the solution, the sodium perborate crystallized at the temperature used in the electrolysis (12°–13° C). The favorable effect of the water-glass is also observed in these experiments, but it is also seen that the influence decreases with the concentration of the borate in the electrolyte, and in such a way that the maximum concentration without water-glass is practically independent of the concentration of the borate, while the decrease is very marked where water-glass is present in the solution.

TABLE V

Ex. No.	Contents per 100 cc of electrolyte	Voltage on cell	Temperature	Maximum concentration
9	12 grs $\text{Na}_2\text{CO}_3$ + 8 grs NaOH + 17 grs Borax	7.4-8.0	10°-14°	4.0
13	12 grs $\text{Na}_2\text{CO}_3$ + 8 grs NaOH + 17 grs Borax + 3 cc water-glass	7.5-8.5	10°-14°	6.6
18	12 grs $\text{Na}_2\text{CO}_3$ + 5.5 grs NaOH + 12 grs Borax	8.0-8.3	11°-14°	4.2
19	12 grs $\text{Na}_2\text{CO}_3$ + 5.5 grs NaOH + 12 grs Borax + 3 cc water-glass	7.2-7.7	10°-13°	5.5
20	12 grs $\text{Na}_2\text{CO}_3$ + 4.5 grs NaOH + 8 grs Borax	7.4-7.9	11°-14°	4.1
21	12 grs $\text{Na}_2\text{CO}_3$ + 4.5 grs NaOH + 8 grs Borax + 3 cc of water-glass	7.5-8.0	11°-14°	5.2

As soon as it is possible to prepare solutions saturated or supersaturated with respect to sodium perborate, the most important question is no longer the maximum concentration but the current efficiency at that concentration of sodium perborate where the solution is saturated.

When in the experiments 20 and 21, the amounts of sodium hydroxide are varied, the time required for the reaching of the maximum concentration varies also and hence the current efficiency. The highest current efficiency obtained in this way at the concentration of the saturated solution, was 35 percent with and 30 percent without water-glass in the electrolyte. At the temperature in use (12°-13° C) the concentration of the saturated solution corresponded to the amount of about 2.7 cc of N/10  $\text{KMnO}_4$  used per cc of the electrolyte.

This is, however, still rather high and it proved more favorable to work with solutions containing no sodium hydroxide at all, hence no metaborate. The maximum concentration certainly decreases markedly when doing so, as the contents of borate in the solution becomes rather small; but at the same time the solubility of the sodium perborate decreases to such a degree that the current efficiency at the concentration of the

saturated solution increases considerably. A further advantage is the possibility of doing away with the diaphragm. This is certainly practicable, also in the previous experiments where sodium hydroxide is used. The losses in current efficiency, due to cathodic reduction of the perborate increases, however, rather markedly with increasing concentration of the perborate. When therefore no diaphragm is used, the decrease in current efficiency is much greater, when the electrolyte contains sodium hydroxide, as compared with the cases where no sodium hydroxide is employed, and the concentration of sodium perborate therefore is much less. The concentration of such a solution, when saturated, corresponds to the amount of only 0.9–1 cc of N/10  $\text{KMnO}_4$  used per cc of the solution. (Cf. ex. No. 22.) The variation of the current efficiency in relation to the concentration of perborate may be seen from Table VI. The solution employed contained

Table VI

Ex. 22 Contents per 100 cc of electrolyte	Amp hrs from start of the experiment	Amount of cc N/10 $\text{KMnO}_4$	Current efficiency in percent
12 grs $\text{Na}_2\text{CO}_3$	0	0	49.5
+ 4.5 grs Borax	0.5	1.1	33.8
+ 0.2 gr $\text{Na}_2\text{Cr}_2\text{O}_7$	1.0	1.85	29.2
	1.5	2.5	

per 100 cc 12 grs of  $\text{Na}_2\text{CO}_3$ , 4.5 grs of crystallized borax, and 0.2 gr of sodium bichromate. The cathode consisted of two zigzag bent nickel wires, one on each side of the anode, of 1.5 mm diameter, and an effective length of 205 mm. The surface was accordingly about  $9.6 \text{ cm}^2$ . The current was 1.6 amperes; the current density about  $17 \text{ amp/dm}^2$ , the anodic current density  $35 \text{ amp/dm}^2$ ; the volume of the solution 85 cc; the temperature  $11^\circ\text{--}13^\circ \text{C}$ ; and the voltage on the cell about 6.5 volts.

As previously mentioned, it is also practicable, instead of sodium carbonate alone, to employ a mixture of sodium and potassium carbonates in the electrolytes. This makes it pos-



sible to increase the total amount of carbonate in the solution, which causes an increase in the maximum concentration of the sodium perborate and a higher current efficiency. The addition of potassium carbonate, however, increases simultaneously the solubility of the sodium perborate, and as we are here concerned chiefly with the current efficiency at the concentration of a saturated solution, this effect to some extent counterbalances the increase in current efficiency. When the amount of potassium carbonate is not too large, this increase in solubility is relatively small. The best results were obtained with a solution containing per 100 cc 10 grs of sodium carbonate, 7 grs of potassium carbonate, 4.5 grs of borax and 0.2 gr bichromate, cf. Table VII. The concen-

Table VII

Exp. 25 Contents per 100 cc of electrolyte	Amp hrs from start of the experiment	Amount of cc N/10 KMnO <sub>4</sub>	Current efficiency in percent
10 grs Na <sub>2</sub> CO <sub>3</sub>	0	0	54.0
+ 7 grs K <sub>2</sub> CO <sub>3</sub> + 4.5	0.5	1.2	40.3
grs Borax + 0.2 gr	1.0	2.45	30.9
Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	1.5	3.0	

tration of the saturated solution in this case corresponded to an amount of 1.1 cc N/10 KMnO<sub>4</sub> used per 1 cc of electrolyte. The temperature was maintained at 10°-13° C, and the voltage was about 6 volts. For the remainder of the experiment the working conditions were the same as those employed in experiment No. 22. Also in this experiment an addition of water-glass proved favorable, when the amount was not too large. In Table VIII are given the results of an experiment which differs from the above experiment only in so far as the electrolyte contained three drops of water-glass per 100 cc. When sodium perborate is to be manufactured on a technical scale, the most ideal condition would be the continuous crystallization of the sodium perborate during the electrolysis, and the simultaneous addition of the raw materials as they are consumed in the process. In order to have the sodium

Table VIII

Exp. 24 Contents per 100 cc of electrolyte	Amp hrs from start of the experiment	Amount of cc N/10 KMnO <sub>4</sub>	Current efficiency in percent
10 grs Na <sub>2</sub> CO <sub>3</sub> + 7 grs K <sub>2</sub> CO <sub>3</sub> + 4.5 grs Borax + 0.2 gr NaCr <sub>2</sub> O <sub>7</sub> + 3 drops water-glass	0	0	56.4
	0.5	1.5	45.0
	1.0	2.3	30.1
	1.5	3.1	

perborate crystallize out without the concentration rising too high above the concentration of the saturated solution, the slow crystallization of the salt makes it necessary to use rather large electrolyzing cells and a relatively small current. In the following are given two experiments, carried out in a relatively large electrolytic cell, with a lower surface of 660 cm<sup>2</sup>, and containing 2.5 liters of electrolyte.

The electrolysis was run for a period of 40 hours. When the concentration of the saturated solution was reached, the solution was inoculated with crystals of sodium perborate. Borax and sodium carbonate were added as they were consumed in the process. In the first experiment—using no water-glass—after crystallization had started and equilibrium attained, the concentration remained between 1.8 and 1.9 cc of N/10 KMnO<sub>4</sub> used per cc of electrolyte. The sodium perborate which crystallized out during the experiment, was carefully washed, dried, weighed and analyzed. The current efficiency was calculated to be 31.8 percent.

In the other experiment, using 2 cc of water-glass per liter of the electrolyte, equilibrium was established at an amount of 2–2.1 cc of N/10 KMnO<sub>4</sub> used per cc of electrolyte, and the current efficiency amounted to 37.5 percent. As the concentration of the saturated solution corresponds to the amount of about 1.1 cc of N/10 KMnO<sub>4</sub> per cc of electrolyte, there is no doubt that the current efficiency can be improved considerably by using still larger electrolytic cells, in which case the equilibrium is established at a lower concentration of perborate. These experiments, carried out by Valeur cleared

up the process for the electrolytical production of sodium perborate in a large measure, and threw light upon the most important factors governing the process. For the technical and commercial utilization of the process, further important problems had to be solved, and the writer therefore, some years later, in the employment of O. Collett and Co., started some new research work in order to develop a technical process for the electrolytic production of sodium perborate. The process was in operation in Germany during the war, and plans were considered to extend the work on a very large scale.

The first experiments were practically a repetition of the experiments already carried out by Valeur, but on a somewhat larger scale. The external cooling with ice water is of course out of the question in a technical process. The solution was therefore cooled by running cold water through the cathode which for this purpose consisted of a pipe of copper, suitably shaped, and coated with a layer of tin or nickel. The results obtained were practically the same as those found by Valeur. It will therefore be sufficient to refer to only one of these experiments, the results of which are shown graphically in Fig. 1.

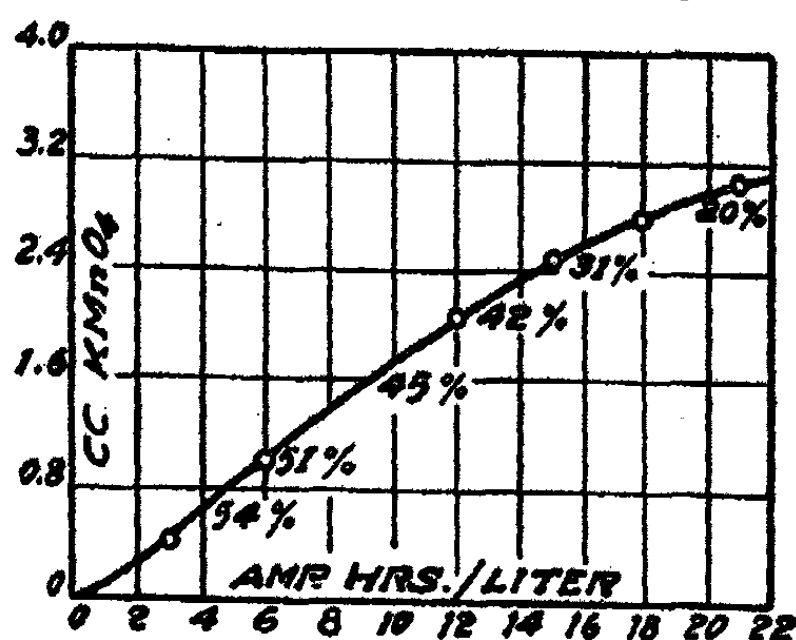


Fig. 1

As abscissa is used the number of ampere hours per liter of the electrolyte, and as ordinate the amount of N/10  $\text{KMnO}_4$  used per cc of the electrolyte, 1 cc of N/10  $\text{KMnO}_4$  corresponding to 7.7 grs of perborate per liter of the electrolyte.

The current was 6 amperes and the voltage on the cell about 5 volts. The volume of the electrolyte was 400 cc and the temperature was kept at 9°–10° C. The electrolyte had the following composition per liter:

100 grs of  $\text{Na}_2\text{CO}_3$

75 grs of  $\text{K}_2\text{CO}_3$

45 grs of Borax

2 grs of Potassium chromate

It is seen from the curve that the current efficiency falls off as the concentration of the sodium perborate increases, and on extrapolation becomes zero. By further electrolysis the concentration of the perborate remains constant, and equal amounts of perborate are formed and decomposed. The solutions of perborate obtained, however, did not appear to be stable. When allowed to stand, the content of perborate gradually decreased. The rate of decomposition varied to some extent, but it was always observed in spite of the use of very pure reagents. This decomposition is inevitable, as it had been stated by Valeur that great surfaces and volumes, as compared with the employed load of ampere, were necessary in order to cut down the concentration of the perborate and to increase the current efficiency. On account of the spontaneous decomposition of the perborate, the beneficial effect of a greater volume is of course limited, as the decomposition is proportional to the volume of the electrolyte employed. The decomposition of the sodium perborate is, as in the case of a solution of hydrogen peroxide, in the main effected by the catalytic action of impurities present in the solution. It was impossible to prepare a solution which was absolutely stable, even at very low temperatures. The decomposition proved chiefly to be due to iron, which is rather peculiar, as iron is generally not supposed to be soluble in sodium carbonate. Efforts were now made to purify the raw materials. The crystallized high grade commercial borax (99.5%  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) may be used directly. The commercial soda ash, however, with 98–99 percent  $\text{Na}_2\text{CO}_3$ , has to be purified, as it always contains traces of iron. The content of sodium

chloride is unimportant, as a concentration of 5 grs of NaCl per liter of the electrolyte does not affect the current efficiency at all. An attempt was made to precipitate and remove the iron from the solution of sodium carbonate by boiling, by addition of several substances, colloids, alumina, ferric oxide, etc.; but all in vain. The only way left was to purify the sodium carbonate by crystallization. From the equation for the formation of sodium perborate from sodium carbonate and borax:

$\text{Na}_2\text{B}_4\text{O}_7 + \text{Na}_2\text{CO}_3 + 4\text{O} \rightarrow 4\text{NaBO}_3 + \text{CO}_2$ , it is noticed that  $\text{CO}_2$  is set free, and that the materials actually consumed are borax and sodium hydroxide. In order to maintain the initial and favorable concentration of borax and sodium hydroxide, these substances must be added to the electrolyte during the process of the electrolysis.

The employment of sodium hydroxide involves another problem, as it is very difficult to obtain this material of the purity required for the perborate electrolysis. It may be obtained from pure sodium carbonate by caustification with pure lime, or sodium carbonate may be used instead of sodium hydroxide, and the  $\text{CO}_2$  formed by the electrolysis removed by treatment of the electrolyte with pure lime. However, either one of these methods is rather expensive, and not very satisfactory. A more favorable method was the caustification of the electrolyte by means of electrolysis. The electrolyte, which in this case was made purposely rich in sodium bicarbonate, was fed to the cathodic compartment of an electrolytic cell, canvas being used as a diaphragm, and electrolyzed until the greater part of the bicarbonates and carbonates of sodium was converted into sodium hydroxide. This process worked very satisfactorily; but as it requires special electrolytic cells, it makes the process more complicated.

Further experiments were therefore carried out in order to find another method for the removal of the excess of carbon dioxide. It had been observed that the carbon dioxide is partly liberated at the anode and thus removed from the electrolyte by the primary electrolytic process. As this fact

may be used for the removal of the carbon dioxide, set free by the formation of sodium perborate, some experiments were carried out in order to determine under what conditions this evolution of carbon dioxide takes place. The method which suggests itself, is to carry out the electrolysis, in such a way that the absorption of the liberated carbon dioxide is cut down to such an extent that the quantity set free corresponds to the consumption of sodium carbonate for the formation of perborate. This proved to be possible by using as an electrolyte a solution containing a large amount of sodium bicarbonate compared with the total amount of carbonate present, and by lessening the submergence of the anode in the electrolyte. It also proved favorable to work with electrolytes containing no or only small amounts of potassium carbonate. The elimination of the potassium carbonate is also desirable from the point of view of regeneration of the substances dissolved in the electrolyte. As the electrolysis proceeds, and new raw materials are added to the system, impurities gradually accumulate in the electrolyte, and the decomposing influence on the perborate becomes more marked. From time to time it is therefore necessary to replace the electrolyte partially by fresh solution. The regeneration of the sodium carbonate and the borax from the old electrolyte does not offer any difficulties, as this is easily done by evaporation and crystallization. The regeneration of the potassium carbonate, however, and further, the purification of the commercial potassium carbonate involve several difficulties. For these reasons it would be a great advantage to use an electrolyte containing borax and sodium carbonate only, and no potassium carbonate at all. The current efficiency certainly would diminish in this case, but at the same time the lesser solubility of the perborate in the electrolyte produces better conditions of crystallization. Experiments along this line were made in connection with the next problem to be solved, namely the crystallization of the sodium perborate from the electrolyte.

From the current efficiency curve it is noticed that the

lower the concentrations of the perborate in the electrolyte the higher the current efficiency. In order to keep the concentration of the perborate low, Valeur in his last experiments used a very large lower surface as compared with the ampere used, and still the concentration maintained at a volume corresponding to the amount of 2 cc of N/10  $\text{KMnO}_4$  used per cc of the electrolyte. If the same relative area were to be used, when working on an industrial scale (one ton per day), this would mean a surface of about an acre. This is of course impossible. At the same time this involves the use of large volumes of electrolyte per ampere, which is unfortunate, because of the spontaneous decomposition of the perborate. The solution of the problem offered several difficulties, which at last were overcome, and it proved possible to reduce the volume of the electrolyte substantially. In one of these experiments 1.8 liters of electrolyte were electrolyzed with 6 amperes at a temperature of  $10^\circ \text{C}$ . The solution had the following compositions per liter:

45 grs of Borax  
130 grs of Sodium carbonate  
45 grs of Sodium bicarbonate  
2 grs of Potassium bichromate  
2 grs of Water-glass.

Potassium carbonate was not used. When equilibrium was established the concentration of the perborate in solution corresponded to an amount of about 1.5 cc of N/10  $\text{KMnO}_4$  used per cc of the electrolyte. The current efficiency, with reference to the washed, dried, and analyzed salt, amounted to about 40 percent.

When the research work on this preliminary smaller scale had led to satisfactory results, and the process had been given a shape suited for development, experiments were started on a large scale, to determine what modifications of the apparatus and process were necessary; to determine, for instance, what form and dimensions of the electrodes were to be used on an industrial scale. The results from these experiments confirmed to the full the results obtained in the

previous experiments, and also furnished the facts and figures necessary for the technical design of the process and the calculation of the costs of production.

As to the latter, these of course depend to some extent on the local conditions; but some figures may be stated, which give an idea of the production costs. The outstanding items are the cost of raw materials, power and labor. The raw materials required per ton of perborate are:

Borax 700 kg  
Soda ash 200 kg

Assuming a production of one ton of sodium perborate per day, and 330 days of operation a year, the electric power required for the electrolysis, calculated as direct current, will be

315 H. P.  
Mechanical power, power for cooling plant 130 H. P.

---

*Total Power, say* 450 H. P.

Number of laborers, about 10

In the case that the perborate electrolysis is operated in connection with another electrolysis, this figure is reduced considerably. The amount of platinum required for this production is about 7 kg.



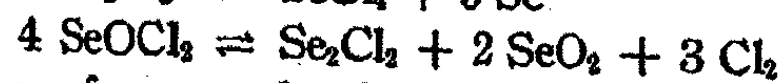
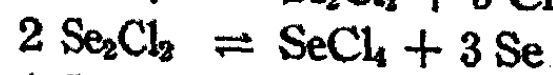
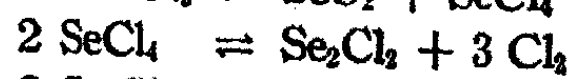
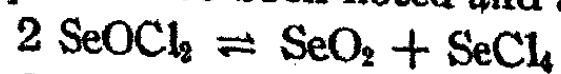
## VAPOR PRESSURE OF SELENIUM OXYCHLORIDE

BY VICTOR LENHER, G. B. L. SMITH AND G. G. TOWN

In the preparation of selenium oxychloride, it has been the practice in this laboratory, for purposes of purification, to distill under reduced pressure. In this paper are presented the observed vapor pressures of selenium oxychloride at temperatures ranging from 85° to 177° and at pressures from 21 mm to 740 mm. Selenium oxychloride, when distilled under considerably reduced pressures, has a light straw color and by analysis shows that it is a quite pure product. Such selenium oxychloride freezes at 10.8° C and boils at 177.2° C at 744 mm pressure.

When selenium oxychloride is distilled under atmospheric pressure, it decomposes slightly as is evidenced (1) by the condensation of small amounts of selenium dioxide on the neck of the distilling flask, (2) by the change of color in the distilling flask from that of a pale straw to a reddish brown, which change on cooling partially reverses, (3) by the slight increase in its boiling point.

At or near the boiling point and under atmospheric pressures, the minor decompositions of selenium oxychloride which take place have been noted and are as follows:



A series of vapor density experiments in the ordinary Victor Meyer apparatus using alpha brom-naphthalene yielding a temperature of 265°-290° in the heating chamber, ranged from 164.4 to 141.5 for the molecular weight, the mean of the observed values being 151.4 by this method. There is apparently a small amount of dissociation of the substance appearing as a factor at these temperatures. By reducing the pressure and thus distilling at a lower temperature these minor decompositions are very largely obviated.

### Apparatus

The apparatus used for the determination of the vapor pressures between 85° and 120° C was a modification of the Ramsay-Young<sup>1</sup> apparatus. This consisted of a distillation chamber with a glass tube sealed on the top, the thermometer being hung to a ground glass stopper in the top of the tube. The selenium oxychloride was introduced from a separatory funnel which was connected to a distillation chamber by means of a glass tube sealed into the side of the chamber in such a manner that the selenium oxychloride would run down the thermometer. The bulb of the thermometer was wound with glass wool which was tied on with the glass wool itself. The chamber was immersed in a phosphoric acid bath. The distillation chamber was connected to a condensing flask by means of a glass tube and ground-glass joint, the condensing flask being immersed in cold water. The condensing flask was in turn connected to the vacuum system. The vacuum system consisted of three equalizing bottles of twenty liters capacity each, a soda-lime tower and a U-tube manometer. A partial vacuum was maintained by a large water pump. When the selenium oxychloride had started to distill, the temperature and pressure were read simultaneously.

Observations were recorded in the modified Ramsay-Young apparatus at pressures up to 105.8 mm. which gave a B. P. of 117.2°. Above this pressure and temperature, it is considered that the method does not give sufficiently accurate results. For the higher temperatures a distillation flask was used. The thermometer was laid in a tube sealed into the side of the distilling flask, the bulb of the thermometer projecting into the neck of the flask. The flask was heated on a sand bath by means of an electric hot plate. The pressure was read directly on a syphon barometer which was connected to the vacuum system. The thermometer was also calibrated in the apparatus against boiling water and boiling selenium oxychloride under atmospheric pressure in order to

<sup>1</sup> Jour. Chem. Soc., 47, 42 (1885).

determine whether the readings were correct at the position in which the thermometer was placed in the apparatus.

#### Experimental

*The Vapor Pressures of Selenium Oxychloride.*—The selenium oxychloride used in these measurements was prepared according to the method given by Lenher,<sup>1</sup> care being taken that it did not contain such impurities as water, selenium dioxide, selenium monochloride, selenium tetrachloride or excess chlorine. Observations were made in the Ramsay and Young apparatus for a period of approximately thirty minutes. The apparatus was always cleaned and thoroughly dried before each set of observations. These precautions were taken to prevent any inaccuracies caused by decomposition products which might have accumulated in the apparatus. For the higher temperatures, where the distillation method was used, the same care was exercised. Tables I–II contain the observed vapor pressures under these conditions.

The effect on the vapor pressure of such substances as may be formed in selenium oxychloride by superheating has been studied at diminished pressures and at the corresponding lower temperatures.

Elementary selenium added in excess exerts practically no measurable effect on the vapor pressures of selenium oxychloride at temperatures between 90 degrees and 120 degrees.

Selenium monochloride dissolved in selenium oxychloride to the extent of 20 percent likewise gives no measurable effect on the vapor pressure at temperatures between 89 degrees and 121 degrees. In a similar manner selenium dioxide added to selenium oxychloride in quantities up to saturation at 20° shows no measurable effect on the vapor pressure of selenium oxychloride at temperatures between 91 degrees and 135 degrees; nor does selenium tetrachloride up to the saturation point at 20° show any effect between 89 degrees and 130 degrees.

<sup>1</sup> Jour. Am. Chem. Soc., 42, 2498 (1920).

TABLE I

Pressure	B. P.	Pressure	B. P.
21	84.3	55.3	102.8
22	85.5	56.3	103.3
23	86.0	56.4	103.4
29.4	89.0	56.7	104.0
29.4	89.1	58.4	104.4
35.6	94.0	60.0	104.8
35.9	94.2	67.0	107.9
36.3	94.7	68.9	108.4
37.0	95.1	68.7	108.8
38.2	95.5	69.0	108.3
38.5 (2 observations)	95.0	73.0	109.1
39.7	95.7	74.9	109.5
39.0	95.8	76.0	109.8
39.4	96.0	78.0	111.2
40.0	96.4	80.0	111.9
40.6	96.8	82.4	112.4
42.0	97.0	83.0	112.8
43.5 (2 observations)	98.5	84.1	112.8
47.7 (2 observations)	100.8	88.8	113.5
48.6	101.0	93.4	114.4
50.4	101.5	97.1	115.7
51.6	102.0	105.5	117.0
52.2	102.2	105.5	117.1
52.5	102.6	105.8	117.2
52.5	102.7	—	—

TABLE II  
DISTILLATION METHOD

Pressure	B. P.	Pressure	B. P.
138	123.5	402	153.5
142	124.7	425	155.0
162	127.0	466	159.0
174	128.5	479	159.6
183	130.5	492	160.5
187	131.5	511	161.8
209	133.5	512	162.0
232	136.5	528	163.2
256	139.0	551	164.5
266	141.3	571	166.5
269	142.0	614	168.0
313	146.0	641	169.0
319	147.0	728	176.4
393.5	152.8	740	177.2
395	153.0	—	—

The following equation gives the vapor pressure of selenium oxychloride deduced from the observations made:

$$\text{Log } P = 5.8503 + .000219T - \frac{830.9}{T-178}$$

In this equation  $P$  = the vapor pressure in mm and  $T$  the corresponding temperatures on the absolute scale.

# CATALYTIC PREPARATION OF ANILINE

BY O. W. BROWN AND C. O. HENKE

## Introduction

Sabatier<sup>1</sup> found that nitrobenzene was reduced by hydrogen in the presence of active nickel, yielding aniline, ammonia, benzene, cyclohexane, cyclohexylamine, dicyclohexylamine, cyclohexylaniline, and a little diphenylamine. With a more active nickel and at a higher temperature, the nitrobenzene was reduced even to ammonia and methane, while with a less active nickel only aniline was produced. He found copper to be a better catalyst than nickel for the production of aniline because its action did not extend to the aromatic ring. In this paper we shall give the results of some studies of this reduction of nitrobenzene to aniline in the presence of nickel and copper catalysts. The object in view was to study quantitatively the behavior of these two catalysts and to determine the various factors affecting their activity, as measured by the yield of aniline secured.

## Apparatus

In order to make these studies an apparatus was required which would permit: (1) an accurate method of measuring the temperature of the gaseous mixture while in contact with the catalyst; (2) an even flow of nitrobenzene which could be easily regulated and accurately known; (3) an even flow of hydrogen which could be easily regulated independently of the nitrobenzene; (4) a means of quantitatively receiving the product, so that it could be quantitatively determined. After many attempts an apparatus was finally devised which fulfilled all requirements, and since it has proved very satisfactory a full description follows.

The apparatus is shown diagrammatically (to scale) in Fig. 1. A is a flowmeter used to measure the rate at which the hydrogen was passed into the furnace. This was cali-

<sup>1</sup> Sabatier: "La Catalyse," 1st Ed., pp. 60, 91 and 107 (1913).

765

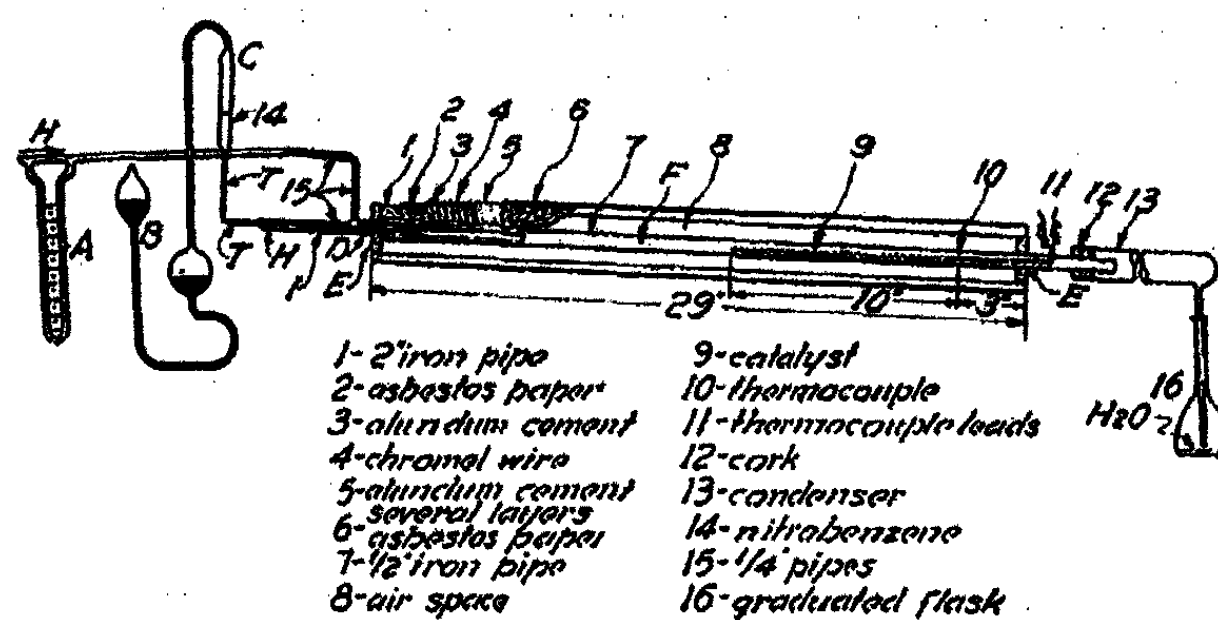


Fig. 1

brated against an electrolytic hydrogen generator, the quantity of hydrogen liberated being calculated from the current used. The nitrobenzene is introduced at A (after disconnecting the rubber tube) by means of a calibrated pipette. C consists of a glass tube, about 7 or 10 mm in diameter, sealed to a capillary tube T which is then bent as shown in the diagram. The capillary of a thermometer serves very well, especially if a thermometer with an unusually fine capillary is selected. This capillary is so fine that pressure is required to force the nitrobenzene through it at a fast enough rate. This pressure is secured by raising the mercury bulb shown at B, the difference in the level of the mercury in the two bulbs, being a measure of the pressure on the nitrobenzene, and hence a measure of the rate of flow of the nitrobenzene. About 35 minutes are required for 2 cc of nitrobenzene to flow through the capillary when the pressure is 3.5 to 14 cm of mercury, the exact pressure depending on the size of the capillary. The rate of flow of nitrobenzene is quite constant since the amount of pressure due to the nitrobenzene is only 0.08 to 0.02 of that due to the mercury which is nearly constant. So that although the column of nitrobenzene decreases to nothing, the pressure remains nearly constant as it is practically all due to the mercury pressure which is changed but slightly. It was found that with a certain pressure of mercury the time required for 2 cc of nitrobenzene to flow through a capillary

was very nearly constant, varying 2 minutes from the mean only occasionally, while usually the time was the same within a minute. Sometimes a small particle of dirt would get into C and then the capillary would need to be cleaned.

#### **Heating Element**

The heating element of the furnace was made in the following way. A 2 inch iron pipe, 29 inches long was first covered with a layer of asbestos paper which was cemented to the pipe with sodium silicate solution. This was then covered with a layer of alundum cement. About 30 or 35 feet of chromel wire, size 16 B and S gauge, was then wound on top of this layer of alundum cement. In starting the winding the end of the wire is doubled for about 2 feet. This doubled end is brought around one end of the pipe and twisted tightly on the pipe, the end sticking out 6 to 10 inches for electrical connection. This first round of doubled wire does not do any of the heating but holds the wire in place and the winding is continued with the main strand of the wire, the rounds being about  $\frac{3}{4}$  inch apart. When the other end of the pipe is reached the wire is again doubled for about 2 feet and instead of going around the pipe in the same direction as before, for the last round the wire is bent back and brought around the pipe in the opposite direction. The bending back of the wire for the last round forms a loop and after bringing the wire around the pipe it is brought through this loop, bent back and twisted tightly with one side of the loop, the end again sticking out 6 to 10 inches for electrical connection. After winding on the wire another layer of alundum cement is applied so that the wire is entirely embedded in alundum cement which keeps it from burning in two. Several layers of asbestos paper are then wrapped around the furnace for heat insulation.

#### **Catalyst Tube**

The tube containing the catalyst was a half inch wrought iron pipe 33 inches long and was held in the center of the heating jacket by the plugs of alundum cement E, E at each end. This provides an air space between the catalyst tube



and the heating element which leads to a more even temperature of the catalyst tube and the catalyst and prevents any spot becoming overheated. The capillary T sticks into the furnace 2 to 3 inches. When an experiment is carried out at a low temperature it should extend farther into the furnace than when a higher temperature is used. If it extends too far into the furnace at the high temperature the nitrobenzene will char in the capillary and finally clog it. The capillary tube T and the hydrogen are led into the catalyst tube through a  $\frac{1}{4}$  inch iron pipe which extends about 8 inches into the furnace. The connection between the capillary tube and the quarter inch iron pipe at H is made air tight by a short piece of rubber tube as is shown in the figure. To keep this rubber tube cool a piece of cloth is tied around the quarter inch iron pipe at I, the ends of which dip into a beaker of water. Due to capillary action the cloth is kept wet and is a means of cooling the iron pipe around which it is wrapped. The quarter inch iron pipe (on the other end of the T) passes through the cap (which is screwed onto the catalyst tube) and is brazed to it at D, in order to make it hydrogen tight. The column of catalyst was 10 inches long and was placed in the tube 3 inches from the end of the heating jacket. The catalyst was put at this place by means of a strip of tin which was bent in the form of a long narrow trough. Thus a definite amount of catalyst, prepared in a certain way, was placed in a certain part of the tube. This left a space in the tube about 12 inches long where the nitrobenzene and hydrogen became thoroughly mixed and heated to the temperature of the catalyst before reaching the catalyst.

#### Temperature Measurement

The temperature was measured by a copper-constantan thermocouple, the voltage being read by a high resistance milli-voltmeter. The thermocouple was made by wrapping copper and constantan (advance) wire (gauge 16) separately with asbestos cord, after which they were wrapped together with the asbestos cord, and then the ends twisted and welded.

This was calibrated in position against tin, lead and zinc. The calibration curve is practically a straight line and does not change appreciably with use. The couple as made is flexible and may be bent. It is put in place through a hole drilled through the catalyst tube at G. In order to make the tube air tight at G it is necessary to put sodium silicate solution of 1.400 sp. gr. between the rounds of the asbestos cord and then a lute between the couple and the pipe. A lute consisting of 30 grams alundum cement, 15 grams ground pumice and 21 cc of a solution of sodium silicate of 1.200 sp. gr. was found to be very satisfactory by the writers. The lute must not be porous and at the same time it must not set so hard that it is difficult to break loose, since the thermocouple must be taken out every time a new catalyst is put in the furnace. As is shown in the diagram the thermocouple extends up the tube to the catalyst, so that the temperature measured is the temperature of the gaseous mixture as it leaves the column of catalyst. This temperature is quite different from that on the outside of the tube in the heating jacket. The temperature inside the catalyst tube was in all experiments kept within 3° of the desired temperature.

The condenser fits on a cork over the catalyst tube. In putting the cork on the catalyst tube, it is best to use a sodium silicate solution as an adhesive between the cork and the pipe in order to make it air tight.

#### **Materials Used**

The nitrobenzene used was purified by shaking it with sodium carbonate solution and then distilling it with steam. The distillate was dried with calcium chloride and then redistilled twice. The hydrogen used was commercial hydrogen put up in steel cylinders. This was purified by passing over red hot scrap copper, through concentrated sulphuric acid and then over stick caustic.

#### **Estimation of Aniline Produced**

The product (which had not already run into the flask) was washed from the condenser into the flask, and, after

diluting to the mark, a 100 cc portion pipetted out, 25 cc concentrated HCl added, and titrated with tenth molar sodium nitrite, starch iodide paper being used as an external indicator. The reaction involved in the titration is a diazotization. This reaction is rapid at first but as the end point is approached it becomes slow. So that the end point is not reached until the solution will turn the starch iodide paper blue after standing several minutes. Any other amine besides aniline will give the same reaction. However the amount of other amines was not large (except in a few instances) so that this error is not great. The nitrite solution was standardized by titrating with a permanganate solution which had been acidified with sulphuric acid and heated to about 60°.

#### Method of Procedure

Before starting an experiment the furnace was heated to the proper temperature in a current of hydrogen (the current of hydrogen was continued during the entire time that the furnace was heating or cooling). After securing the proper temperature and adjusting the flow of hydrogen, 2 cc of nitrobenzene was put into C from a calibrated pipette. The rubber tube was then put on C again and the mercury bulb raised to the desired height, the time being noted. During the experiment the temperature was kept within 3 degrees of the desired temperature. When the last of the nitrobenzene flowed through the capillary the time was again noted and from the time required for it to flow through the capillary the rate of flow in grams per hour was calculated. This latter only occasionally varied as much as 6%. The pipette, under the conditions under which it was used, delivered 2.322 grams of nitrobenzene. After the last of the nitrobenzene had passed into the furnace the current of hydrogen was continued at least 20 minutes before disconnecting the condenser from the catalyst tube. This allowed all of the products of the reaction to be washed out of the furnace into the condenser.

**Preparation of Nickel Catalyst**

The nickel catalyst was prepared by igniting the nitrate and then reducing the oxide in hydrogen. The nickel nitrate used contained: 0.081% Fe, 0.386% Co, 0.003% SO<sub>3</sub>, 0.001% Cl and a trace of copper. The nitrate, with the addition of nitric acid, was ignited in a small porcelain evaporating dish in an electrically heated muffle. The temperature of ignition was measured by a copper-constantan thermocouple, the junction being in the dish just above the nickel oxide. The nickel oxide, after cooling, was powdered and put in the furnace as previously described. About 16 grams of the oxide were used each time.

**Experimental Results with Nickel**

Various investigators heretofore have paid but little attention to the temperature of ignition of the nitrate. Usually the temperature is reported as a "low red heat" or a "dull red temperature" which are rather indefinite and may admit of a variation of 100 degrees or even more. The effect of the temperature of ignition is given in Table I. The nickel oxide was not kept at the indicated temperature for any length of time but was merely heated to that temperature and then allowed to cool.

TABLE I

Temperature of catalyst—192°.

Rate of flow of hydrogen—17 liters per hour.

Rate of flow of nitrobenzene—3.9 grams per hour.

Excess of hydrogen—710%.

Catalyst	Temperature of ignition of nitrate °C	Material yield in % of theory
A5	353	84
A6	412	87
A9	475	87
A8	535	68

In each case in the above table the nickel oxide was reduced and heated in hydrogen to 322° before use. It was then used until it gave concordant results. Four or five

experiments were required and the average of two or three is given in the table.

From the table it will readily be seen that the temperature of ignition is very important and that ignition at a dull red temperature means very little. A difference of 60° in temperature of ignitions means a difference of 19% in material yield. With different experimenters not accustomed to judging the temperature of a furnace from its color a dull red temperature may admit of a variation of 100°. In the first three of the above experiments the product was colorless, the material unaccounted for probably being reduced still further, for Sabatier has shown that nickel is an excellent catalyst for taking nitrobenzene to cyclohexane and ammonia or even to methane and ammonia.

In studying the effect of heating the reduced nickel in hydrogen, 450° was chosen as the best temperature of ignition of the nitrate. Hydrogen was passed through the tube containing the nickel oxide as it was heated so that reduction did not take place at any particular temperature. The reduced nickel however was always heated to a definite temperature in the stream of hydrogen before any experiments were made. It seems to the writers that the highest temperature to which the catalyst was heated is the important factor and not the temperature at which the reduction actually took place. The effect of heating the nickel in hydrogen to various temperatures is given in Table II.

In these ten experiments, each time after heating to the indicated temperature and cooling to the correct temperature experiments were made until constant results were obtained. The average of the constant results is given in the table. The catalyst was not kept at the indicated temperature for any length of time but was merely heated to that temperature and then allowed to cool.

The results of Table II are plotted graphically in Curves A and B of Fig. 2. From the graph it is apparent that the activity of the catalyst is affected tremendously by the temperature to which it has been heated in hydrogen. Thus

TABLE II

Temperature of catalyst—192°.  
 Rate of flow of hydrogen—17 liters per hour.  
 Rate of flow of nitrobenzene—3.7 grams per hour.  
 Excess hydrogen—750%.

After heating catalyst in hydrogen to °C	Material yield in % of theory
335	69.0
390	84.0
435	90.8
475	90.9
322*	88.0
352	91.0
383	92.7
444	89.9
475	69.8
535	22.1

after heating to 335° the yield is 69% while after heating to 435° it is 90.8%. This increase in yield of aniline is probably due to a decrease in the activity of the nickel catalyst. For active nickel will reduce nitrobenzene to ammonia and cyclohexane or even to methane which would mean a low yield of aniline. However if the activity of the nickel is decreased still further, the yield of aniline decreases instead of increasing. Thus after heating to 444° the yield is 90.0% while after heating to 535° the yield is only 22%. The very active nickel prepared by heating to a low temperature in hydrogen

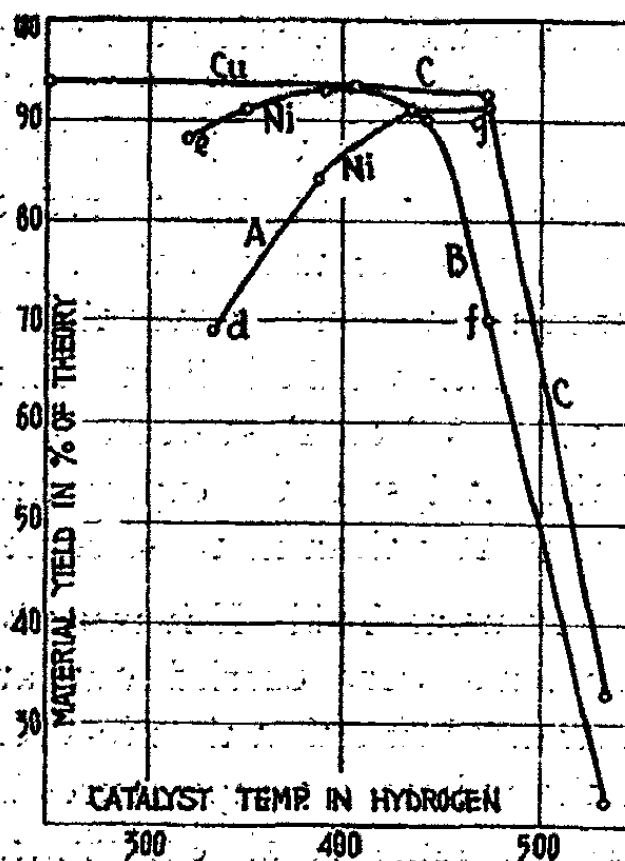


Fig. 2

\* Prior to this experiment the catalyst was oxidized by heating it in a current of air to 485°. It was then reduced again and the succeeding experiments made.

gives a low yield of aniline because it carries the reduction on farther than the aniline stage. Less active nickel prepared by heating to about  $440^{\circ}$  gives a high yield of aniline, while nickel still less active, prepared by heating to  $535^{\circ}$  gives a very low yield of aniline, the nitrobenzene being only partly reduced.

The importance of the history of the catalyst will also be noted by comparing Curves A and B. The experiments represented by the two curves were carried out under the same conditions except that the catalyst had been oxidized after making the experiments shown in A and before making those shown in Curve B. Point *d* of Curve A is lower than point *e* of Curve B. The activity of the catalyst represented by point *d* was greater than that represented by point *e*, for in the experiment represented by *d* the low yield is due to the fact that the nickel carried the reduction farther than the aniline stage and is not due to incomplete reduction of the nitrobenzene. However the low yield of the experiment represented at *f* is due to incomplete reduction of the nitrobenzene and since *f* is lower than *g*, the activity of the catalyst in the experiment at *g* was greater than in the experiment represented by *f*. This would indicate that the oxidation and reduction of the nickel catalyst decreased its activity since the activity of the catalyst in the experiments represented by the Curve A is greater than in those represented by Curve B.

In using Table II it must be remembered that all the experiments were carried out at the same temperature, the difference being that the nickel catalyst was heated in hydrogen to the indicated temperatures before use. The catalyst used was the same in all experiments. After heating to the indicated temperature it was cooled to  $192^{\circ}$  in each case, and the experiment carried out at this temperature.

In the experiments of Table II results were constant almost immediately except after heating to  $475^{\circ}$  and  $535^{\circ}$ . The experiments, after heating to these two temperatures, are given, in the order in which they were made in Table III.



TABLE III

After heating nickel catalyst of Table II in hydrogen to 475°. All conditions the same as in Table II.

Experiment number	Material yield in % of theory	Experiment number	Material yield in % of theory
102A4	91.6	110A4	69.8
103A4	87.1	111A4**	87.1
104A4	79.9	112A4	61.6
105A4	75.7	113A4	48.6
106A4*	74.5	114A4	38.2
107A4	69.8	115A4*	46.4
108A4	84.9	116A4	32.8
109A4	69.5	117A4	22.1

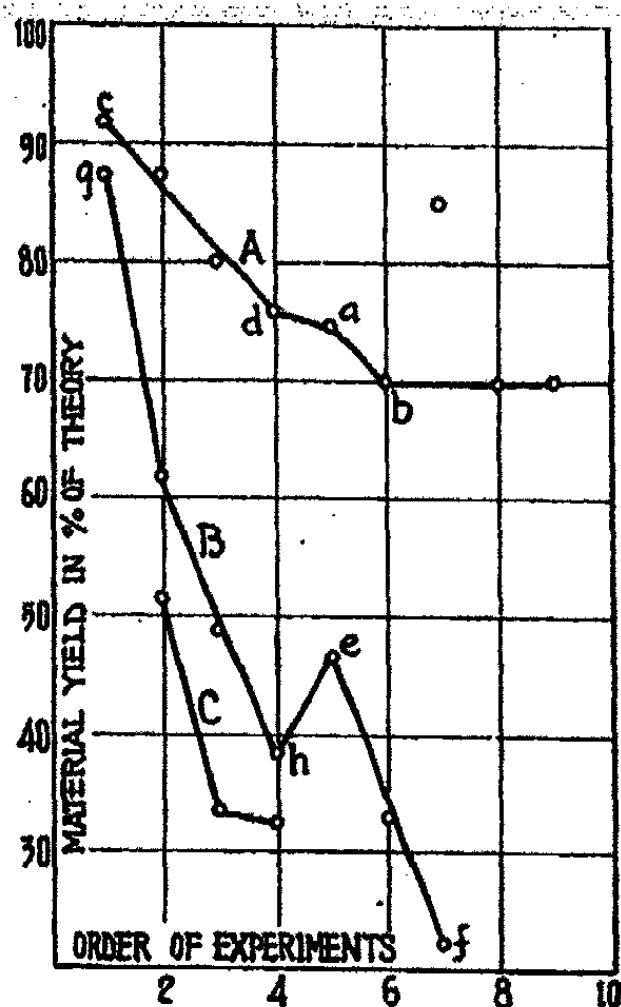


Fig. 3

- A. After heating Ni to 475°  
 B. After heating Ni to 535°  
 C. After heating Cu to 535°

The results of Table III are shown graphically in Fig. 3. The abscissa gives the order in which the experiments were carried out while the ordinate gives the percentage yield. Experiments 102A4 to 110A4 inclusive are plotted in Curve A and 111A4 to 117A4 inclusive in Curve B. The activity of the catalyst as measured by the material yield of aniline produced decreased continuously with use and finally became constant giving a material yield of 69.8% aniline. It will be noted that experiments 106A4 and 115A4 are higher than the preceding experiments would indicate. Both of these were the first experiments made in

\* The first experiment after the catalyst had been idle overnight in an atmosphere of hydrogen.

\*\* Prior to experiment 111A4 the catalyst was heated in hydrogen to 535°.



the morning after the catalyst had been idle overnight in an atmosphere of hydrogen. Thus the catalyst seemed to recuperate when idle. Also experiment 110A4 gave a material yield of 69.8%, then after heating in hydrogen to 535°, experiment 111A4, the first experiment after heating to 535°, gave a material yield of 87.1%, which would indicate that the catalyst is activated by merely heating in hydrogen. One comparing the curves of Fig. 3 it will be seen that the efficiency of the catalyst drops much more rapidly after heating to 535° than when heated to 475°. Also the slope of *ab* is practically the same as that of *cd* which would mean that the activity of the catalyst decreased linearly. The same thing holds for Curve B. The experiment represented by point *a* was the first experiment in the morning. The same thing is indicated by the other curve, the experiment represented by the point *e* being the first experiment in the morning.

After experiment 117A4 this same catalyst was oxidized by heating in a current of air to 465°. It was then reduced and heated in hydrogen to 260°. Experiments carried out under the same conditions as 117A4 then gave 90% material yields of aniline. This indicates that oxidation restored the activity of the catalyst.

The catalyst used to determine the best temperature for carrying out the reduction with nickel as catalyst was prepared by ignition of the nitrate at 414°; this oxide was reduced at 322°, used in a few experiments and then heated in hydrogen to 400°. The results of experiments at different temperatures are given in Table IV.

It will be seen from Table IV that the best temperature for the reduction with nickel as catalyst is about 192°.

This is the temperature at which the effect of the rate of flow of the hydrogen was studied. The catalyst used for this was prepared by igniting the nitrate at 475°, heating the nickel, after reduction, to 352°, using in a few experiments and then heating to 400°. The results are given in Table V.

From the table it will be seen that one may pass too large a current of hydrogen as well as too little hydrogen. At 69

TABLE IV  
 Rate of flow of hydrogen—17 liters per hour.  
 Rate of flow of nitrobenzene—3.9 grams per hour.  
 Excess of hydrogen—710%.

Temperature of catalyst, °C	Material yield in % of theory
243	87.0
225	91.9
208	94.9
192	95.2
172	94.3
156	88.3

TABLE V  
 Temperature of catalyst—192°.  
 Rate of flow of nitrobenzene—3.8 grams per hour.

Hydrogen per hour in liters	Excess of hydrogen in %	Material yield in % of theory
8.5	300	87.6
23	1000	94.3
46	2100	95.8
69	3290	91.4
92	4380	85.1

and 92 liters of hydrogen the product had a slight yellowish color while in all the other experiments the product was colorless. Thus at these rapid rates of hydrogen the time of contact of the nitrobenzene with the catalyst was evidently too short. At the lowest rate considerable of the nitrobenzene was probably reduced farther than aniline, for the product was practically colorless.

A study of the effect of the rate of flow of nitrobenzene was then made. The same catalyst was used as in Table V. The results are given in Table VI.

TABLE VI  
 Temperature of catalyst—192°.  
 Rate of flow of hydrogen—17 liters per hour.

Nitrobenzene per hour in grams	Excess of hydrogen in %	Material yield in % of theory
11.6	170	94.0
5.34	490	94.8
3.1	900	95.8

With the rate of flow of hydrogen constant the rate of the nitrobenzene has, within rather wide limits, but little effect. Of course increasing the rate of nitrobenzene a great amount would undoubtedly cut down the yield. On the contrary with the rate of nitrobenzene constant the rate of flow of hydrogen had a big effect, as is shown by the results of Table V. This would indicate that the time of contact has an importance of the first order and that the percentage excess of hydrogen is of secondary importance. Also it would appear that the rate of flow of the gaseous mixture through the tube is more important than the percentage excess of hydrogen present.

#### Preparation of Copper Catalyst

The copper catalyst was prepared by igniting the nitrate and then reducing the oxide obtained in hydrogen. The copper nitrate used contained 0.001% Fe, 0.001% Cl and 0.001% SO<sub>3</sub> according to the maker. The nitrate, with the addition of nitric acid, was ignited under the same conditions as the nickel catalyst. About 29 grams of the oxide were used each time.

#### Experimental Results with Copper

The effect of the temperature of ignition is given in Table VII.

TABLE VII

Temperature of catalyst—253°.  
Rate of flow of hydrogen—17 liters per hour.  
Rate of flow of nitrobenzene—3.7 grams per hour.  
Excess of hydrogen—750 %.

Catalyst	Temperature of ignition of nitrate, °C	Material yield in % of theory
B5	353	95.8
B9	414	97.5
B8	472	90.7
B11	535	90.2

In each case in the above table the copper oxide was reduced and heated in hydrogen to 314° before use. It was

then used until it gave constant results. The average of two or three experiments is given in the table.

The results of Table VII are plotted in Fig. 4, Curve B. The graph indicates that the temperature of ignition is very important up to about 475° after which it does not have such a great effect, the catalyst ignited at 535° giving practically the same result as that ignited at 475°. Curve A in Fig. 4 is plotted from Table I and shows the effect of the tempera-

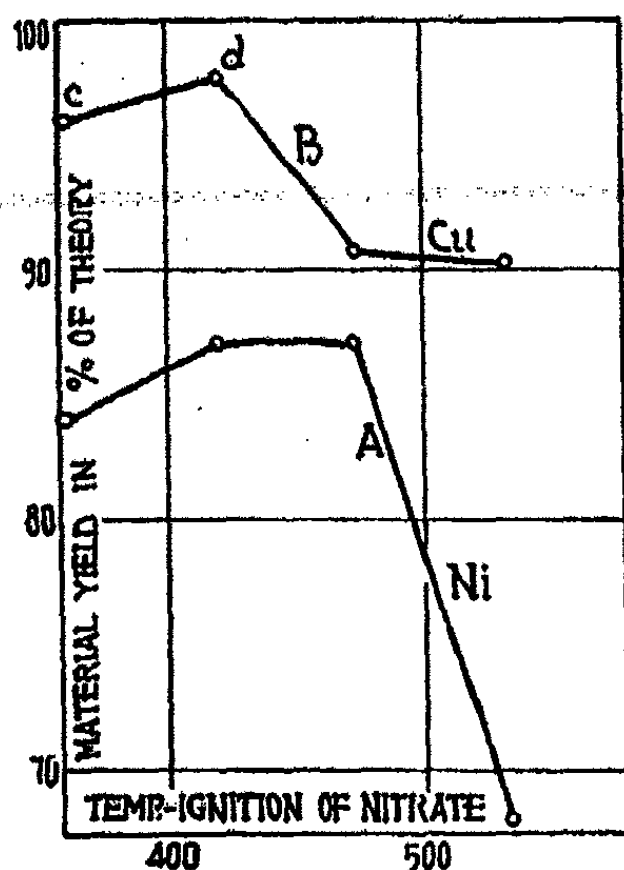


Fig. 4

ture of ignition upon the activity of the nickel catalyst. A temperature of 475° caused a decrease in the aniline yield with the copper catalyst but not with the nickel catalyst. However, an ignition temperature of 535° caused a much larger decrease in yield of aniline with nickel than with copper. The decrease in yield with nickel is about three times the decrease with copper which would indicate that the nickel was more easily killed by heating to a high temperature than the copper.

The effect of heating the copper catalyst in hydrogen is given in Table VIII. This catalyst was ignited at 420°

TABLE VIII

Temperature of catalyst—253°.  
Rate of flow of hydrogen—17 liters per hour.  
Rate of flow of nitrobenzene—3.9 grams per hour.  
Excess of hydrogen 710%.

After heating catalyst in hydrogen to °C	Material yield in % of theory
253	93.8
407	93.2
475	92.2
535	32.8

reduced at 250°, used in several experiments and then oxidized by heating in a current of air to 475°, after which it was reduced and the experiments indicated in the table carried out.

The results of Table VIII are plotted in Curve C of Fig. 2. The activity of the catalyst is not affected greatly until one gets above 475° when it is decreased tremendously. The difference between copper and nickel is again quite evident in this figure. The curve for copper does not have the first rise which the other two curves have, since the active copper does not attack the aromatic ring while the active nickel does. Also the activity of the copper is not killed so easily as that of the nickel.

After repeatedly oxidizing and reducing the copper catalyst it gave 80% yields of aniline again. The oxidation did not bring its activity back as high as it was before heating to 535° in hydrogen while in the case of nickel 90% yields were obtained after oxidizing and reducing once. This indicates that the activity of the nickel catalyst is more easily restored than that of the copper catalyst.

After heating the nickel catalyst in hydrogen to 535° the first experiment gave a high yield but this decreased after a few experiments to 22%. With copper no high yields were secured and the drop in activity was almost immediate as is shown in Table IX.

TABLE IX  
After heating copper catalyst of Table VIII in hydrogen to 535°. Conditions same as in Table VIII.

Experiment number	Material yield in % of theory
93B4	51.2
94B4	33.4
95B4	32.8

These results are plotted in Curve C of Fig. 3. The average of the last two results is the one that is given in Table VIII.

When a new catalyst was reduced or when an old catalyst was oxidized and reduced it did not show its full activity

immediately but sometimes as many as five or six experiments were necessary to bring it up to its full activity. This fact is brought out by the data in Table X. The experiments recorded in Table X are representative of this unexpected behavior which was observed many times. The catalyst used in Table X was prepared by ignition of the nitrate at 414°. The oxide was then reduced and heated in hydrogen to 314°.

TABLE X

Temperature of catalyst—253°.  
Rate of flow of hydrogen—17 liters per hour.  
Rate of flow of nitrobenzene—3.9 grams per hour.  
Excess of hydrogen—710%.

Experiment number	Material yield in % of theory	Experiment number	Material yield in % of theory
198B9	78.8	224B9	94.0
199B9	93.6	230B9**	58.9
200B9	94.0	231B9	89.3
201B9	97.7	232B9	89.0
202B9	97.4	233B9	96.2
220B9*	71.4	235B9***	44.8
221B9	84.3	236B9	52.3
222B9	84.9	237B9	53.6
223B9	90.5		

The results of Table X are shown graphically in the four curves of Fig. 5. All four curves show a low first yield and a subsequent increase with use. If Curves C and B had been carried out one experiment farther it is probable that A, B and C would have reached about the same figure of 97%. Although Curve D may have reached this same figure, not enough experiments were carried out to prove that it would. In each of the four curves the second experiment is consider-

\* Prior to Experiment 220B9 the catalyst was oxidized by heating in a current of air to 414°, after which it was reduced and heated in hydrogen to 314°.

\*\* Prior to Experiment 230B9 the catalyst was oxidized by heating in a current of air to 414°, after which it was reduced and heated to 253°.

\*\*\* Prior to Experiment 235B9 the catalyst was oxidized by heating in a current of air to 414°, after which it was reduced and kept in a current of hydrogen, at a temperature of 253° for 8 hours before use.

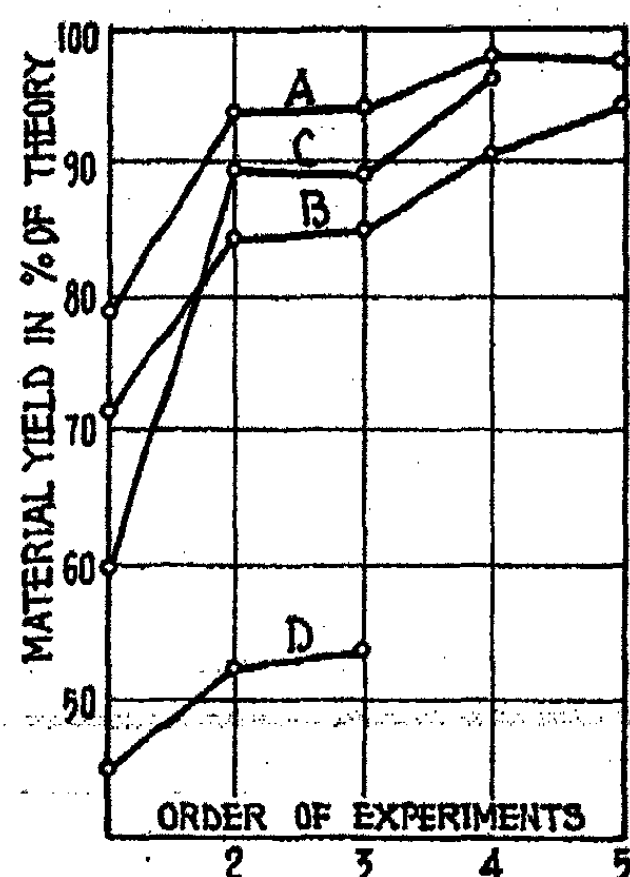


Fig. 5

ably higher than the first one, while the third is nearly the same as the second experiment, after which it again increases. Curves A and B show a higher yield in the first experiment than do Curves C and D. In the case of Curves A and B the catalyst was heated in hydrogen to 314° before use while in C and D the maximum temperature was 253°. It was thought at first that probably the catalyst was not completely reduced in A, B and C and so in D the catalyst was heated in hydrogen for 8 hours at 253° before making the first experiment, while the others had been heated in hydrogen only about an hour. However Curve D shows lower results than the other three which proves conclusively that the low first yield was not due to incomplete reduction of the catalyst. In fact the three experiments of Curve D indicate that a longer time is necessary for the catalyst to attain its full activity when reduced in hydrogen for a long period than when reduced for a short period.

On the adsorption theory of contact catalysis one might explain this by assuming that in order for the copper to act as a catalyst it must adsorb both the nitrobenzene and the hydrogen. Now if the copper has been kept in hydrogen for a long time it has covered its entire surface with a layer of adsorbed hydrogen. Then when the nitrobenzene vapors pass over it they do not come in contact with the copper but with this adsorbed layer of hydrogen. Consequently the nitrobenzene is not adsorbed by the copper and a low yield of aniline results. But some of the adsorbed hydrogen reduces some nitrobenzene and in these places little nuclei of

adsorbed nitrobenzene are formed which gradually increase and result in a gradual increase in yield of aniline produced.

This increase in activity was not observed with nickel except occasionally and then the increase was only slight. Also it did not increase after the second experiment. On the contrary heating in hydrogen seemed to be beneficial to the nickel catalyst, as was brought out in the discussion under Table III. With nickel the first experiment in the morning after lying idle in an atmosphere of hydrogen overnight was higher than the previous or succeeding experiments would indicate. On the other hand with copper it was observed many times that the first experiment in the morning was lower than the previous or succeeding experiments would indicate, the second experiment under duplicate conditions being 2 to 4% higher than the first.

When a copper catalyst is prepared under correct conditions it retains its activity for a long time. However if the nitrate is ignited at too low a temperature it loses its activity in a short time. This is shown in Table XI. The catalyst for these experiments was prepared by igniting the nitrate at 353° and reducing the oxide and heating to 314° in hydrogen.

TABLE XI

Temperature of catalyst—253°.

Rate of flow of hydrogen—17 liters per hour.

Rate of flow of nitrobenzene—3.7 grams per hour.

Excess of hydrogen—750%.

Experiment number	Material yield in % of theory	Experiment number	Material yield in % of theory
111B5	95.0	119B5	86.5
112B5	96.0	120B5	88.1
113B5	95.7	121B5	84.0
114B5	89.0	122B5	66.2
115B5	89.3	123B5	70.3
116B5*	92.2	124B5	79.1
117B5	91.2	125B5	70.0
118B5	91.2	—	—

\* This experiment was carried out with a rate of flow of hydrogen of 5.7 liters per hour and hence is not comparable to the others.



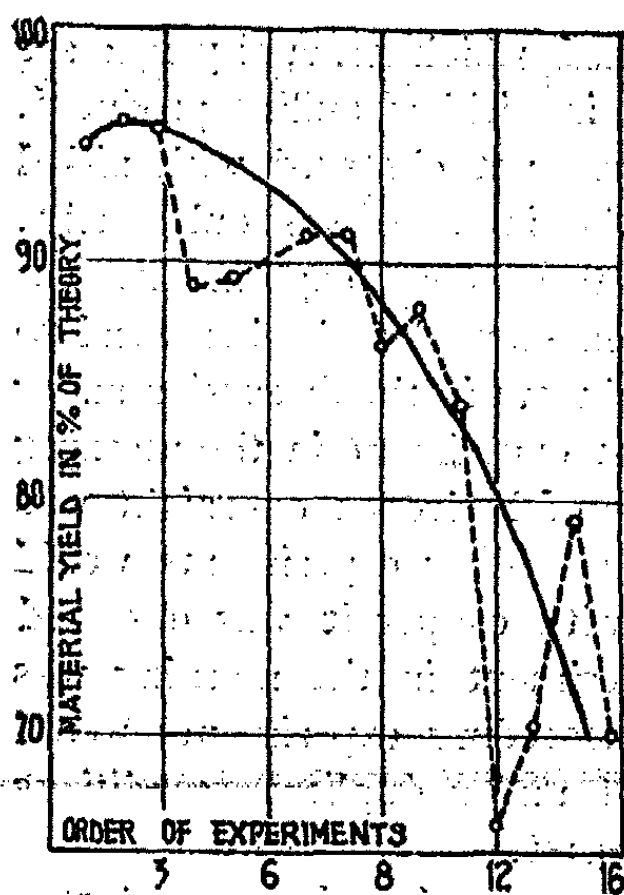


Fig. 6

The results of Table XI are plotted in Fig. 6. The full line shows the general tendency while the dotted line goes through all the points. Although the results are irregular they unmistakably point to a decrease in activity, which is evidently due to ignition at too low a temperature for other catalysts ignited at higher temperatures and used under the same conditions did not show this decrease in activity. The irregularity of the results is not experimental error but shows that the catalyst is on the border line between a good and a bad catalyst. Results are also irregular when using a copper catalyst that has been ignited at 475° or 535°; however, when using a copper catalyst that was ignited at 414°, reduced and heated in hydrogen to 314° and used at about 260° results are not irregular.

Since the data in Table X show that a copper catalyst does not reach its full activity until it has been used in five or six experiments and since this catalyst decreases in activity continuously one is led to believe that if this catalyst had not decreased in activity the highest yield would have been more than 96%, probably near 100%. Then the point *c* of Curve B in Fig. 4 would have been higher than point *d* of the same curve. Then this curve would show a continual decrease in activity with increase in temperature of reduction.

The catalyst used to determine the best temperature for carrying out the reduction with copper as catalyst was prepared by ignition of the nitrate at 414°. The resulting oxide was reduced and heated in hydrogen to 314°, used in several experiments and oxidized and reduced twice at the same tem-

perature. The results of experiments at different temperatures are given in Table XII.

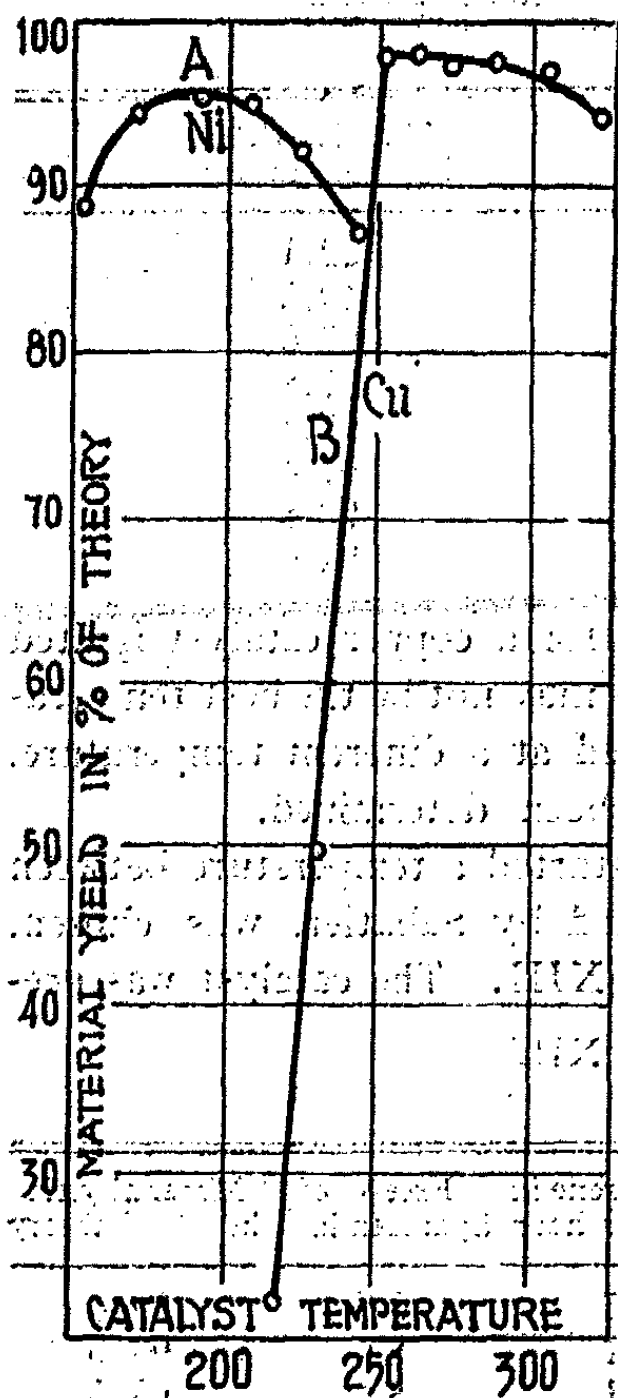


Fig. 7

The results of Table XII are plotted in Fig. 7. Curve B. It will be noted that the first three points fall on a straight line. Also between 217° and 253° one degree difference in temperature means a difference in yield of 2.1%. The extremely narrow temperature range within which the activity of the catalyst is at its best will also be noted, a range of only about 30°.

The results of Table IV with nickel as catalyst are plotted in Curve A of Fig. 7. The best temperature for nickel is much lower than for copper, being about 192° for nickel. The optimum temperature range for nickel is likewise very narrow.

Sabatier<sup>1</sup> states that the reduction of nitrobenzene by hydrogen in the presence of

finely divided copper starts at 230° and that the reaction is rapid and very regular between 300° and 400°. The difference in the optimum temperature as found by us may be due to the fact that we measured the temperature of the gaseous product as it came off the catalyst while Sabatier measured the temperature with a mercury thermometer on the outside of the catalyst tube.

<sup>1</sup> Local citation.

TABLE XII

Rate of flow of hydrogen—17 liters per hour.  
 Rate of flow of nitrobenzene—3.9 grams per hour.  
 Excess of hydrogen—710%.

Temperature of catalyst ° C	Material yield in % of theory
217	22.1
232	49.5
253	97.6
263	97.8
274	97.1
286	97.4
305	96.8
322	94.0

Also the best temperature for a copper catalyst ignited and reduced at one temperature may not be the best temperature for one ignited and reduced at a different temperature. However this point has not been determined.

When this work was first started a temperature between 300° and 400°, as recommended by Sabatier, was chosen. The results are given in Table XIII. The catalyst was pre-

TABLE XIII

Temperature of catalyst—377°.

Experiment number	Hydrogen in liters per hour	Nitrobenzene in grams per hour	Excess of hydrogen in %	Material yield in % of theory
13B2	20	4.1	800	90.6
14B2*	20	4.1	800	90.6
19B2*	20	4.1	800	63.5
24B2	20	4.1	800	27.3
29B2**	17	3.3	840	85.5
33B2	17	3.3	840	83.9
38B2	17	3.3	840	74.1
39B2	17	3.3	840	72.7
40B2	17	3.3	840	68.0
42B2	17	3.3	840	63.3
43B2	17	3.3	840	56.2

\* The experiments not listed were made under different conditions and so are not comparable with those listed in the table.

\*\* Prior to Experiment 29B2 the catalyst was oxidized at 475° and reduced and heated in hydrogen to 400°.

pared by ignition of the nitrate at  $550^{\circ} \pm 25^{\circ}$  and reduction of the oxide at  $440^{\circ}$ .

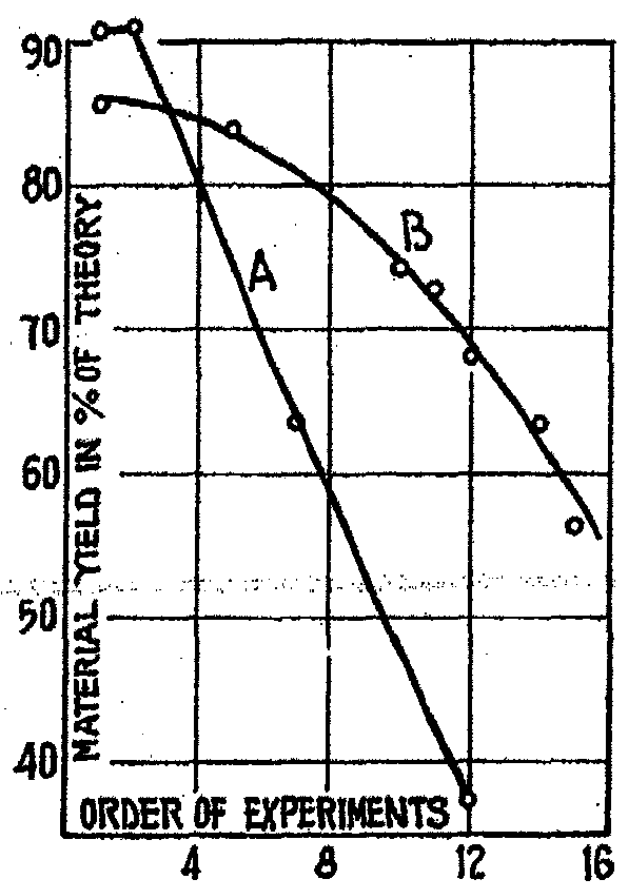


Fig. 8

The results of Table XIII are plotted in Fig. 8. As abscissa are plotted the experiments in the order in which they were carried out. Curve A represents experiments 13B2 to 24B2, inclusive, while Curve B represents experiments 29B2 to 43B2, inclusive. The results indicate that the activity of the catalyst decreases with use if used at too high a temperature,  $377^{\circ}$  being then too high a temperature. In the first experiment the products condensed nicely in the condenser, but

after a few experiments white fumes (very difficult to condense) appeared which increased in amount with each succeeding experiment and the yield in aniline decreased. With a slower rate of flow of the nitrobenzene the decrease in activity is not so rapid as with a higher rate as is shown by the fact that Curve B does not drop so rapidly as Curve A. Likewise the activity of a catalyst used at  $286^{\circ}$  decreased from 96 to 76% in 26 experiments which indicated that  $286^{\circ}$  was also slightly too high. At  $253^{\circ}$  the catalyst showed no appreciable decrease in activity. Probably about  $260^{\circ}$  is the best temperature for carrying out the reduction with copper as catalyst.

The effect of the rates of flow of hydrogen and nitrobenzene upon the yield of aniline was also studied. The results are given in Table XIV. The catalyst used in these experiments was prepared by igniting the nitrate at  $414^{\circ}$  and reducing the oxide at  $314^{\circ}$ . This was used in a few experiments and was oxidized and reduced twice at the same temperature before being used in the experiments given in the table.

TABLE XIV  
Temperature of catalyst—286°.

Experiment number	Hydrogen in liters per hour	Nitrobenzene in grams per hour	Excess of hydrogen in %	Material yield in % of theory
157B6	5.7	4.0	160	90.5
153B6	11.4	4.0	420	95.8
154B6	28.5	4.0	1200	95.5
155B6	46	4.0	2000	90.8
156B6	69	4.0	3040	81.7
158B6	5.7	5.6	90	79.5
159B6	11.4	5.6	270	86.1
160B6	17	5.6	450	89.9
161B6	28.5	5.6	830	84.8
162B6	46	5.6	1400	88.6
163B6	69	5.6	2160	72.5
164B6	92	5.6	2920	61.5
165B6	5.7	7.3	40	51.4
166B6	11.4	7.3	180	70.0
167B6	17	7.3	320	68.1
168B6	28.5	7.3	610	65.5
169B6	46	7.3	1150	61.8
170B6	69	7.3	1620	54.9
171B6	92	7.3	2200	41.3

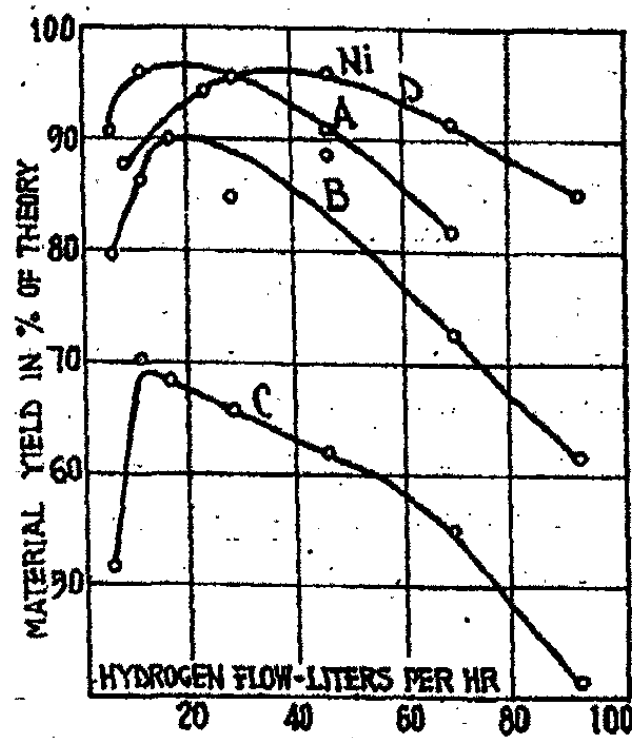


Fig. 9

- A. 4 grams nitrobenzene per hour  
 B. 5.6 grams nitrobenzene per hour  
 C. 7.3 grams nitrobenzene per hour  
 D. 3.8 grams nitrobenzene per hour

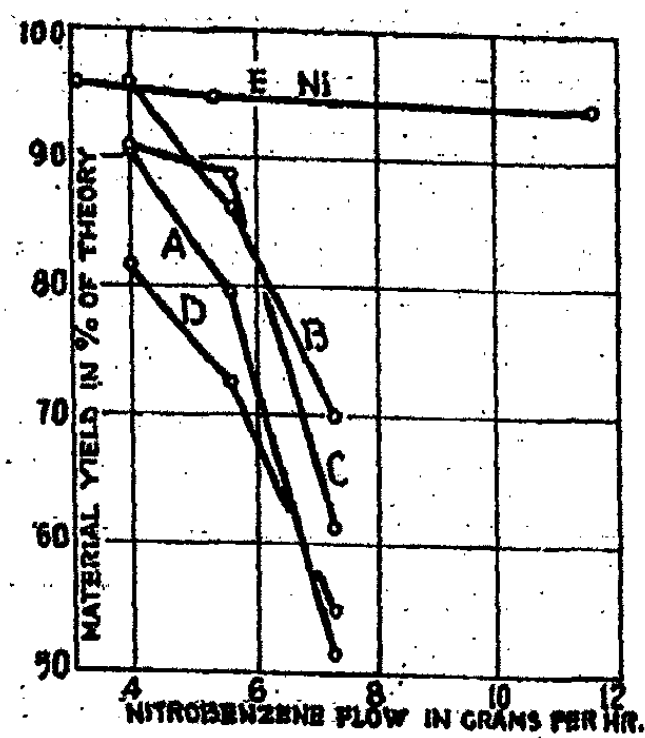


Fig. 10

- A. 5.7 liters  $H_2$  per hour  
 B. 11.4 liters  $H_2$  per hour  
 C. 46 liters  $H_2$  per hour  
 D. 69 liters  $H_2$  per hour  
 E. 17 liters  $H_2$  per hour (Ni)

The results of Table XIV are plotted in Figs. 9 and 10. In Fig. 9 the yield of aniline is plotted against the rate of flow of hydrogen expressed in liters per hour. The Curves A, B and C for the three different rates of flow of nitrobenzene are very similar. With each increase in rate of nitrobenzene the percentage yield of aniline increases. Curve D is drawn from the data of Table V with nickel as catalyst. A large excess of hydrogen does not decrease the yield with nickel as much as with copper. This illustrates the greater activity of the nickel catalyst as the time of contact of the nitrobenzene with the catalyst does not need to be so long with nickel as with copper.

In Fig. 10 the yield of aniline in percent is plotted against the rate of flow of nitrobenzene expressed in grams per hour. The Curves A, B, C and D are all similar, the percentage yield of aniline being higher the lower the rate of the nitrobenzene. Curve E is drawn from the data of Table VI with nickel as catalyst. This is vastly different from the other curves the yield dropping less than 2% when the rate is increased from 3.1 to 11.6 grams per hour, while with copper the yield drops from 95.8 to 70%, a decrease of nearly 26% when the rate of nitrobenzene is increased from 4 to 7.3 grams per hour. Hence the nickel can be used at a much greater rate than the copper. There was also a great difference in the physical appearance of the two catalysts after having been used. The nickel catalyst after use was a loose, non-coherent mass of black nickel, while the used copper catalyst was a compact red mass which was coherent. It could be shaken out of the furnace as a stick and was strong enough to be held in a horizontal position by holding one end. The older the copper catalyst the more firmly it was packed together. If by some means the copper catalyst could be kept from becoming packed, it might act at as fast a rate as the nickel.

The effects of length of time of heating in hydrogen has not been thoroughly studied although it appears that with copper merely keeping at an elevated temperature in hydrogen

decreases its activity, while with nickel the reverse is true. This was brought out in the discussion under Tables III, IX and X. The results of Table X do not show any decided effects of repeated oxidation and reduction of the copper catalyst.

After using many other catalysts (the results of which will be given in a paper in a later number of this journal) it was suspected that the iron tube might have some catalytic effect upon the reduction of the nitrobenzene. A new iron tube just like the previous ones was put in the furnace. This had been cleaned with nitric acid (1:1). After cleaning with the nitric acid it had been washed well with water in order to remove any nitrate that may have been formed by the action of the nitric acid upon the iron pipe. Before use the new tube was heated in a current of hydrogen at 395° for one hour. It was then used in several experiments the results of which are given in Table XV.

TABLE XV

Rate of flow of hydrogen—17 liters per hour.  
Rate of flow of nitrobenzene—3.9 grams per hour.  
Excess of hydrogen—710%.

Experiment number	Temperature °C	Material yield in % of theory
12HO	305	57.3
13HO	268	23.8
14HO	230	10.7
15HO	305	32.0

From the data of the table it is evident that the iron tube has considerable activity, although it decreases rapidly with use. Thus in the first experiment the yield of aniline was 57.3% while in the fourth experiment, which was carried out under the same conditions, the yield of aniline was 32.0%.

The next experiment was with an iron tube that had not been cleaned with nitric acid, but was put in the furnace just as received without making any attempt to remove any dirt or grease. This was heated in a current of hydrogen to 410°, then allowed to cool to 300° and an experiment carried out

under the same conditions as the first experiment of Table XV. The first experiment gave a yield of 28.2% aniline, as compared to a yield of 57.3% when cleaned with nitric acid.

Three tubes lettered L, M and N were then tried to see whether they would give similar results. In each case a new uncleaned tube was used. This was heated in a current of hydrogen to 565° before use. The results are given in Table XVI, several experiments being carried out with each tube, which are listed in the order in which they were made.

TABLE XVI

Rate of flow of hydrogen—17 liters per hour.

Rate of flow of nitrobenzene—3.9 grams per hour.

Excess of hydrogen—710%.

Experiment number	Temperature of catalyst ° C	Material yield in % of theory
1L	322	26.9
2L	322	33.2
3L	322	31.3
4L	305	14.7
5L	305	12.2
1M	335	41.4
2M	335	25.7
3M	335	17.5
4M	320	13.5
1N	305	20.4
2N	305	19.4
3N	305	14.7
4N*	305	18.2
5N	305	15.0

The results do not show exactly the same behavior with each tube, which is as one would expect. However it will be noted that with use the yields at 300° approach a value of from 12 to 15%. The yield is highest at first and decreases with use. Experiment 1L, however is lower than the succeeding one, which we are unable to explain, except that it be an error.

\* This was the first experiment after the catalyst had been idle for about two hours and indicates that the catalyst (iron pipe) recuperates when idle in an atmosphere of hydrogen.



**Summary of Results.**

1. A suitable apparatus for the systematic study of catalysis in the vapor phase has been described.
2. The most favorable temperature of ignition of nickel nitrate for the reduction of nitrobenzene to aniline has been found to be about  $450^{\circ}$ .
3. It has been shown that merely heating the reduced nickel in hydrogen suffices to decrease the activity of the nickel. The most favorable temperature for heating in hydrogen was found to be about  $380^{\circ}$  since a lower temperature produced a more active nickel which carries the reduction too far.
4. After heating the reduced nickel catalyst in hydrogen to a high temperature, it did not lose its activity immediately, but lost it with use, its activity decreasing almost linearly.
5. The best temperature for carrying out the reduction with nickel as catalyst was found to be about  $192^{\circ}$ .
6. From a study of the rates of flow of hydrogen and nitrobenzene it appears that the rate of flow of the gaseous mixture through the tube is of more importance than the percentage excess of hydrogen present.
7. The best temperature for the ignition of copper nitrate for the reduction of nitrobenzene to aniline was found to be about  $415^{\circ}$ . At lower temperatures the copper loses its activity with use and does not give as high yields as when ignited at about  $415^{\circ}$ .
8. Heating the copper catalyst in hydrogen reduced its activity but little until it was heated above  $475^{\circ}$ , its activity being 60% lower (as measured by aniline yield) when heated to  $535^{\circ}$  than when heated to  $475^{\circ}$ .
9. The copper catalyst lost its activity almost immediately, when heated to a high temperature ( $535^{\circ}$ ) in hydrogen, while the nickel catalyst lost its activity with use.
10. A new copper catalyst or one that has been oxidized and reduced gains in activity with use for four to six experiments before it gives constant results. Long reduction in

hydrogen increases the length of time required for it to attain its maximum activity.

11. The best temperature for carrying out the reduction of nitrobenzene with copper as catalyst was found to be about 260°. It was pointed out that probably the best temperature for copper when prepared in one way would not be the best temperature for copper when prepared in another way.

12. The activity of a copper catalyst decreases when used at too high a temperature (377°). The decrease is more rapid with a more rapid rate of flow of nitrobenzene.

13. A study of the rates of flow of hydrogen and nitrobenzene showed: (1) with a constant rate of flow of hydrogen the lower the rate of flow of nitrobenzene the greater the yield of aniline; (2) with a constant rate of flow of nitrobenzene, an increase in the rate of flow of hydrogen first increases the yield of aniline and then decreases it, the increase and decrease being much more marked with copper than with nickel; (3) it seems that the time of contact of the gaseous mixture with the catalyst is of more importance than the percentage excess of hydrogen present.

14. It has been shown that the activity of an ordinary wrought iron pipe is considerable. Its activity decreases with use. Its activity is greater when cleaned with nitric acid before being put in the furnace than when put in the furnace and used without being cleaned with nitric acid.

15. The activity of nickel and copper catalysts, for reducing nitrobenzene to aniline, is restored by oxidation and reduction although not to so great an extent with copper as with nickel.

### Conclusions

Although a higher material yield of aniline can be obtained with copper as catalyst than with nickel as catalyst, yet the writers are of the opinion that nickel would be better and cheaper in commercial practice than copper because it can be used at a much greater rate. The best temperature for igniting the nickel nitrate is about 450°, the best tempera-

ture to which to heat the nickel in hydrogen after reduction is about 380° and the best temperature for carrying out the reduction is about 190°.

*Laboratory of Physical Chemistry  
Indiana University  
Bloomington*

## NEW BOOKS

**A Manual of Flotation Processes.** By Arthur F. Taggart. 23 × 15 cm: pp. xv + 181. New York and London: John Wiley and Sons, 1921. Price: \$3.00.—In the preface the author says: "Flotation concentration includes within its scope almost as many processes as all other methods of ore concentration combined, the only elements common to all the processes being selection, or concentration, and separation of the concentrate from the tailing by flotation of the former.

"Widespread understanding of the physical principles underlying flotation phenomena and of the diversity of flotation processes has been delayed for divers reasons. The apparent complexity of the phenomena and the difficulties of investigation are sufficient to explain some of the delay, but much of it is chargeable to the stand of patent-owning corporations in their attempt to establish a monopoly on flotation processes. These companies have steadfastly opposed dissemination of knowledge of the art by their employees and licensees, notwithstanding the moral and legal duty of a patentee to make full and truthful disclosure of all he knows concerning the subject matter of his patent; by threats of litigation sown broadcast they have succeeded in causing a veil of secrecy to surround the operations of non-licensees; and by their unfounded claims that all flotation processes prior to that described in U. S. Patent 835,120 were laboratory curiosities or commercial failures, and that those subsequently discovered were merely improvements of that process, they have caused the spread of wrong ideas on the part of many of those interested."

The subject is treated in four chapters: introduction; testing laboratory equipment; testing; mill data. Of these the first is the one which will appeal most to those interested in the theoretical side of the subject. The author starts off, p. 1, with the statement that "minerals that float have a metallic, adamantine, or resinous luster. Minerals with vitreous, pearly, or earthy luster do not float, as the term is at present used, in the art of concentration." In a sense this may be true empirically, but it ignores the radical distinction between calcium carbonate and calcium sulphate, for instance, and seems like an unnecessarily unfortunate way of wording things.

The distinction between pulp-body concentration processes and bubble-column concentration processes, pp. 3, 6, 7, 8, has never been brought out so clearly before. "Froth flotation comprises two entirely different types of processes which resemble each other only in the fact that in both the concentrate is removed in the form of a froth composed of gas, liquid, and solid matter, preponderantly sulphide mineral. The processes differ fundamentally both in the place in which concentration is done and in the mechanism of the selection of sulphide from gangue. On the basis of the first difference the processes may be classified as pulp-body concentration processes and bubble-column concentration processes.

"Pulp-body-concentration processes may be subdivided, on the basis of the method of introducing the bubble-making gas, into four types: (1) chemical-generation; (2) pressure-reduction; (3) boiling; and (4) agitation. All four types

depend upon the fact that in a pulp, the liquid part of which is saturated with a gas, preferential precipitation of the gas on the sulphide particles can be brought about by so changing the conditions of temperature and pressure that the liquid is, under the changed conditions, supersaturated. This preferential precipitation of gas from the supersaturated liquid is enhanced, if the sulphide particles are coated with an oily substance, and the presence of such a substance also makes greater the force of adherence between the precipitated bubbles and sulphide particles. As a result of this preferential precipitation of gas on sulphide particles in the pulp, and its adhesion thereto, there are formed in the body of the pulp agglomerates consisting of one or more gas bubbles with sulphide particles firmly cemented to them. These agglomerates later rise to the surface in the form of a froth which is separated as concentrate. Observation of any of the pulp-body-concentration processes shows clearly this phenomenon of rising agglomerates whose color indicates distinctly that concentration has been completed at the surfaces of the bubbles composing them *below the surface of the pulp*, that is, within the pulp body. . . .

"The agitation-froth process depends upon local supersaturation of the water of a pulp with air by the mechanical action of a swiftly revolving beater and the simultaneous precipitation of air in the form of bubbles, preferentially on the surface of the particles of metalliferous mineral, to effect the same result effected in the previously mentioned processes of the pulp-body-concentration type. . . . The excess bubbles which never go through the solution stage, in this as in the other pulp-body-concentration processes, in part coalesce with the bubbles already formed on sulphide surfaces; in part pass with the pulp into the froth-separating chamber and there, rising, add buoyancy to the froth and serve to pick up particles dropped by the bursting of other bubbles; in large part, however, they rise to the surface of the pulp in the agitating compartment and are lost to the process.

"The froths produced in pulp-body-concentration processes are small-bubble, coherent and persistent, and characteristic. The volume of gas effectively utilized in floating the mineral is of the order of 20 to 50 cu. ft. of solid floated.

"In the bubble-column process substantially all of the concentration is done in a column of bubbles above and floating on the surface of the body of pulp. In this process the volume of gas effectively used to produce concentration is enormously greater than in pulp-body concentration, being of the order of 1000 to 2000 cu. ft. of solid floated. The result is that the froth is fragile and evanescent and strikingly different from that characteristic of the other class of processes. Further investigation of the process, by observation of the operation in glass-sided machines, makes apparent the following facts: (1) The bubbles are much larger than in pulp-body processes; (2) they are more numerous; (3) they rise through the pulp more rapidly; (4) they arrive at the surface of the pulp with a solid load composed of sulphide and gangue in the same proportions that these exist in the pulp through which they have passed; (5) concentration begins at the bottom of the bubble column (i. e., the surface of the pulp body) and progresses upward. The actual mechanism of the concentration itself can be observed by studying the bubble column with a hand glass. Such study shows that in the bubble walls there is a differential draining of the gangue and sulphide particles; that the average downward velocity of the sulphide particles is less than the average upward velocity of the bubbles; that the average downward

velocity of the gangue is greater than the average upward velocity of the bubbles; and that, as a result, the sulphides are lifted up and away from the gangue. It is apparent, also, from such study, that the sulphide particles in the bubble column are nowhere firmly adherent to bubbles, as they are in the pulp-body processes.

"Pneumatic bubble-column machines are typified by the Callow cell. In this device air is introduced into the pulp through a porous medium. Canvas, cotton twill, blanket, carborundum, concrete and other porous substances are used as media for the distribution of the entering air. In pneumatic machines the pulp is relatively quiescent, the bubbles are larger than in agitation-type machines and hence rise rapidly. No pressure is exerted to force them into solution nor is there any local release of pressure to cause air already in solution to precipitate. The result is that no selection of sulphide particles takes place beneath the pulp surface. The bubbles rushing upward through the pulp mechanically push a certain amount of pulp above them as they emerge, with the result that the walls of the emerged bubble contain a solid load of the same composition as that in the body of the pulp. At the pulp surface the speed of the rise of the bubble abruptly lessens and the solid particles which now form a part of the bubble film begin to drain away rapidly. At the same time the bubble is lifted by the bubbles which follow it to the pulp surface. The solid particles drain away at different rates, the gangue particles much the more rapidly, so that, if the air supply and consequent rate of rise of bubbles is properly adjusted, the average downward velocity of the gangue will be greater than the average upward velocity of the bubble, and it will largely settle back into the pulp, while the average downward velocity of the sulphide will be less than that of the bubble, with the result that the sulphide will be carried up and away from the gangue and may be separated as concentrate."

Froth flotation, properly practiced, will recover from 60 to well over 95 percent of the sulphide mineral content of an ore in the form of a concentrate containing from ten to forty percent gangue. The author states, p. 13, that "In the agitation-froth process, the recoverable mineral content of an ore, the amount of a given oil necessary, the percentage of solids in the pulp treated, the grade of concentrate and the recovery attained are strictly dependent variables. This interdependence may be stated as follows:

1. In order to recover a given percentage of the recoverable mineral in an ore in the form of a concentrate of a given grade, if the percentage of solids is fixed, the amount of a given oil necessary is in direct proportion to the amount of recoverable mineral in the feed.

2. In order to recover a given percentage of the recoverable mineral in an ore in the form of a concentrate of a given grade, if the grade of the feed is kept constant, the amount of a given oil necessary is in almost direct proportion to the percentage of moisture in the pulp.

"These relations have been proven conclusively for the agitation-froth process and should, therefore, hold for the other pulp-body-concentration processes. Some similar relation is indicated for bubble-column process, but the writer is aware of no exhaustive and conclusive work in this direction, and the dissimilarity in the mechanism of the two types of processes forbids reasoning across from the one to the other.

"The size of the particles in a flotation pulp affects the percentage of solids and the amount of oil necessary. It is not unlikely, also, that it has some effect on the necessity for other agents. If the solids are coarse it is necessary to run with a thick pulp in order to attain a good recovery. A thick pulp, in general, results in a low-grade concentrate. Hence a coarse feed is likely to mean a low-grade concentrate. More oil is, in general, necessary, if the feed is coarse. This is probably due to the fact that, owing to the lesser covering power of the coarse material, more of the stabilization of the froth must be done by the oil. The necessity for flocculation of very fine material is not present in the case of coarse feed. Hence the necessity of an electrolyte to produce such flocculation is lacking and the conclusion follows that a coarsely ground pulp from a given ore is less likely to require the use of acid or alkali than a finely ground pulp from the same ore....

"The purpose of the oil in froth-flotation is: (1) to form, together with water and solid of the pulp and the gas introduced into the pulp, a froth; and (2), to aid in the selection of the particles of mineral of metallic, resinous or adamantine luster in the pulp from the gangue minerals. Not all oils will perform both of these functions with all ores in all processes. Newly refined paraffin hydrocarbons, if pure, will not froth to a sufficient extent to make them efficient flotation agents in the agitation-froth or pneumatic processes. Certain other substances, although possessing the property of froth formation in these processes, exclude practically all solid matter from the froth. Saponin is such a substance. Certain other agents, such as soap, cause the formation of a froth containing solid matter, but this froth results in no useful concentration. Finally, a considerable number of oil substances such as essential oils and coal-tars and wood-tars and their fractions and derivatives cause not only copious frothing but, with certain ores, efficient selection of metalliferous mineral from gangue. With other ores the selection is nil or wholly inefficient. It may be put down as an axiom of the art that no one substance is universally applicable as an 'oil' in froth-flotation concentration of all ores."

"Mobile and highly soluble oils can be employed in smaller quantity, all other conditions being equal, than viscous and relatively insoluble oil. This follows naturally from the preceding discussion. Mobile and highly soluble oils are easily dispersed in an extremely high state of subdivision, while viscous and slightly soluble oils are dispersed more slowly and to no such high degree. In pulp-body concentration the function of the oil is to coat the mineral particles. In bubble-column processes it is essential that the rising bubbles become oiled. An extremely thin film is all that is necessary. But in order to insure that the sulphide particles in the one case and the air bubbles in the other shall come into contact with oil, a certain minimum spatial distribution of the oil in the pulp is necessary. In order to insure this minimum spatial distribution with a viscous and relatively insoluble oil, necessarily in relatively large masses as compared with the particles of a mobile and highly soluble oil, a greater amount of the former must be used. Owing to the greater size of the masses of the viscous and insoluble oil the films on the particles and the bubbles will exceed the effective minimum, and further the amount of excess oil which does no coating but which is necessarily present in order to accomplish the required spatial relation will, in this case, exceed in bulk that unused in the case of the mobile or highly soluble agent.



"Above a certain minimum quantity, all other conditions being constant, the amount of oil necessary in the agitation-froth process varies directly with the amount of recoverable mineral in the ore. This is easily proven experimentally and can be predicted from theoretical considerations as follows: The maximum surface that can be covered by a given quantity of a given oily substance is measured by the area of the film, one molecule thick, which can be obtained from the given amount of agent. In any successful agitation-froth flotation operation it is essential that all of the sulphide mineral particles be coated to at least this extent. This coating cannot be accomplished without the presence of an excess of the agent in the pulp. Hence the minimum quantity of agent necessary is some probably fixed excess over that required to coat the sulphide particles with a layer one molecule deep, which excess depends upon the degree and duration of agitation, the kind of agent, and the thickness of the pulp. Any increase in the amount of metallic mineral in the pulp means an increase in the area to be covered by the oil and hence an increase in the amount of oil that must be provided.

~~"Above a certain minimum quantity, all other things being constant,~~ the amount of oil necessary in the agitation froth process to make a given recovery from a given ore with a given grade of concentrate varies directly with the percentage of moisture in the pulp, within the efficient working range of moisture percentages which is from, say, 65 to 70 percent to 90 or 95 percent. This is confirmed by experimental data and follows logically from a theoretical analysis. As has been previously stated, a certain minimum spatial distribution of the particles of oil in the pulp is necessary in order that the metalliferous mineral particles may be coated during the time that the pulp is under treatment. If the volume of pulp carrying a given amount of solid matter is increased, then the number of particles of oil necessary to produce the minimum spatial distribution of the same throughout the total volume of pulp will likewise be increased.

"The following relations between quantity of oil and size to which the ore is ground are experimentally proven: (1) If a pulp containing solid matter ground to a given degree of fineness is being concentrated by flotation with a given minimum quantity of a given agent the same metallurgical results can be obtained with a smaller quantity of agents, if the solids are more finely ground. Conversely more oil must be used, if the grinding is so changed that the product to be floated is coarser. The explanation of this observed phenomenon is, probably, that a certain degree of stability is essential in the froth and that this stability may be provided by either oil or solid matter. If the covering and hence stabilizing power of the solid is increased by finer subdivision, the oil is relieved of part of its duty and less of it, therefore, is necessary. *Vice versa*, if the covering and stabilizing power of the solid is decreased, as by coarser grinding, more burden is placed on the oil and it must be increased in quantity."

"The rôle of the minor agents is to increase the grade of concentrate, i. e., aid in selection, and to a lesser extent, aid recovery. Various theories have been advanced to explain their action. In general they are electrolytes, and ingenious hypotheses have been based on assumed accentuation, due to their ions, in the difference in magnitude of the electrical charges said to exist at the surfaces of the solid particles in the pulps. Excluding for the present the cases in which the minor agent reacts chemically with the principal agent or oil, it is a commonly observed experimental fact that successful use of a minor agent is



accompanied by increased flocculation of the flotation pulp, particularly of the flotation tailing. It is furthermore usually true that the tailing from an unsuccessful flotation operation is slow-settling, indicating a lack of flocculation. Hence we may set down as an empirical rule that a suitable minor agent will be one that flocculates the pulp.

"Concentrate handling consists in breaking down froth concentrate, thickening the same by settling, and filtering the thickened product. Sampling and transporting from thickener to smelter also offer problems, but these are not part of the subject matter under present discussion. A few general principles are all that can be set forth to aid the experimenter.

"Froth may be broken down by impact or by the force of surface tension or both. Unfortunately the same forces also tend to make froth. Hence it is essential that they be utilized in a different way or to a different extent when the end in view is froth destruction. If a small amount of froth is placed on a body of fresh water or water but slightly contaminated with a frothing agent; the tension of the water surface will pull the froth mass apart into individual bubbles and will then so extend most of the individual bubbles, especially the larger ones, that the films will rupture and the solid load will sink. The bubble film may also be ruptured by piercing or puncturing. In practice this is accomplished by directing a spray of water upon the froth. A froth is a system in more or less unstable dynamic equilibrium under the forces of gravity, surface tension and viscosity. Anything that tends suddenly to upset the equilibrium of the system will tend to break down the froth. A sudden change in surface tension can be brought about by spraying with a substance or solution whose surface tension is different from that of the bubble films.

"The three phenomena outlined in the last paragraph are all utilized in froth breaking. General practice in the mills is to run the froth concentrate through launders to Dorr tanks fitted with a peripheral curb to prevent froth overflow, and to spray the surface of the tanks, particularly near the center, usually with fresh water, in order to puncture the bubble films. Occasionally the water used is contaminated with a substance which markedly lowers the surface tension. This upsets the equilibrium of the forces acting in the bubble films, in addition to the puncturing effect. This latter procedure is necessary only in the case of obstinately persistent froths.

"Froths carrying a high percentage of solids are more persistent than those with a low percentage and more elaborate froth breaking equipment is necessary for their treatment. Such froths result from ores carrying a high percentage of mineral or high percentages of kaolinized matter. They result also from agitation methods of froth formation as differentiated from pneumatic methods.

"Certain flotation agents, notably petroleum products and wood-tar oils, produce persistent froths. Also the froths produced with more than one percent of oil on the ore are harder to break down than those produced with small quantities."

It is evident that when air comes out of a supersaturated solution it will come out most readily at those points from which air is displaced least readily by water. It is not so clear why it is difficult to make an actual bubble attach itself to the sulphide particles. One must assume that, for some unspecified

reason, the bubble does not come in actual contact with the sulphide particles. Since the author is writing a manual of flotation processes rather than a theoretical treatment, he does not go into this point and he also does not discuss the effect of copper on zinc ores in Tennessee. While one regrets that these points could not have been included, it is a pleasure to bear witness that the author has written an admirable book, and one that is entirely free from the air of mystery which pervades most articles and books on the subject of ore flotation. It is not an exaggeration to say that this is the only book on flotation which is really worth reading.

Wilder D. Bancroft

*Lehrbuch der Metallographie.* By Gustav Tammann. Second revised edition. 25 X 16 cm: pp. xviii + 402. Leipzig: Leopold Voss, 1921. Price: Paper, 98 marks, bound 110 marks. As the author states in the preface, the book is based entirely on the phase rule classification. He takes up, in order, one-component, two-component, and three-component systems. Under one-component systems we get a discussion of rate of crystallization, of the simpler changes of state, and of the effect of mechanical treatment. Under two-component systems, we get the structure diagram proper, and the methods of thermal analysis and of microscopic analysis. Two chapters are given to the physical and chemical properties of binary alloys. After a discussion of crystallization in three-component systems, there are a few pages given to the general subject of the phase rule.

On p. 46 the author quotes the work of Sieverts on the increase of solubility of hydrogen in copper, nickel, and iron with rising temperature; but neither offers any explanation of it nor calls attention to the unexpectedness of the phenomenon. On the next page he discusses temper colors as due to thin films without reference to Mallock's work in which it seemed to be shown that the colors are not due to thin films. On p. 58 he carries out strongly against Bellby's amorphous layer theory; but in what seems to the reviewer a half-hearted way. The importance of carrying the war into Africa does not seem to have occurred to him. While Tammann is probably right and Bellby wrong, nobody would guess it from reading the literature on the subject. One must congratulate Bellby and his supporters on the extraordinarily good showing they have made with practically no facts to support them.

The same rather unfortunate way of wording things appears on p. 62 where the author says that a metal will be plastic when the force necessary to break it is large relatively to the forces necessary to cause slipping. This is true but it is a re-statement of the fact of plasticity and not an explanation.

Since the author does not believe in the production of an amorphous phase when a metal is rolled cold, he has to account for the decrease in apparent density. He ascribes this, p. 114, to the production of microscopic voids arising from the displacement caused by the cold working. A strong point in his favor is that bismuth shows a decrease in density although bismuth expands on freezing. He does not seem to be well-advised in claiming, p. 117, that a shearing force is equivalent thermodynamically to a uniform pressure.

On p. 182 the author states that eutectics do not necessarily consist of thin plates but that, in the case of cadmium and zinc, the eutectic is made up

of rods of cadmium surrounded by rods of zinc. This is so interesting that one would have liked to know to what extent this phenomenon is general. In this case, zinc is apparently the external phase. With bismuth and gold, bismuth is the external phase, though present only in relatively small amount. With chill-cast copper-lead alloys, the lead is the internal phase. Nobody seems to know whether there is always an external and an internal phase or whether we may have interlacing systems. When we have one phase the external one, what are the factors which determine which phase is which?

On p. 236 the author follows many metallographists in concluding that because cementite is said to be less stable than graphite at 1000°, it is necessarily less stable at all temperatures. The reviewer feels that there is need for a careful, critical study of the evidence on which people base the belief that ferrite and graphite are the only stable phases at ordinary temperatures. The author believes that there are two forms of cementite, p. 245; the cementite in pearlite and the cementite as produced direct from the melt. This is very important if true. Tammann considers that martensite is an instable form of alpha iron, p. 248. The book was written too soon to permit of a discussion of Jeffries' conclusions in regard to martensite, though it is quite possible that the author would not have considered them at all, for he states in the preface that the volume is based so far as possible on his own work.

On p. 264 the author states that the gamma solid solutions of the copper-tin alloys consist of  $Cu_3Sn$  with an excess of copper or tin. While this may be true, there is absolutely no experimental evidence for it and it does not make for progress to conceal our ignorance by assertions of this sort. Tammann is not alone to blame for this. Practically all the modern metallographists give free rein to their fancy when dealing with solid solutions and show no hesitation in describing constituents for which there is no experimental evidence. It must be counted to Tammann's credit that he makes no guess, p. 268, as to the hypothetical compounds occurring in the copper-zinc solid solutions.

While the conductivities of the fused tin-lead alloys are approximately an additive property, this is not true for the sodium-potassium melts, p. 312, where the conductivity-concentration curve passes through a marked minimum. With sodium and mercury there are apparently two minima. While one minimum could be accounted for by postulating the existence of a compound in the melt, it is difficult to see how to account for two.

On p. 390 the author states that the alloys of aluminum and antimony, iron and chromium, and iron and molybdenum behave like a two-component system on slow crystallization and like a three-component system on rapid crystallization. This means that there are two modifications of something in the melt which change relatively slowly one into the other.

*Wilder D. Bancroft*

*Die Methoden der organischen Chemie. By J. Houben. Vol. I. 27 × 18 cm; pp. XXVI + 1121. Leipzig: George Thieme, 1921. Price: paper, 420 marks; bound, 450 marks. This stupendous volume is the first in a completely revised edition of Weyl's work of the same title. The new edition will run to four volumes and will be absolutely indispensable if the other three volumes are anything like as valuable as this one, which covers the general presentation.*

The sub-heads are: organic ultimate analysis; simplified ultimate analysis; ultimate analysis with the Berthelot bomb; organic ultimate micro-analysis; gas analysis; proximate analysis; colorimetry; capillary and adsorption analysis; heating; cooling; drying; stirring and shaking; pressing and centrifuging; clarification; decolorizing; filtration; washing and decantation; analysis and ultra-filtration; solvents; precipitation and salting-out; crystallization; extraction and shaking-out; evaporation and concentration; distillation; sublimation; autoclaves and sealed tubes; special methods of purification; preparation and purification of some gases; crystallographic methods; melting points; boiling points; solubilities; densities; molecular weights; rotation of plane of polarization; index of refraction; fluorescence; conductivity; calorimetry of organic compounds; heats of reaction; flash-points and inflammation temperatures; viscosity; recognition of dyes.

The micro-analysis methods now developed, p. 130, make it possible for anybody to do combustion with 5-10 mg of substance while an expert can get along with 1-2 mg by taking all sorts of precautions. This is of such importance that these methods should be taught in every chemical laboratory. Twenty pages are given to capillary and adsorption analysis, pp. 272-291. This includes the use of the capillarimeter, the stalagmometer, and the viscostagonometer; Goppelsroeder's capillary analysis; and Wislicenus' method of adsorption with fibrous alumina. It is claimed for Goppelsroeder's method that in aqueous solution one can detect strychnine hydrochloride at a dilution of 1/1600,000, strychnine nitrate at 1/13,000,000, eosin at 1/58,000,000 and magenta at 1/185,000,000.

Under clarification, p. 388, are included the carrying down of suspended matter by alumina, barium sulphate, and kieselguhr. The author (Herzog) recommends precipitating gelatinous material with tannin; but he points out that the same result can be obtained by adding alcohol and distilling it off. Under these conditions the gelatinous materials form flocks which can be filtered. The theory of this appears not to have been given. Under decolorizing, p. 389, the use of charcoal is the important thing. Merck is quoted as saying in 1917 that a vegetable charcoal had been made which was fully as good as any animal charcoal. Decolorizing agents of an entirely different type are sulphurous acid and permanganate. Dialysis and ultrafiltration receive about twenty-five pages, pp. 428-453. Gold-beaters' skin is much better for dialysis than parchment paper. The pores of ordinary filter paper are given as  $3.3\mu$ ; those of extra hard paper as  $0.9-1.5\mu$ ; while the earthenware filters run as low as  $0.16\mu-0.18\mu$ . With the most recent Pukall filters one can take the albuminoids out of milk completely. For ultra-filtration proper only collodion membranes are used at present.

The earliest case of salting out a dye occurred in 1740 when Barth precipitated indigo carmine from solution by addition of sodium chloride, p. 493. Now many dyes are purified by a salting-out process. The sodium salts of the sulpho acids can be obtained readily by salting-out with sodium chloride and ammonium sulphate is a standard reagent in preparing proteins. These different cases are not necessarily the same because we are probably dealing with true solutions with the sulpho acids while the proteins are in colloidal solutions. It is not always possible to draw an absolutely sharp line. Methylene blue forms true solutions ordinarily but addition of enough caustic soda makes it colloidal and then precipitates it.

In the chapter on the recognition of dyes, pp. 1023-1072, the author (Schneider) makes the usual differentiation into acid, basic, direct, mordant, sulphur, vat, and pigment dyes. As a means of determining the class to which an unknown dye belongs, the author adopts the methods of Heermann and of Ganswindt: dyeing on wool without mordant for acid dyes; dyeing on chrometanned wool for mordant dyes; dyeing on wool with sodium sulphate for direct dyes, or on cotton in presence of much sodium chloride; dyeing on cotton mordanted with tannin for basic dyes. The sulphur and vat dyes can be recognized by their behavior with sulphide and hydrosulphite solutions, respectively.

Wilder D. Bancroft

*Analytische Chemie.* By Th. Döring. 22 × 15 cm; pp. 97. Dresden and Leipzig: Theodor Steinkopff, 1921. Price: Paper 60 cts.—During the war the Germans were cut off from a knowledge of what the rest of the world was doing in a scientific way and since the war the rate of exchange has made it difficult for them to get the necessary books, to say nothing of the time wasted if each man looked through everything to find out what had been done in the lines that appealed especially to him. In order to meet this difficulty Liesegang has started a scientific series, each volume of which shall give in a condensed form the progress made in some branch during the period from 1914 to 1919. The first volume is on analytical chemistry, the second is on general geology and stratigraphy, while subsequent volumes will deal with electrochemistry, inorganic chemistry, organic chemistry, foods, theoretical physics, optics and wave theory, atomistics and electronics, mineralogy, etc.

In the preface the author says that recent progress in analytical chemistry has been along three lines: introduction of new reagents such as nitron, benzidine, etc.; improvements in instruments; application of physical chemistry. The subject is presented under five heads: general; detection, separation, and quantitative determination of cations; detection, separation, and quantitative determination of anions; determination of carbon, oxygen, and included gases in commercial metals, with special reference to iron; elementary analysis of organic substances.

As a substitute for platinum the author recommends the gold-palladium alloy, p. 1. On page 3 attention is called to Chamot's use of silk fibre stained with Congo red for microchemical investigations. On p. 8 Kolthoff's work on the effect of salts on indicators seems important. Hedwall's detection of calcium carbonate in a mixture of calcium, strontium, barium, by heating to a temperature at which calcium carbonate alone loses carbon dioxide, p. 12, is an interesting application of physical chemistry. The reviewer was also interested in the estimation of perchlorate with methylene blue, p. 72, though chiefly on account of the color changes involved.

The book seems a very good one and the value of it is not limited to the Germans. All chemists will find this concise statement of the recent developments in analytical chemistry of value to them.

Wilder D. Bancroft

*Mr. J. Witzemann*

**THE TRANSITION FROM CRYSTALLOID TO COLLOID  
PROPERTIES WITHIN HOMOLOGOUS SERIES**

BY EDGAR J. WITZEMANN<sup>1</sup>

The properties of colloidal and crystalloidal solutions are generally discussed from the standpoint of their differences and less frequently from the standpoint of their similarities.<sup>2</sup> The former is done for convenience in presentation; the latter because they really are quite similar and as Einstein emphasized in a mathematical treatment of the subject,<sup>3</sup> there is a gradual transition from crystalloid to colloid properties. There is in living organisms a special case of gradual transition from crystalloid to colloid properties within homologous series. This transition is not static but represents a dynamic equilibrium which is, so far, largely peculiar to the living organism and which seems to be an indispensable characteristic of life as we know it.

The biological aspects of the general problem of colloidal transition fall apart into three considerations.

(1) The factors that influence this transition in general with a given group of compounds.

(2) The condensation  $\rightleftharpoons$  hydrolysis equilibrium by which the transition is made from one end of the series to the other.

(3) The biological factors that sensitize and speed up this equilibrium.

In this paper we shall discuss this problem of transition mainly with respect to the first of these considerations in order to determine whether the relations involved can be considered in simple terms of chemical constitution, for instance. It seemed likely that to consider all solutions as a continuity would aid eventually in understanding certain aspects of many

<sup>1</sup> Contribution from the Otho S. S. Sprague Memorial Institute, Rush Medical College, Chicago, Ill.

<sup>2</sup> Zsigmondy-Spear: "Chemistry of Colloids," p. 23 (1917).

<sup>3</sup> Einstein: Ann. Phys., (4) 17, 549 (1905); 19, 371 (1906); Zeit. Elektrochemie, 14, 235 (1908).

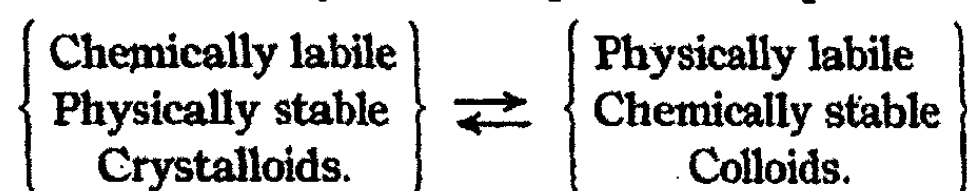


biological problems such as diabetes mellitus for instance in which the organism can convert a colloid (starch) into a crystalloid (glucose) but cannot get it back again into the colloid state (glycogen) adequately.

The main components of living organisms (other than water) are the so-called biocolloids (lipoids, carbohydrates and proteins) and the simple molecules or crystalloids of which they are built up. These biocolloids as a group differ from other colloids in the degree to which they show certain typical characteristics of colloids. For instance they are in general more completely reversible than most other colloids. In fact they show two interesting kinds of reversibility.

(1) These colloids as a group may be taken out of or put into colloid-solution as often as desired, and in general if nothing is done to them that is incompatible with the life of the organism from which they are derived, they show little tendency to become irreversible. In any case the biocolloids are the type substances of the reversible colloids.

(2) In the living organism they exhibit a tremendous capacity for reversibility of the equilibrium represented thus:



A large portion of the physical chemical philosophy of the cell is graphically summarized in this equilibrium. The chemical processes of life take place in chemically stable colloidal systems built up from crystalloids by virtue of chemical transformations of other portions of the same crystalloids.

The formulation of this reversible equilibrium visualizes some interesting paradoxical situations. Both sides contribute indispensably to the joint result—namely, life—but from the viewpoint of either side of the equation the material on the other side is playing a passive rôle. Its effects are indirect. Assigning "social" attributes to the molecules in question we have here a kind of chemical "altruism." Moreover the system contains both a dilute and concentrated solution since the

discontinuous phase contains a lower concentration of water (in biological systems) than the continuous phase. Therefore if condensation reactions thrive best in the more concentrated phase hydrolytic reactions should thrive best in the other. This discontinuity moreover gives rise to a differentiation in the energy components of the two phases the full consequences of which are yet to be appreciated and concerning which more will be said below.

These two types of reversibility so important to the chemical organization of life seem to fit these biocolloids peculiarly for their rôle in life processes as we know them. The chemist cannot aid materially in the dynamic interpretation of these processes until he can connect these two groups of spontaneous effects with the properties of the compounds in question and at the same time formulate his interpretation so that these transformations are seen to take place in accordance with the known principles of thermodynamics. Recent experience in the interpretation of the transformations of colloidal manganese dioxide<sup>1</sup> on the basis of equilibria sensitive to changes in temperature, in concentration and in the nature of the reagents suggested that perhaps the transition from crystalloid to colloid properties and *vice versa*, considered above, could be interpreted on the basis of chemical constitution. The results of such an inquiry are briefly stated in what follows.

#### The Fatty Acids

The commonest biocolloids constitute three complex homologous series—namely, the fats, carbohydrates and proteins—all of which are homogeneous or heterogeneous in their chemical components. For the sake of definiteness and simplicity it will be best to consider the fats first and these preferably in the form of their sodium and potassium soaps or salts. These compounds have the simplest chemical structure and within a truly homologous series show a strikingly definite transition from simple crystalloid qualities, in the lower members, to definite colloid properties in the higher members. The

<sup>1</sup> Jour. Am. Chem. Soc., 35, 1079 (1915); 39, 25 (1917).



main facts concerning this series will be recalled in connection with the brief review given in the following paragraphs.

(1) It is well known that after butyric acid the fatty acids rapidly become increasingly insoluble in water. Thus from complete miscibility in water for the lower acids there is a gradual passage to almost complete insolubility and immiscibility in the higher members.

(2) On the contrary the sodium and potassium salts of fatty acids are much more soluble, except the lowest members of the series, than the corresponding free acids. With increasing molecular weight the aqueous solutions tend to become more and more colloidal. Here, too, we have a gradually decreasing miscibility with increasing molecular weight manifested in a somewhat different way.<sup>1</sup> Thus the substitution of the hydrogen atom in the carboxyl group with potassium or sodium increases the range of solubility of the fatty acids and increases their capacity to take up water in the case of the higher acids in which colloidal solutions are formed.

(3) If we accept the main idea of the solvate theory of solution, namely, that solvent and solute interact in some way, then in the case of the fatty acid series the introduction of sodium or potassium in the carboxyl group increases the affinity of the molecule for water. Since a fatty acid is a constant (the carboxyl group) attached to a variable (the hydrocarbon group) it would obviously be unreasonable to expect the entire series of soaps to interact with water in exactly the same way. Now it is well known that water forms hydrates with formic and acetic acids and the alkali salts of lower fatty acids;<sup>2</sup> but the idea that these hydrates vary in complexity and stability for different fatty acids has not been much used as a working conception. Thus the long-known anomalous volatility of the lower fatty acids<sup>3</sup> on distilling dilute aqueous solu-

<sup>1</sup> Cf., for instance, Mayer, Schaeffer and Terroine: *Comptes rendus*, 146, 484 (1908).

<sup>2</sup> Jones: *Carnegie Inst. Publications*, No. 210 (1915); Cf. summary and list of earlier publications at the end. Turner: "Molecular Association" (1915).

<sup>3</sup> Duclaux: *Ann. Chim. Phys.*, 2, 289 (1874).

tions had no simple rational interpretation until recently the principle of decreasing stability of the fatty acid hydrates with increasing hydrocarbon function was used to supply one.<sup>1</sup>

(4) The idea that these compounds interact with the solvent is supported by many well-known lines of evidence only a few of which will be mentioned.

If the growing insolubility of the acids in water is due to the increasing significance of the hydrocarbon function and this group and the carboxyl act in an opposite sense on the solubility as may be concluded from much data in the literature<sup>2</sup> then the substitution of hydrogen in water with hydrocarbon groups should increase the solubility of fatty acids in the solvent. Now it is well known that soaps and fatty acids give true solutions with alcohols to a higher point in the series and to higher concentrations than they do with water. Moreover if the presence of the hydroxyl group in water is associated with the favorable effect of the carboxyl group on the solubility of the fatty acid, then the introduction of hydroxyl groups in the hydrocarbon group of a higher fatty acid should favor solubility of the fatty acid in water. That the hydroxy fatty acids are more soluble and interact more strongly with water is well known.

Other effects of the hydrocarbon depending on the character of the carbon chain, the number of carbon atoms in it and the position of the substituents, all have marked influences upon the solubility, but these factors do not modify the minimal statements given above concerning the influence of the two component groups of a fatty acid upon its general behavior toward water.

#### **Physical and Chemical Theories of Solution**

In order to make this discussion of the problem of the transition from crystalloid to colloid properties within a homologous series concrete it seems necessary to compromise the immortal controversy between the physical and chemical

<sup>1</sup> Witzemann: *Jour. Am. Chem. Soc.*, 41, 1946 (1919).

<sup>2</sup> For example cf. Auwers: *Zeit. phys. Chem.*, 42, 542 (1902).

theories of solution.<sup>1</sup> After what was said in the preceding paragraphs it seems clear that whether the one or the other theory most nearly expresses the facts will depend upon the chemical constitution of the solvent and the solute in question. Thus hydrocarbons in hydrocarbons give solutions in which the two components of the two systems of molecules differ quantitatively in composition but not qualitatively. We should here expect a minimum of chemical interaction and many of the properties of the solution should represent the algebraic sum of those of the components. Such solutions would best conform with physical theories. With water and hydrocarbons we have no chemical resemblance and have no way of knowing *a priori* how these two substances will interact. Having found that they do not interact to form a solution we have two possible ways of modifying the mixture in order to attain solubility. We may chemically make the hydrocarbon more like water by putting a carboxyl or hydroxyl group into its molecule or we may make the water more like hydrocarbon by replacing a hydrogen atom with a hydrocarbon group. Both systems now interact and will conform more or less closely with the physical or chemical theory of a solution depending upon the nature of the groups involved, *i. e.*, in which component the concession to the chemical constitution of the other was made.

As a qualitative statement the above is probably generally accepted. The difficulties arise in attempting to apply quantitative definitions and are partly due to the fact that our qualitative conceptions are not yet sufficiently clear. Moreover there is a tendency to set up discontinuities in our consideration of these phenomena where gradual transitions only exist. In this way imaginary boundaries are set up which we find ourselves more reluctant to cross as the data in the two fields multiply.

---

<sup>1</sup> Cf. P. Walden; "Die Lösungstheorien in ihrer geschichtlichen Aufeinanderfolge," Ahrens Sammlung Chem. u. Chem.-Techn. Vorträge, 15, Nos. 8-18 (1910).

In a recent study of water in the state of vapor, Oddo<sup>1</sup> pointed out that the more rarefied water vapor becomes, or the lower the vapor pressure, the greater the percentage of water dissociated into  $H^+$  and  $OH^-$  ions. On the other hand Oddo also found that after a certain vapor pressure was attained the percentage of ionic dissociation continues to decrease but that the percentage of molecular association rapidly increases. Oddo concluded that it seems that nature likes about so many particles of the constituents of water in a given volume and tends to break them apart or double them up in the attempt to maintain this number.

Jones<sup>2</sup> observed similar effects with mixtures of alcohol and water and acetic acid and water.

"An associated liquid tears down the molecules of an electrolyte dissolved in it, into simpler parts or ions; and it might be expected that such a liquid would tear down molecules of another associated liquid, a nonelectrolyte, not into charged parts or ions, but into simpler molecules. Alcohol and water are associated liquids, as has been shown by the surface tension method of Ramsay and Shields. Do these diminish the association of one another?

"That this is the case was shown by Murray.<sup>3</sup> He worked with associated liquids, water, formic and acetic acids. He determined the molecular weight of each of these liquids in the other two and found that the molecular weight became smaller the more dilute the solutions. This showed that the solvent, i. e., the liquid present in the larger quantity, was tearing down the molecular complexes of the dissolved liquid or the one present in the smaller quantity."

#### Application of Le Chatelier's Principle

The above graphic statements of Oddo and Jones seem to resemble the qualitative statement of the second law of Thermodynamics known by chemists as the Theorem of Le Cha-

<sup>1</sup> Gazz. chim. ital., 45 I, 319 (1915).

<sup>2</sup> Carnegie Inst. Washington Pub., No. 210, 163 (1915).

<sup>3</sup> Am. Chem. Jour., 30, 193 (1903).

telier, by physicists as the Theorem of De Maupertuis or the Principle of Least Action, by biologists as the Law of the Survival of the Fittest, and by economists as the Law of Supply and Demand.<sup>1</sup> If this apparently universal principle governing natural phenomena can be adequately applied to a formulation of the phenomena of true and colloidal solution it would constitute a simplification of the problem and an advance at the same time. The example cited by Jones will serve to discuss the proposition concretely and thus to test the applicability of this Principle of Le Chatelier of the problem of solution.

Pure liquid acetic acid and liquid water are largely dimolecular. When a little of the acid is dissolved in the water dimolecular acid and water break up and acetic acid hydrate is one of the products. The total number of dimolecular molecules is less than the sum of the dimolecular molecules originally present in the two component liquids. This distribution of acetic acid in water thus really involves two effects. (1) It involves the tendency on the part of the acid to distribute itself in the volume available as though it alone were present. This involves the breaking up of some associated molecules and some ionic dissociation analogous to what Oddo pictured for water. (2) It involves the interaction of these components of the acid system with the components of the water already present and this involves the formation of the various ion and molecule hydrates. The whole system of changes can be expressed in a series of equilibria<sup>2</sup> and the final condition of the system undoubtedly conforms with the Second Law of Thermodynamics, of which Le Chatelier's Principle is the qualitative statement.

When additional acid is added, the whole cycle of changes and adjustments is repeated until presently enough acid has been added so that it becomes obvious from molecular weight determinations such as those cited above that a smaller

<sup>1</sup> Paraphrased from a paper by W. D. Bancroft: *Jour. Am. Chem. Soc.*, 33, 91 (1911).

<sup>2</sup> Cf., for instance, Witzemann: *Jour. Am. Chem. Soc.*, 39, 25 (1917).

proportion of dimolecular acetic acid molecules is now being broken up. Into such a solution we could pass monomolecular acetic acid vapor and find it in the aqueous solution largely as dimolecular acid. Such a solution presents three kinds of acetic acid—ionized acid, monomolecular acid, and dimolecular acid—all in equilibrium with each other. The system is a completely reversible and reproducible one and may be prepared from any of the three acid components and water by adjusting the concentration of the water. Whether all three kinds of acid were present in the solution when equilibrium was attained after the first addition is probably not certainly known, but that as the concentration increases the dimolecular kind of acid increases faster than the other two kinds is clearly indicated by much experimental data. Since all of these kinds of acid are freely soluble in water the system is commonly considered to be homogenous. That it is not truly homogeneous is obvious.

The particular heterogeneity in which we are interested at this point is that involved in the formation of dimolecular acid from and in the presence of monomolecular acid within the aqueous solution. Here we have the spontaneous formation of a more condensed system within a less condensed one. Or using colloid chemical terminology a discontinuous phase (or concentrated solution of the colloidal substance) within a continuous phase (a dilute solution of the colloidal substance in the solvent). What may appear to be an unimportant distinction in the case of acetic acid as discussed ceases to be so if we take the sodium or potassium salts of the lower and higher fatty acids as well. One of the best-known facts of colloid chemistry is the fact that in passing up this series the significance of the ionized and monomolecular molecules diminishes more and more while the typical colloidal polymolecular molecules dominate more and more. Here we have developed for identical molecular concentrations of various salts the series of effects observed with variable concentrations of acetic acid.

The discussion in the preceding paragraphs confirms the

impression that the process of formation of both true and colloidal solutions, although not understood in its details, is obviously amenable to Le Chatelier's Principle. The molecular state of the fatty acids and their salts in solution presents no sharp break but rather a gradual transition from a less obvious to a more obvious heterogeneity. This change is seen to coincide with the increase in the hydrocarbon function of the molecule and since the other chemical function (carboxyl) is constant for the series the change must be definitely attributed to the constitutive influence of the hydrocarbon group. Consequently the decreasing dispersibility of these higher fatty acid salts is to be attributed to the increasing hydrocarbon function. Because of the chemical simplicity and stability of this group these salts and their derivatives should be expected to play the important biological rôle that they do.

#### **Differentiation of Energy in the Two Phases**

The fact that the soaps are not uniformly dispersed in aqueous solution but that the solution represents a concentrated solution suspended in a dilute one gives rise to an unequal distribution of energy between the two phases of the solution. The situation from the standpoint of energy is analogous to the behavior of compressed carbon dioxide. When the pressure is released the kinetically cool gas escapes into a warmer atmosphere. In expanding a portion of the gas is heated while the remainder is cooled. The end products are relatively warm carbon dioxide gas and cold carbon dioxide snow. A marked heterogeneity in the energy content of carbon dioxide was produced on releasing the relatively homogenous carbon dioxide into a similarly homogeneous atmosphere. A singularly parallel stepping up and down of the energy content of the component molecules of a quantity of soap occurs when it is dispersed in water. In the case of soap, however, we obtain a differentiated system that is stable in comparison with the carbon dioxide system. Since differentiation of heat energy content as in the case of carbon dioxide gives rise to unstable systems in which energy equalization occurs rapidly



if unhindered, it is obvious that the energy differentiation induced in these colloidal systems involves other kinds of energy than heat energy. The electrically charged colloidal particles (in so far as they are not due to ions) and the surface energies so pronounced in the colloidal state represent at least two known types of differentiation of other energies that are involved here.

This heterogeneity of energy distribution in colloids is conditioned by the orientation of the molecules within the system as a whole and manifests itself as surface energy only at the boundaries of the phases, as is shown by the interesting results of Harkins<sup>1</sup> for instance. These effects are particularly striking with simple compounds like the alkali soaps, the molecules of which have two ends of widely different chemical constitution. The same type of orientation probably is not conspicuous in the polysaccharides and proteins in which the active groups substituted in the hydrocarbon residues are rather evenly distributed through the large molecule.

Since the amount and kind of energy in the environment of molecules is an important factor in determining chemical reactivity, it is clear that such spontaneous differentiations of energies in colloidal systems would be desirable in the chemical organization of life because it would contribute so much to the chemical versatility of the organism. To have chemically cold, moderate and hot regions within submicroscopic distances of each other would be a great engineering advantage when the diversity of the chemical needs and processes of an organism are considered.

In summarizing for the fatty acid series we may say that increasing hydrocarbon function in this series gives rise to an increasing tendency to form two solutions in water at the same time (a concentrated and a dilute one) and that this material differentiation is associated with a differentiation in the amounts and kinds of energy present in the two phases of the

---

<sup>1</sup> Jour. Am. Chem. Soc., 39, 541 (1917).



solution. Moreover it is clear that these transformations are taking place in accordance with Le Chatelier's Principle. Such characteristics as these, together with the fact that these systems are self-reproducing from the components, admirably fit these compounds as biocolloids.

#### The Biocolloids Proper

In the above we have traced the transition from crystalloid to colloid properties in a simple homologous series of compounds. The even more typical biocolloids such as the hexose—polysaccharide series and the amino acid—polypeptide—protein series are not so simply constituted.

Both series are built by condensation reactions from simple crystalloids and thus show the same gradual transition from crystalloid to even more characteristic colloidal properties than are observed with the soaps, in passing up the series. Both series may be considered as substituted hydrocarbons and their differences may be ascribed to the degree and nature of this substitution. In the carbohydrate series the substitution consists mainly in OH groups and the compounds of the entire series are in general feebly acid in nature and generally not highly reactive chemically except under special chemical conditions. The proteins on the other hand are built up of crystalloid components in which the basic amino group balances the acid carboxyl group. When the protein molecule is synthesized from a variety of these compounds with a hexose, purine, phosphoric acid molecule, etc., introduced here and there we have *a priori* a system that will be chemically temperamental or stable, depending upon the quantitative chemical nature of its environment.

The constitutional reason for the colloidal state in the higher carbohydrates and proteins is not exactly the same as that given in the case of soaps. In the soaps we had but two groups—the hydrocarbon and the carboxyl groups—which, according to Auwers' classification of groups with reference to their effects upon molecular association,<sup>1</sup> have an opposite

<sup>1</sup> Zeit. phys. Chem., 42, 542 (1902).

effect upon molecular association of compounds in which they are substituted. In this series the increasing hydrocarbon function acts to decrease the affinity of the fatty acid for water and to increase its affinity for molecules of its own kind. In the case of the carbohydrates the increasing function is approximately CHOH of which group the OH, according to Auwers' classification, has distinct tendencies to facilitate molecular combination with other OH containing compounds, such as water. We therefore have greater solubility of the carbohydrate compounds than is shown by the corresponding hydrocarbons. That starch and cellulose are not freely soluble in water, however, shows that an unlimited number of OH groups does not secure unlimited solubility. In fact the facts in this connection are perhaps the best proof that the solvent interacts with the solute. It is a well-known fact that polyhydroxy compounds have a tendency to undergo condensation reactions by which two molecules react with the splitting out of a molecule of water giving rise to many simple and mixed complexes. Such condensations are however not limited to the kind just described. Anhydrides of some of these compounds are under some conditions more easily formed than the condensation products mentioned above. This is particularly true with  $\gamma$ -hydroxyorganic acids which give lactones so easily. The known chemistry of cellulose, for instance, is at present best explained by considering it as an anhydride of the  $\gamma$ -oxido form of glucose.<sup>1</sup> Compounds that so readily give rise to lactones and inner anhydrides have little tendency to add water at these points. In interacting with water they have a greater tendency to interact by means of their free OH groups to form hydrates than to add water at the anhydride oxygen rings and linkings. That is, the secondary valences of oxygen are more unsaturated toward water under these conditions than the anhydride linkages.

The same problem may be considered concretely in another way. The polysaccharide molecular complex contains many

---

<sup>1</sup> Hibbert: *Jour. Ind. Eng. Chem.*, 13, 256, 334 (1921).

OH groups the secondary valence energy of which is saturated off by adjoining OH groups in the same complex. When this complex network of OH groups interacts with a simple set of OH groups like that of water ( $H_2O$ ), the latter becomes molecularly dissociated and bound by the complex as hydration water without markedly dispersing the complex polysaccharide as a whole. Only as the final result of many such interactions with water molecules does a higher polysaccharide become dispersed in such solvents as water. Such a complex polysaccharide as starch should therefore be expected to swell and disperse slowly in water.

The process becomes still more concrete when pictured in terms of such simple electronic conceptions of valence as that of J. Stark,<sup>1</sup> details concerning which need not be given here.

In the protein molecule the changing functions, besides the hydrocarbon part, are the  $NH_2$  and  $CO_2H$  residues which according to the same classification of Auwers also tend to facilitate molecular association with water. On the basis of the chemical nature of these groups the protein molecule interacts with water in some respects like the higher carbohydrates, but because the structural variety of groups in proteins is much greater the possibilities for sensitive influences become much greater. There is however no question about the gradual transition from crystalloid to colloid properties on passing up and down the series. Moreover it seems clear that if the above statements are of value in clarifying the relations in the fatty acid and carbohydrate series they are of value in the protein series although the relations are still somewhat more obscure on account of the more complex structure of these compounds and our ignorance of the influence of these various structural factors upon the properties of protein.

#### General Résumé

One of the most persistent problems of biological chemistry is the question as to how such chemical systems as con-

<sup>1</sup> Cf. P. Ruggli: Ahrens Sammlung Chem. u. Chem.-Techn. Vorträge, 19 (1912-3) for a review and refs.

stitute living organisms can come about. It is only as this question can be answered more or less clearly in chemical terms that the chemical dynamics of life processes become more amenable to attack with the conventional tools of chemistry. The above paragraphs constitute a partial answer to the question and state pretty clearly in terms of chemical constitution why the indispensable heterogeneity of the aqueous systems constituting living organisms exists and how it is spontaneously brought about. It is shown that the emulsoid structure of biocolloids constitutes a gross heterogeneity which is also present in a much less conspicuous form in the lower crystalloid members of the same homologous series. In this way it becomes clear that the particular properties of biocolloids arise from the cumulative effect of certain groups in the molecule. This effect of chemical constitution is especially easy to trace with the soaps and less easy with the carbohydrates and proteins.

The discussion also brings out the fact that there is associated with this material heterogeneity a well-known heterogeneity of energy. It is shown on the basis of a simple example how such heterogeneities may arise spontaneously upon releasing one system into another. The best known energy differentiation under these conditions is the much-discussed surface energy. In this discussion it appears that the surface energy phenomena in solutions are energy differentiations definitely associated with material differentiations and these in turn are due to chemical constitution and that changes in the latter necessarily involve the whole series of effects. Even the earliest students of chemical constitution knew that changes in constitution involved changes in solubility and therefore in the secondary effects of solubility. We however have been slow in following their lead particularly in considering the biocolloids.

So far as biological phenomena are concerned these two heterogeneities have in the past been regarded as associated with some vital force. But even now, when the aid of a hypothetical vital force is not so often called upon, these hetero-

genities are frequently thought to be maintained in organisms by a constant expenditure of energy obtained from chemical reactions in the organism. Considerations developed in this paper indicate that certainly part of this heterogeneity occurring in the structure of organisms arises from a predisposition on the part of the component substances themselves to give rise to these effects. Such colloidal systems as those prepared from simple biocolloids are self-reproducing from the components: they arise spontaneously and require no unusual outlay of energy for their construction and maintenance.

Wm. Ostwald<sup>1</sup> has said that the two known laws of thermodynamics will take on a new comprehensiveness when we have learned to include the phenomena of biology among the data covered by what is still called thermodynamics. It is therefore particularly interesting to find that the qualitative statement of the second law known as Le Chatelier's Principle is so easily rediscovered in the phenomena of true and colloidal solutions so fundamentally involved in biological phenomena. This leads one to assert, whatever the errors made above may be, that the fundamental idea is right, since the most comprehensive statement yet developed concerning natural phenomena is so readily discovered to be operative in these phenomena of solution when the data are considered in this way.

---

<sup>1</sup> Cf., for instance, "Der energetische Imperativ," pp. 12-13 (1913).

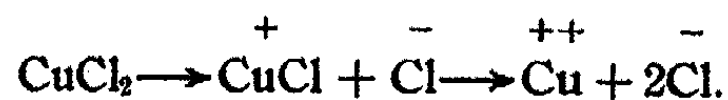
# A SPECTROPHOTOMETRIC STUDY OF SOLUTIONS OF CUPRIC CHLORIDE

BY FREDERICK H. GETMAN

## Introduction

Although the absorption of light by solutions of copper salts has been the subject of numerous investigations extending over a period of nearly fifty years, apparently the first trustworthy quantitative data is that furnished by Ewan<sup>1</sup> in 1892. He investigated solutions of the chloride, sulphate, and nitrate of copper. His apparatus was so arranged that the spectrum of a thin layer of a concentrated solution could be compared directly with a thick layer of a dilute solution, the product of thickness and concentration in each case being maintained constant. The conclusions reached by Ewan may be briefly summarized as follows: (1) The absorption spectra of the three salts change on dilution. (2) The changes in the spectra are such that they tend to become identical in dilute solutions. (3) In concentrated solutions the greater part of the absorption is due to the molecules, while in dilute solutions it is due almost wholly to the ions.

In a second paper, Ewan<sup>2</sup> confirmed his earlier results and pointed out that the changes in the absorption spectrum of cupric chloride on dilution are such as to indicate a progressive ionization as expressed by the equations



The fact that dilute solutions of different salts of copper give identical absorption spectra was brought out in a striking manner in the well-known investigation of Ostwald<sup>3</sup> on the color of salt solutions, and was cited by him as furnishing

<sup>1</sup> Phil. Mag., 33, 317 (1892).

<sup>2</sup> Proc. Roy. Soc., 56, 286 (1894); 57, 117 (1895).

<sup>3</sup> Zeit. phys. Chem., 9, 579 (1892).

further evidence in favor of the theory of electrolytic dissociation.

Kastle,<sup>1</sup> in a paper treating of the colors exhibited by various copper salts in solution, concluded that neither the dissociation nor hydrate theories furnished adequate explanations of the observed color phenomena and, in consequence, advanced the suggestion that the color of a salt solution is not dependent upon the color of the ion, but rather upon the color of the base or that of the acid, either or both of which may be colored. He further suggested that the base or the acid producing the color may possess, according to circumstances, two or more distinct colors.

Knoblauch,<sup>2</sup> and later Grünbaum,<sup>3</sup> showed that the absorption spectrum of copper sulphate is nearly independent of the concentration: in other words, the copper ion and the molecule of copper sulphate seem to possess the same absorbing power.

The addition of sulphuric acid or sodium sulphate to solutions of copper sulphate was shown by Magnanini<sup>4</sup> to produce almost no change in the absorption spectrum, thus confirming the results of Knoblauch and Grünbaum.

Changes in both concentration and temperature have long been known to exert a marked influence on the absorption of the copper halides, an increase in either of the foregoing variables causing an increase in the absorption of the shorter wave-lengths. These changes were attributed by Hartley,<sup>5</sup> and also by Sabatier,<sup>6</sup> to the breaking down of hydrates in solution. On the other hand, Donnan and Bassett,<sup>7</sup> as well as Moore,<sup>8</sup> have furnished evidence to prove that the formation

---

<sup>1</sup> *Am. Chem. Jour.*, **16**, 326 (1894).

<sup>2</sup> *Ann. Phys.*, [3] **43**, 738 (1891).

<sup>3</sup> *Ibid.*, [4] **12**, 1004 (1903).

<sup>4</sup> *Rend. Accad. Lincei*, [4] **7**, II, 308, 356 (1891).

<sup>5</sup> *Trans. Roy. Soc., Dublin*, [2] **7**, 253 (1900).

<sup>6</sup> *Comptes. rendus*, **118**, 1042, 1144, 1260 (1894).

<sup>7</sup> *Jour. Chem. Soc.*, **81**, 939 (1903); *Zeit. phys. Chem.*, **53**, 317 (1905).

<sup>8</sup> *Zeit. phys. Chem.*, **55**, 641 (1906).

of complex ions, rather than dehydration in solution, is the cause of the observed changes in absorption.

Two investigations of special importance are those of Müller<sup>1</sup> and Vaillant.<sup>2</sup> Each of these investigators carried out a series of spectrophotometric measurements of several different copper salts with a view to determining the relation between the degree of electrolytic dissociation and the absorption of their solutions. For the wave-lengths at which measurements were made ( $640\mu\mu$  to  $608\mu\mu$ ) and for all solutions containing less than one mol of solute per liter, the absorption was found to be a function of the degree of dissociation. Divergences from the simple linear relation established by Vaillant were observed with the higher concentrations and were attributed to partial dehydration of the solute. Vaillant also studied solutions in methyl and ethyl alcohols, as well as in glycerine, with the following results: (1) In the organic solvents investigated, the coefficients of absorption are independent of the nature of the solvent and also of the concentration; (2) if a concentrated solution of a salt is added to a dilute aqueous solution of another salt having a common ion, the value of the absorption coefficient tends to approach that of the solution in the organic solvent.

The absorption spectra of solutions of copper sulphate in both water and methyl alcohol were studied by Carrara and Minozzi.<sup>3</sup> As a result of their investigation, they were led to conclude that each solvent exerts a specific influence on the absorbing power of the ions and the undissociated molecules.

Jones and his students<sup>4</sup> photographed the absorption spectra of a large number of salts in aqueous and alcoholic solutions, both alone and in the presence of certain dehydrating agents. From the spectrograms thus obtained, and from other

---

<sup>1</sup> Ann. Phys., [4] 12, 76 (1903).

<sup>2</sup> Ann. Chim. Phys., [7] 28, 213 (1903).

<sup>3</sup> Gazz. chim. ital., 27, II, 465 (1897).

<sup>4</sup> Carnegie Institution of Washington Publication, No. 60.



experimental data, Jones was led to attribute the absorption of light by solutions to the vibration of minute particles of the dissolved substance, and to consider that these vibrations are damped by the condensation of water molecules on the absorbers. Dehydrating agents, rise in temperature, or increase in concentration were believed to effect a breaking down of these complexes, or "solvates" as he termed them, into simpler absorbers and thus, owing to increased resonance, he was able to account for the observed widening of the absorption bands. A narrowing of the absorption bands was found to follow the addition of water to non-aqueous solutions. From this he concluded that the degree of solvation in non-aqueous solutions is less than in aqueous solutions. The work of Jones seems to indicate not only that both ions and undissociated molecules tend to undergo solvation, but also that with increase in concentration, and consequent decrease in dissociation, the total amount of combined solvent at first decreases and then gradually increases.

The absorption spectra of several copper salts, in both aqueous and non-aqueous solutions, have been studied by Cooper,<sup>1</sup> whose results may be considered to be in agreement with those of Jones.

Sidgwick and Tizard<sup>2</sup> conclude, from a series of quantitative colorimetric measurements of a number of different copper salts, that the point at which the solutions change in color from green to blue is that at which the number of complex ions becomes negligible. The solution then contains no molecules

other than  $\overset{+}{\text{CuA}}_2$  and the ions  $\overset{++}{\text{CuA}}$ ,  $\overset{-}{\text{Cu}}$  and  $\overset{-}{\text{A}}$ . According to this explanation, the absorption will be due to  $\overset{+}{\text{CuA}}_2$ ,

$\overset{+}{\text{CuA}}$  and  $\overset{++}{\text{Cu}}$  and the change of color on dilution will be

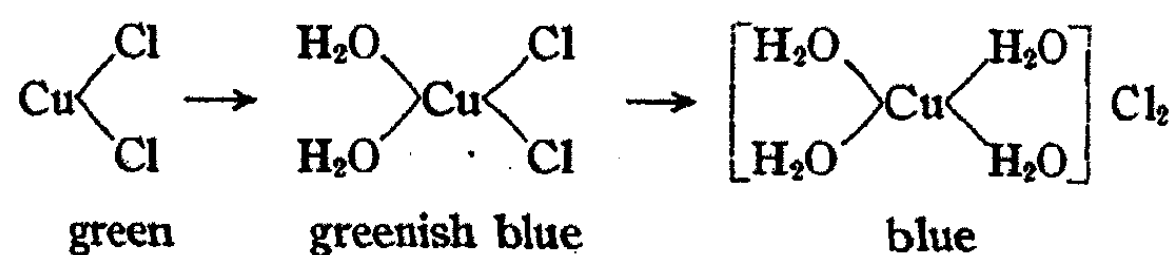
caused by the production of  $\overset{++}{\text{Cu}}$  at the expense of the other two absorbers.

<sup>1</sup> *Astrophys. Jour.*, 31, 339 (1910).

<sup>2</sup> *Jour. Chem. Soc.*, 93, 187 (1908); 97, 957 (1910).

A spectrophotometric study of solutions of copper sulphate up to 0.4 *N* by Hildebrand<sup>1</sup> showed that the absorption is strictly proportional to the concentration.

The investigations of Hantzsch<sup>2</sup> are without doubt among the most important in this field. His conclusions, based upon a large number of observations, may be summarized as follows: (1) Acids, bases and salts having completely saturated complex ions are optically unchangeable whether dissociated or not, no matter what the colorless anion or cation may be with which they are associated. (2) Acids, bases or salts which are unsaturated, but which may become saturated, on the addition of a definite number of molecules of water, ammonia or the like, suffer a change in their absorption until a fully saturated complex is formed, after which no change in the absorption occurs on the addition of an excess of the combining substance. For example, anhydrous copper sulphate,  $\text{CuSO}_4$ , undergoes a change in color when dissolved in water, or ammonia, forming either  $\text{Cu}[(\text{H}_2\text{O})_4]\text{SO}_4$ , or  $\text{Cu}[(\text{NH}_3)_4]\text{SO}_4$ ; on adding more water, or ammonia, no further change in the absorption is produced. (3) If the colored complex is stable only when a large excess of solvent is present, the absorption may change not only with increasing dilution, but also in passing from one solvent to another. In this case, Hantzsch assumes the existence of intermediate complexes, the changes in absorption being attributed to the corresponding changes in the unstable intermediate complexes. Thus, on dilution of a concentrated solution of cupric chloride, the solute is supposed to undergo the following changes:



<sup>1</sup> Zeit. Elektrochemie, 14, 349 (1908).

<sup>2</sup> Ber. deutsch. chem. Ges., 41, 1216, 4328 (1908); Zeit. phys. Chem., 63, 373 (1908); 72, 362 (1910).

As we review the different hypotheses that have been advanced in explanation of the phenomena of absorption of light by solutions, it is apparent that in nearly all of them the existence of ions and molecules, either solvated or unsolvated, has been assumed. It is interesting to note that as long ago as 1893, Werner<sup>1</sup> wrote these significant words: "Die erste Bedingung zur elektrolytischen Dissoziation eines Salzes ist die Fähigkeit seines Metallatoms, sich mit einer bestimmten Anzahl von Wassermolekülen zu einem Radikal zu verbinden, in dem wir uns die Wassermoleküle so angeordnet zu denken haben, dass eine direkte Bindung zwischen dem Metallatom und dem Sauerest nicht mehr eintreten kann." That is to say, in every electrolytically dissociated salt solution, the cations are not present merely as electrically charged metallic atoms, but rather as atoms holding in combination as many molecules of the solvent as correspond to the co-ordination number of the metal. From this it appears that the solvate theory and the dissociation theory are to be regarded as complementary. In this connection Hantzsch (*loc. cit.*) has pointed out that the combined theories can be applied equally well to the explanation of the phenomena of absorption presented by organic compounds, and to the even more obscure phenomena presented by inorganic compounds.

Notwithstanding the fact that such a large amount of work has been done on the spectroscopy of salt solutions, one fails to find in reviewing the literature sufficient reliable quantitative data with which to test the various theories which have been advanced in connection with the phenomena of absorption. In the hope of contributing something to this interesting and important field, the following investigation of the absorption of light by solutions of cupric chloride alone, and in the presence of several dehydrating agents, was undertaken.

#### Definitions

If  $I$  denotes the intensity of a beam of light which has traversed a thickness,  $l$ , of any absorbing medium, we may

<sup>1</sup> *Zeit. anorg. Chem.*, 3, 206 (1893).

write

$$-dI = kI dl. \quad (1)$$

Denoting the intensity of the incident light by  $I_0$  and integrating equation (1), we have

$$\int_{I_0}^I \frac{dI}{I} = -k \int dl,$$

or

$$\log_e \frac{I}{I_0} = -kl. \quad (2)$$

Equation (2) may be written in the exponential form, as follows

$$I = I_0 e^{-kl}. \quad (3)$$

The constant  $k$ , which is dependent upon the wave-length and also upon the nature of the absorbing medium, is known as the *absorption index*. Bunsen and Roscoe<sup>1</sup> introduced the term *extinction coefficient* to denote the thickness of the absorbing medium which is necessary to reduce the intensity of the light to one-tenth of its original value. Hence, if we represent the extinction coefficient by  $\epsilon$ , equation (3) may be written

$$I = I_0 10^{-\epsilon l},$$

or

$$\epsilon = \frac{1}{l} \log_{10} \frac{I_0}{I}. \quad (4)$$

The value of  $\log_{10}(I_0/I)$  corresponding to the extinction coefficient, is frequently referred to as the *density* of the medium. It is often convenient to express the absorption of a solution in terms of the so-called *molecular extinction coefficient*: this quantity is defined by the equation  $M = m/\epsilon$ , where  $m$  denotes the gram-molecular concentration of the solution.

#### Apparatus and Method

A Hilger wave-length spectroscope equipped with a prism of dense optical glass (refr. index 1.74) and fitted with a shutter eye-piece, was used in conjunction with a Nutting photometer<sup>2</sup>

<sup>1</sup> Pogg. Ann., 101, 238 (1857).

<sup>2</sup> Bull. U. S. Bureau of Standards, Reprint No. 155.

to measure the absorption of the different solutions investigated. The more concentrated solutions were examined in absorption tubes 10 cm. in length, while for dilute solutions special tubes 50 cm. in length were employed. A special 6-volt tungsten filament lamp served as the source of light and, to prevent diffuse illumination, this was enclosed in a sheet-iron housing which was perforated with a small hole directly opposite to the incandescent filament. Without entering into the details of the construction of the Nutting photometer, it will be sufficient to state that the optical system of the instrument is so arranged that a tri-partite field is projected upon the slit of the spectroscope. The outside portions of the field correspond to the light which has traversed the solution, while the central portion corresponds to that which has traversed the pure solvent. The intensity of the central portion can be varied by rotating a Nicol prism, and the amount of rotation required to match the intensities of the central and outer portions of the field is read on a divided circle. There are two scales on this divided circle, one graduated in degrees and the other in densities: the relation of one scale to the other is given by the formula

$$\log \sec^2 \phi = D,$$

where  $\phi$  and  $D$  denote the angular and density readings, respectively. To determine the optical density of any given solution, the wave-length drum of the spectroscope is set at the particular wave-length desired and then, after matching the central and outside portions of the field by means of the Nicol prism, the density is read directly from the graduated circle. On multiplying the value of the density thus found by the reciprocal of the thickness of the absorbing medium, the extinction coefficient is obtained.

The absorption of each solution was compared directly with that of the pure solvent, the latter having been distilled as in the preparation of water for measurements of electrical conductivity.

The mother solutions were prepared from the purest

obtainable materials and were standardized analytically. All dilutions were made with calibrated volumetric apparatus and special precautions were taken to protect the solutions from the action of sunlight.

#### Experimental Data

The following tables (Tables I to VII) give the experimental data: the first column of each table gives the wavelengths in micromillimeters ( $\mu\mu$ ) at which the optical densities were measured, while the succeeding columns contain the corresponding values of the extinction coefficients. The figures at the head of each column give the concentrations of the solutions expressed in mols per liter. It was found to be quite difficult to secure satisfactory duplication of results with solutions more dilute than about 0.5 molar, and for that reason no data are recorded for solutions less than 0.8443 molar. Tables II to VII show the effect on the absorption of an 0.8443 M solution of cupric chloride produced by the addition of various dehydrating agents.

TABLE I  
Cupric Chloride  
Mean Temp. 28.3°

$\lambda$	2.2622 $\epsilon$	2.149 $\epsilon$	2.036 $\epsilon$	1.923 $\epsilon$
540	—	—	0.285	0.270
535	0.257	0.246	0.233	0.222
530	0.206	0.199	0.190	0.183
525	0.171	0.167	0.156	0.152
520	0.148	0.140	0.134	0.124
515	0.131	0.126	0.114	0.106
510	0.125	0.116	0.106	0.097
505	0.129	0.117	0.102	0.092
500	0.140	0.129	0.107	0.093
495	0.168	0.154	0.120	0.101
490	0.280	0.200	0.150	0.125
485	—	—	0.195	0.166
480	—	—	0.270	0.230

TABLE I (Continued)  
 Cupric Chloride  
 Mean Temp. 28.3°

$\lambda$	1.519 $\epsilon$	1.435 $\epsilon$	1.182 $\epsilon$	0.8443 $\epsilon$
560	—	—	—	0.260
555	—	—	—	0.214
550	—	—	—	0.180
545	—	—	0.210	0.150
540	0.227	0.211	0.176	0.126
535	0.187	0.172	0.145	0.106
530	0.153	0.144	0.119	0.087
525	0.130	0.122	0.098	0.073
520	0.110	0.102	0.083	0.061
515	0.093	0.084	0.068	0.051
510	0.080	0.072	0.057	0.043
505	0.072	0.061	0.047	0.036
500	0.064	0.054	0.041	0.030
495	0.065	0.049	0.036	0.026
490	0.070	0.050	0.033	0.023
485	0.083	0.056	0.032	0.021
480	0.100	0.066	0.033	0.020
475	0.127	0.080	0.037	0.020
470	0.164	0.100	0.044	0.022
465	—	0.130	0.054	0.025
460	—	—	0.066	0.029

TABLE II  
Cupric Chloride + Hydrochloric Acid  
Mean Temp. 26.7°

$\lambda$	CuCl <sub>2</sub>			HCl		
	0.8443 $\epsilon$	0.461 $\epsilon$	0.922 $\epsilon$	0.199 $\epsilon$	1.844 $\epsilon$	2.305 $\epsilon$
560	0.260	0.260	0.250	0.267	—	—
555	0.214	0.214	0.214	0.217	0.225	0.227
550	0.180	0.180	0.180	0.181	0.185	0.185
545	0.150	0.100	0.150	0.153	0.156	0.159
540	0.126	0.126	0.126	0.128	0.131	0.132
535	0.106	0.106	0.106	0.108	0.111	0.114
530	0.087	0.087	0.087	0.087	0.094	0.097
525	0.073	0.075	0.077	0.075	0.081	0.086
520	0.061	0.063	0.067	0.064	0.073	0.081
515	0.051	0.059	0.053	0.059	0.056	0.066
510	0.043	0.044	0.048	0.050	0.065	0.081
505	0.036	0.038	0.043	0.047	0.066	0.089
500	0.030	0.033	0.041	0.047	0.072	0.105
495	0.026	0.030	0.041	0.049	0.083	0.130
490	0.023	0.029	0.044	0.056	0.104	0.173
485	0.022	0.030	0.049	0.067	0.138	—
480	0.020	0.032	0.057	0.085	0.190	—
475	0.020	0.037	0.069	0.115	—	—
470	0.022	0.044	0.087	0.153	—	—
465	0.025	0.055	0.120	—	—	—
460	0.029	0.070	—	—	—	—
455	0.035	0.090	—	—	—	—
450	0.046	—	—	—	—	—
445	0.068	—	—	—	—	—



TABLE III  
Cupric Chloride + Potassium Chloride  
Mean Temp. 26.3°

$\lambda$	CuCl <sub>2</sub>		KCl		
	0.8443 ε	0.395 ε	0.789 ε	1.578 ε	1.973 ε
560	0.260	0.260	0.255	0.258	0.259
555	0.214	0.214	0.214	0.208	0.214
550	0.180	0.180	0.180	0.176	0.173
545	0.150	0.150	0.150	0.146	0.142
540	0.126	0.126	0.126	0.122	0.116
535	0.106	0.106	0.106	0.104	0.096
530	0.087	0.087	0.089	0.088	0.082
525	0.073	0.073	0.075	0.072	0.070
520	0.061	0.062	0.060	0.062	0.063
515	0.051	0.054	0.054	0.054	0.055
510	0.043	0.044	0.046	0.048	0.053
505	0.036	0.039	0.042	0.045	0.052
500	0.030	0.034	0.039	0.044	0.055
495	0.026	0.031	0.037	0.047	0.065
490	0.023	0.029	0.035	0.053	0.080
485	0.022	0.028	0.036	0.064	0.102
480	0.020	0.029	0.037	0.080	0.124
475	0.020	0.030	0.040	0.105	—
470	0.022	0.034	0.048	0.137	—
465	0.025	0.040	0.060	—	—
460	0.029	0.050	—	—	—
455	0.035	0.070	—	—	—
450	0.046	—	—	—	—

TABLE IV  
 Cupric Chloride + Lithium Chloride  
 Mean Temp. 27.2°  
 CuCl<sub>2</sub> LiCl

$\lambda$	CuCl <sub>2</sub>		LiCl			
	0.8443 $\epsilon$	0.5543 $\epsilon$	1.1086 $\epsilon$	1.0629 $\epsilon$	2.2172 $\epsilon$	2.7715 $\epsilon$
560	0.260	0.260	—	—	—	—
555	0.214	0.214	0.219	0.214	0.214	0.220
550	0.180	0.180	0.184	0.183	0.183	0.188
545	0.150	0.154	0.151	0.150	0.155	0.156
540	0.126	0.127	0.128	0.126	0.131	0.134
535	0.106	0.107	0.108	0.106	0.112	0.114
530	0.087	0.089	0.088	0.089	0.096	0.100
525	0.073	0.075	0.075	0.077	0.085	0.090
520	0.061	0.061	0.064	0.067	0.077	0.087
515	0.051	0.051	0.054	0.059	0.073	0.088
510	0.043	0.043	0.047	0.054	0.073	0.094
505	0.036	0.037	0.042	0.051	0.078	0.108
500	0.030	0.033	0.039	0.050	0.092	0.131
495	0.026	0.029	0.039	0.055	0.119	0.170
490	0.023	0.028	0.041	0.064	0.150	0.222
485	0.022	0.029	0.047	0.084	0.190	—
480	0.020	0.032	0.060	0.106	—	—
475	0.020	0.032	0.078	0.140	—	—
470	0.022	0.046	0.110	—	—	—
465	0.025	0.058	—	—	—	—
460	0.029	0.073	—	—	—	—
455	0.035	0.095	—	—	—	—

TABLE V  
 Cupric Chloride + Calcium Chloride  
 Mean Temp. 23.9°

$\lambda$	CuCl <sub>2</sub>		CaCl <sub>2</sub>			
	0.8443 $\epsilon$	0.4606 $\epsilon$	0.9312 $\epsilon$	1.3819 $\epsilon$	1.8425 $\epsilon$	2.3031 $\epsilon$
560	0.260	0.259	0.258	0.258	0.262	0.275
555	0.214	0.215	0.215	0.215	0.221	0.228
550	0.180	0.180	0.180	0.180	0.186	0.196
545	0.150	0.150	0.150	0.150	0.156	0.169
540	0.126	0.126	0.126	0.128	0.130	0.154
535	0.106	0.106	0.106	0.108	0.114	0.145
530	0.087	0.087	0.087	0.093	0.103	0.140
525	0.073	0.073	0.073	0.081	0.098	0.150
520	0.061	0.061	0.061	0.074	0.099	0.169
515	0.051	0.052	0.054	0.070	0.106	0.200
510	0.043	0.043	0.050	0.071	0.120	0.260
505	0.036	0.038	0.047	0.077	0.148	—
500	0.030	0.033	0.047	0.087	0.190	—
495	0.026	0.031	0.050	0.104	0.236	—
490	0.023	0.031	0.057	0.135	—	—
485	0.022	0.034	0.070	0.195	—	—
480	0.020	0.039	0.090	—	—	—
475	0.020	0.047	0.120	—	—	—
470	0.022	0.059	0.165	—	—	—
465	0.025	0.073	—	—	—	—
460	0.029	0.089	—	—	—	—
455	0.035	0.130	—	—	—	—

TABLE VI  
 Cupric Chloride + Aluminium Chloride  
 Mean Temp. 25.2°

$\lambda$	CuCl <sub>2</sub>			AlCl <sub>3</sub>		
	0.8443 $\epsilon$	0.2382 $\epsilon$	0.4763 $\epsilon$	0.7143 $\epsilon$	0.9526 $\epsilon$	0.1908 $\epsilon$
555	0.214	0.214	0.218	0.214	0.218	0.217
550	0.180	0.180	0.183	0.183	0.183	0.184
545	0.150	0.150	0.153	0.153	0.156	0.156
540	0.126	0.126	0.129	0.130	0.131	0.136
535	0.106	0.106	0.109	0.110	0.112	0.118
530	0.087	0.087	0.092	0.093	0.098	0.105
525	0.073	0.073	0.076	0.079	0.088	0.098
520	0.061	0.062	0.066	0.070	0.084	0.102
515	0.051	0.052	0.058	0.065	0.083	0.110
510	0.043	0.045	0.052	0.062	0.086	0.122
505	0.036	0.039	0.048	0.063	0.095	0.140
500	0.030	0.035	0.046	0.068	0.113	0.180
495	0.026	0.032	0.048	0.077	0.145	0.235
490	0.023	0.030	0.053	0.095	0.200	—
485	0.022	0.030	0.061	0.130	—	—
480	0.020	0.032	0.074	0.160	—	—
475	0.020	0.035	0.097	—	—	—
470	0.022	0.041	0.128	—	—	—
465	0.025	0.050	—	—	—	—
460	0.029	0.063	—	—	—	—
455	0.035	0.085	—	—	—	—
450	0.046	0.122	—	—	—	—

TABLE VII  
Cupric Chloride + Zinc Chloride  
Mean Temp. 27.7°

$\lambda$	CuCl <sub>2</sub>		ZnCl <sub>2</sub>
	0.8443 $\epsilon$	1.251 $\epsilon$	2.085 $\epsilon$
560	0.260	0.263	0.263
555	0.214	0.227	0.226
550	0.180	0.191	0.191
545	0.150	0.163	0.163
540	0.126	0.136	0.137
535	0.106	0.113	0.115
530	0.087	0.095	0.097
525	0.073	0.079	0.082
520	0.061	0.067	0.070
515	0.051	0.057	0.060
510	0.043	0.048	0.051
505	0.036	0.042	0.044
500	0.030	0.037	0.039
495	0.026	0.033	0.035
490	0.023	0.031	0.033
485	0.022	0.031	0.036
480	0.020	0.036	0.040
475	0.020	0.042	0.047
470	0.022	0.050	0.055
465	0.025	0.063	0.069
460	0.029	0.079	0.090
455	0.035	0.106	0.125
450	0.046	—	—

#### Discussion of Results

In a discussion of the foregoing experimental results, it is essential that we ascertain whether in solutions of cupric chloride absorption is proportional to concentration and, furthermore, whether any simple relation exists between absorption and dissociation.

The generalization connecting absorption and concentration, commonly known as Beer's law,<sup>1</sup> may be stated as follows: Any change in the thickness of an absorbing layer of a solution exerts the same influence on its absorbing power

<sup>1</sup> Pogg. Ann., 86, 78 (1852).

as a corresponding change in concentration. Therefore, if  $c$  denotes the concentration, equation (3) may be written

$$I = I_0 e^{-kcl}; \quad (6)$$

the product,  $cl$ , of course being constant. Hence, for an ideal solution, it follows that the ratio of the concentration to the extinction coefficient should be a constant. On the other hand, for solutions of electrolytes in which the ions and the molecules do not possess the same absorbing power, it has been pointed out by Rüdorff<sup>1</sup> that the ratio should vary in the following manner: (1) If absorption is due solely to ions, the ratio should decrease with decreasing concentration; (2) if absorption is due entirely to undissociated molecules, the ratio should increase with decreasing concentration. Therefore, in order to test the validity of Beer's law in the case of solutions of cupric chloride, the values of the extinction coefficient for four different wave-lengths have been calculated from the data of Table I. The results of this calculation are given in Table VIII, where it will be seen that the values of  $M$  depart more and more from constancy as the shorter wave-lengths are approached.

TABLE VIII

Conc.	$\lambda = 535$ M	$\lambda = 510$ M	$\lambda = 500$ M	$\lambda = 490$ M
2.2622	8.802	18.10	16.16	8.078
2.149	8.736	18.53	16.66	10.745
2.036	8.738	19.21	19.03	13.57
1.923	8.657	19.83	20.68	15.38
1.519	8.123	18.99	23.73	21.70
1.435	7.797	19.93	26.57	28.69
1.182	8.145	20.72	28.80	35.79
0.8443	7.965	19.64	28.14	36.71

From this we conclude that, in the case of cupric chloride, Beer's law is only applicable in the region of the longer wave-lengths, and that in that region, both ions and molecules must possess nearly equal absorbing powers.

<sup>1</sup> Jahrb. Elektronik, 3, 423 (1907).

As has already been mentioned, both Müller and Vaillant (loc. cit.) made a series of careful spectrophotometric measurements of a number of different copper salts with a view to determining whether any simple relation exists between the absorption and dissociation of their solutions. On the assumption that Beer's law holds for ions as well as for molecules, we may express the absorption of any salt solution as the sum of the absorptions of the molecules of the solute and its products of dissociation. Thus, if a solution of a binary salt, the percentage dissociation of which is  $\alpha$ , be placed in a tube of length  $l$ , we may express the absorptions of the different constituents, for any particular wave-length by the following equations—

$$I_1 = I_2 e^{-ac(1-\alpha)l}, \quad (7)$$

$$I_2 = I_0 e^{-bc\alpha l}, \quad (8)$$

$$I_3 = I_0 e^{-b'\alpha l}, \quad (9)$$

where  $c$  is the equivalent concentration, and where  $a$ ,  $b$ , and  $b'$  are the absorption coefficients of the molecule and its two ions, respectively. Since all three species are present together, we may write  $I = I_0 e^{-c[a(1-\alpha) + (b+b')\alpha]l}$ . (10)

For the chlorine ion  $b' = 0$ , hence on simplifying, we have

$$I = I_0 e^{-cml}, \quad (11)$$

where  $m = a - (a - b)\alpha$ . (12)

But  $m$  can be calculated from equation (11), since both  $c$  and  $l$  are known and the ratio  $I/I_0$  can be determined with the spectrophotometer. From the value of  $m$  thus obtained, the constants  $a$  and  $b$  in equation (12) can be evaluated, and therefore the values of  $m$  at different concentrations, as calculated by means of equations (11) and (12) for any given wave-length, can be compared. The results thus obtained by Vaillant with solutions of cupric chloride for  $\lambda = 640$ , are given in Table IX.

TABLE IX  
 $a=2.08$                        $b=1.31$

Conc.	$\alpha$	$m(\text{obs.})$	$m(\text{calc.})$
0.0103	0.91	1.38	1.38
0.0197	0.89	1.44	1.40
0.103	0.72	1.46	1.53
0.197	0.67	1.57	1.57
0.675	0.48	1.72	1.72
0.820	0.46	1.70	1.73
4	0.24	1.92	1.90
6	0.14	2.77	1.98
8	0.09	3.08	2.01

It would appear, from the agreement of the two sets of values, that a linear relation exists between  $m$  and  $\alpha$ , at least in the more dilute solutions, and from this we might infer that the absorption follows Beer's law. When, however, we attempt to apply this relation for wave-lengths in the vicinity of the minimum in the absorption curves it ceases to hold, even in the most dilute solutions. Thus, the existence of a simple linear relation between absorption and dissociation is found to be more apparent than real, and the agreement between the values of  $m$ , as calculated by means of equations (11) and (12), is probably fortuitous.

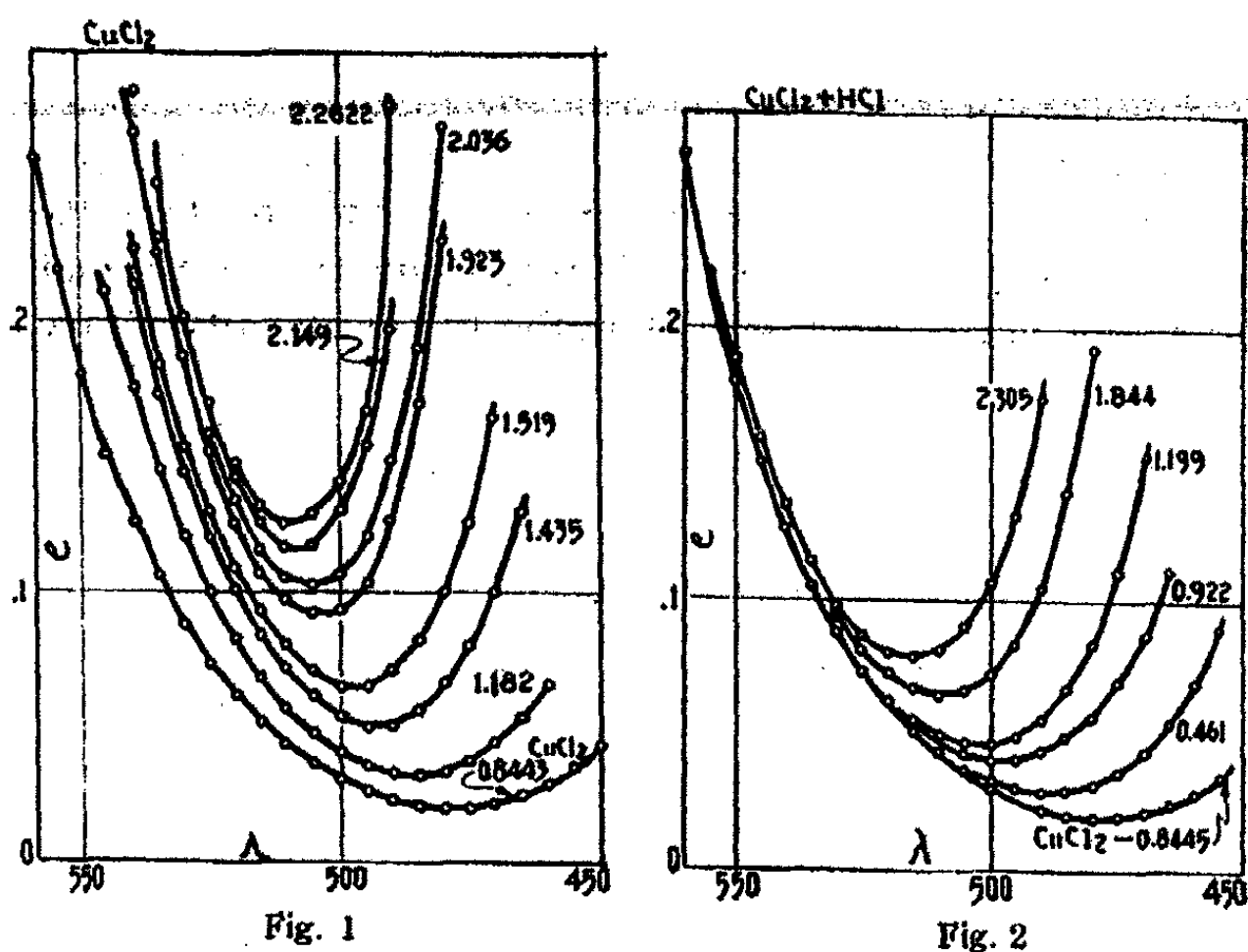
It will be seen from Fig. 1, that with increasing concentration there is a marked displacement of the absorption minima toward the red end of the spectrum. Since the wave-length corresponding to the minimum in the absorption curve of any particular solution determines its predominant color, it follows that the change in the absorption of solutions of cupric chloride resulting from change in concentration can be measured by the corresponding displacement in the absorption minima. The following different hypotheses have been advanced in explanation of the displacement of the absorption minimum, or predominating color, of solutions of cupric chloride resulting from change in concentration.

(1) *Dissociation Hypothesis.*—According to Ostwald,<sup>1</sup> the

<sup>1</sup> Lehrbuch der allgemeinen Chemie, 1, 799.



blue color of very dilute solutions of cupric chloride is due to the presence of  $\text{Cu}^{++}$  ions, whereas the color of the more concentrated solutions is due to the presence of both ions and undissociated molecules, the yellow color of the latter together with the blue color of the former causing the solution to appear green. This seemingly satisfactory and simple hypothesis is open to several objections, among which may be mentioned its failure to account for the presence of complex anions containing copper which subsequent investigations have proved to be present in concentrated solutions.



(2) *Hydrolysis Hypothesis.*—The change from blue to green, in solutions of cupric chloride, has been attributed by Engel<sup>1</sup> to the development of hydrochloric acid due to the hydrolysis of the salt, with the resultant formation of double salts having the formulas,  $\text{CuCl}_2 \cdot \text{HCl} + 3\text{H}_2\text{O}$  and  $\text{CuCl}_2 \cdot 2\text{HCl} + 5\text{H}_2\text{O}$ . These salts, or chloro-acids, as Werner terms them, have actually been isolated by Engel.<sup>2</sup> While Engel's hypothesis is undoubt-

<sup>1</sup> Bull. Soc. chim., (3) 6, 239 (1891).

<sup>2</sup> Comptes rendus, 106, 273 (1888); 107, 178 (1888).

edly erroneous, it deserves to be mentioned because of its possible bearing upon the change in color produced by the addition of colorless chlorides to solutions of cupric chloride.<sup>1</sup>

(3) *Hydrate Hypothesis*.—The change in color of a dilute aqueous solution of cupric chloride which results from increase in either concentration or temperature, or from the addition of various dehydrating agents, has led to the view that the blue solutions contain a definite hydrate of cupric chloride, while the green solutions contain either the anhydrous salt or a lower hydrate. Much experimental evidence has been advanced by Hartley<sup>2</sup> and others in support of this hypothesis, especially in connection with similar phenomena observed in solutions of salts of cobalt. While the hypothesis serves to explain many of the experimentally observed facts, it lacks completeness.

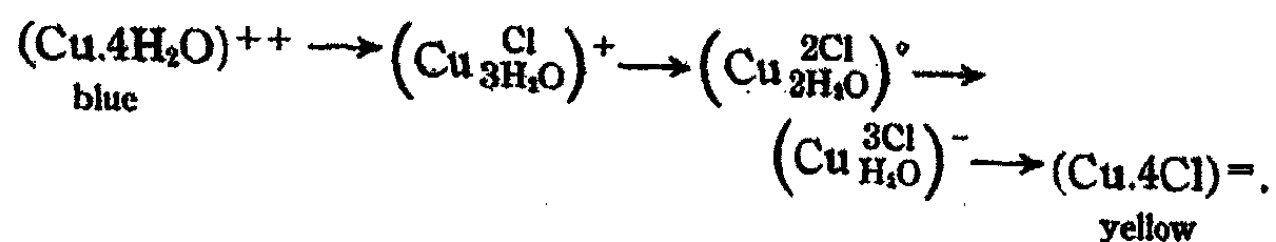
(4) *Solvate Hypothesis*.—Closely related to the foregoing, is the so-called solvate hypothesis of which the late H. C. Jones was the protagonist. According to this hypothesis there exists in a solution a series of hydrates, or solvates, the composition of which is conditioned primarily by the law of mass action. Although there is a large amount of experimental evidence which points to the existence in solution of complexes involving both solute and solvent, it is extremely doubtful whether as many molecules of solvent are actually associated with a single molecule of dissolved substance as Jones' calculations indicate.

(5) *Complex Ion Hypothesis*.—This hypothesis was advanced by Donnan and Bassett (*loc. cit.*) to account for the changes of color observed in solutions of the chlorides of copper, cobalt and iron. When a concentrated solution of cupric chloride was placed in the bend of a U-tube and the two arms were filled with a dilute solution of some colorless

<sup>1</sup> See Le Chatelier: *Bull. Soc. chim.*, (3) 6, 3, 84, 209 (1891).

<sup>2</sup> *Trans. Roy. Soc., Dublin*, (2) 1, 253 (1900); Wyruboff: *Bull. Soc. chim.*, (3) 5, 460 (1891); Potilitzin: *Ber. deutsch. chem. Ges.*, 17, 276 (1884); Charpy: *Comptes rendus*, 113, 794 (1891); Etard: *Comptes rendus*, 113, 699 (1891); 120, 1057 (1895).

salt, such as potassium chloride, Donnan and Bassett found, on passing an electric current through the solutions, that the green layer migrated toward the anode. In this way, as well as by means of other lines of experimentation, they proved beyond a doubt that complex anions containing copper are present in concentrated solutions of cupric chloride. Similar results were obtained at about the same time by Kohlschütter,<sup>1</sup> in a series of determinations of the transference number of copper in solutions of cupric chloride. In attempting to formulate their views as to complex ions and undissociated molecules, Donnan and Bassett sought to emphasize the probability of a relationship between the degree of dissociation and the degree of hydration, as had been suggested ten years earlier by Werner (*loc. cit.*). Their hypothesis may be briefly summarized by the following scheme:



It will be seen that the hypothesis advanced by Hantzsch (*loc. cit.*), an outline of which has already been given in the introduction to this paper, may be looked upon as a modification of the complex ion hypothesis. This hypothesis has been adversely criticized by Lewis<sup>2</sup> and also by Jones.<sup>3</sup> Lewis bases his criticism largely upon the experimentally established fact that the change in color, resulting from the addition of calcium chloride to a solution of cobalt chloride, is conditioned almost wholly by the active mass of the water, whereas, according to the complex ion hypothesis, the change should be solely dependent upon the chlorine ion concentration. Jones' criticisms of the hypothesis may be summarized as follows: (a) Rise in temperature has been shown by experiment to produce the same qualitative effect upon absorption as in-

<sup>1</sup> Ber. deutsch. chem. Ges., 37, 1153 (1904).

<sup>2</sup> Zeit. phys. Chem., 56, 223 (1906).

<sup>3</sup> Carnegie Institution Monograph, No. 110.

crease in concentration, whereas, according to the views advanced by Donnan and Bassett, rise of temperature and increase in concentration should produce opposite effects; (b) experiment shows that absorption bands widen with increase in temperature, whereas, if complex ions are present they would break down with rise in temperature and a narrowing of the bands should result; (c) it is difficult to explain, on the hypothesis of Donnan and Bassett, the change in the absorption spectrum which results when the same substance is dissolved in different solvents.

Notwithstanding these criticisms, the complex ion hypothesis appears to the author to offer the most satisfactory explanation of the available experimental data.

The importance of the results of spectroscopic investigation of the metalamines in connection with the complex ion hypothesis of absorption appears to have been overlooked. In reviewing the work of Miss French,<sup>1</sup> and others, we find that when water is substituted by chlorine in the complex cations of the tetrammino- and pentammino-chromium salts, the absorption minima are displaced toward the red end of the spectrum or, in other words, chlorine is found to exert a bathochromic influence on absorption. This bathochromic influence of chlorine offers a very satisfactory explanation of the change from blue to green in a solution of cupric chloride with increase in concentration, provided we accept the view that absorption in dilute solutions is due to complex hydrated copper ions, and that absorption in concentrated solutions is due to similar ions in which water has been replaced by chlorine. Furthermore, the absorption spectra of a series of aquoammino-chromium chlorides show that, as the number of water groups is replaced by ammonia groups, the absorption is displaced toward the ultra-violet. In this case, ammonia exerts a hypsochromic influence. As is well known, when a solution of cupric chloride is treated with ammonia, the color of the solution changes to a deep, azure blue, owing to the

---

<sup>1</sup> "Absorption Spectra of Certain Chromium Salts." Diss. Zürich.

formation of tetrammine cupric chloride,  $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$ . Here again, the replacement of water by ammonia causes a displacement of the absorption toward the ultra-violet. It may be inferred then, that ammonia and chlorine produce opposite effects when replacing water groups in complex ions; in fact, if a chlorine atom and an ammonia molecule are simultaneously introduced into the same complex ion, each replacing a molecule of water, the absorption is found to remain practically unchanged. All of the available experimental evidence, therefore, appears to justify the following generalization: *Substitution of a chlorine atom for a water molecule in a complex ion, displaces the absorption minimum toward the red end of the spectrum, whereas substitution of an ammonia molecule for a water molecule in a complex ion, displaces the absorption minimum toward the violet end of the spectrum.*

Jones (loc. cit.) determined qualitatively the effect of the chlorides of calcium and aluminium upon the absorption spectra of several colored, metallic chlorides, and Vaillant (loc. cit.) made a spectrophotometric study of the same effect over a limited range of wave-lengths. The results of these investigations show that a marked displacement in the absorption bands occurs, and that the direction of the displacement is the same as that produced by increasing either the temperature or the concentration of the solution of the colored salt. The cause of the displacement was believed to be the removal of water from the solvates by the added chlorides, each of which is known to possess marked dehydrating properties. The conclusions drawn from these experiments have been criticized on the ground that the dissociation of the colored salt is depressed by the addition of a salt having a common ion. These criticisms cease to have weight, however, if we accept the validity of the generalization advanced by Hantzsch, that absorption is independent of the degree of dissociation. In order to determine quantitatively the effect on the absorption of cupric chloride of added electrolytes having a common ion, we have determined the extinction coefficients of a series of binary mixtures in each

of which the concentration of the copper salt was kept constant, while the concentration of the added chlorides was progressively increased. The concentration of the cupric chloride was so chosen that while the color of the solution was distinctly blue, its strength was sufficient to insure sharp readings on the spectrophotometer. The method of making up the mixed solutions was as follows: A definite volume of the mother solution of cupric chloride was measured out by means of a burette into a measuring flask of known capacity; a definite volume of the mother solution of the colorless salt was then measured out by means

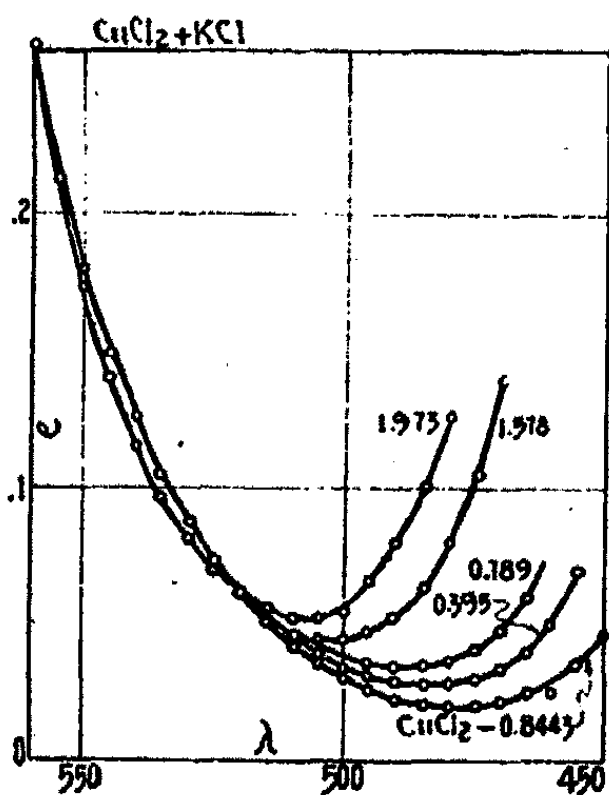


Fig. 3

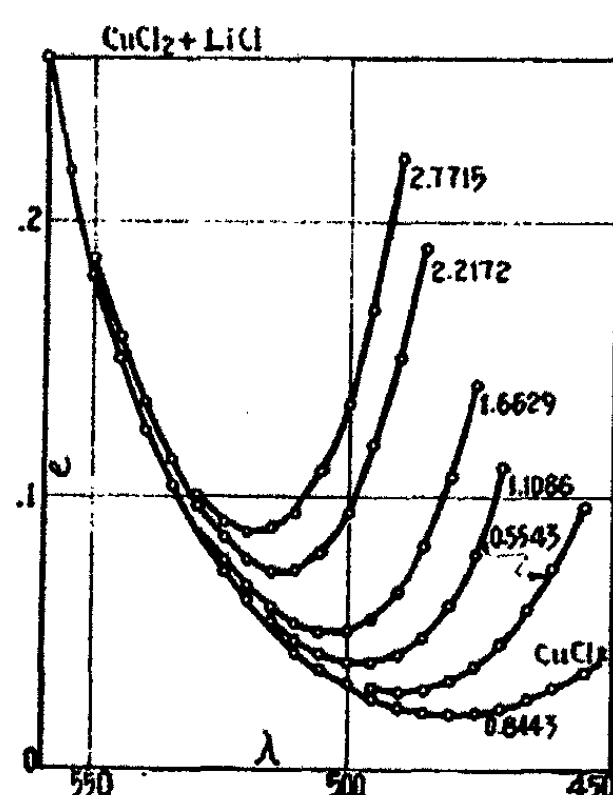


Fig. 4

of a second burette into the same flask, and the combined solutions made up to the mark by the addition of water. In any series of solutions of the same two salts, the mass of the cupric chloride and the total volume of the solution were kept constant. The concentration of the mother solution of cupric chloride was 1.6886 M, and in each case the measuring flask was half-filled with the solution, thus making the solution to which the colorless chlorides were added 0.8443 M. The effect of the addition of the different chlorides to 0.8443 M cupric chloride is shown by the data of Tables II to

VII, and also by the curves of Figs. 2 to 7. It will be seen that in every case there is a marked displacement of the absorption minima toward the red end of the spectrum. This, of course, is the direction we should expect the displacement to take if water is removed from the absorbing complexes that have been assumed to be present in the solutions. It is of further interest to note that, although the displacement produced by zinc chloride is relatively small, the direction of displacement is similar to that produced by the other chlorides. According to Donnan, zinc chloride causes the color of a solution of

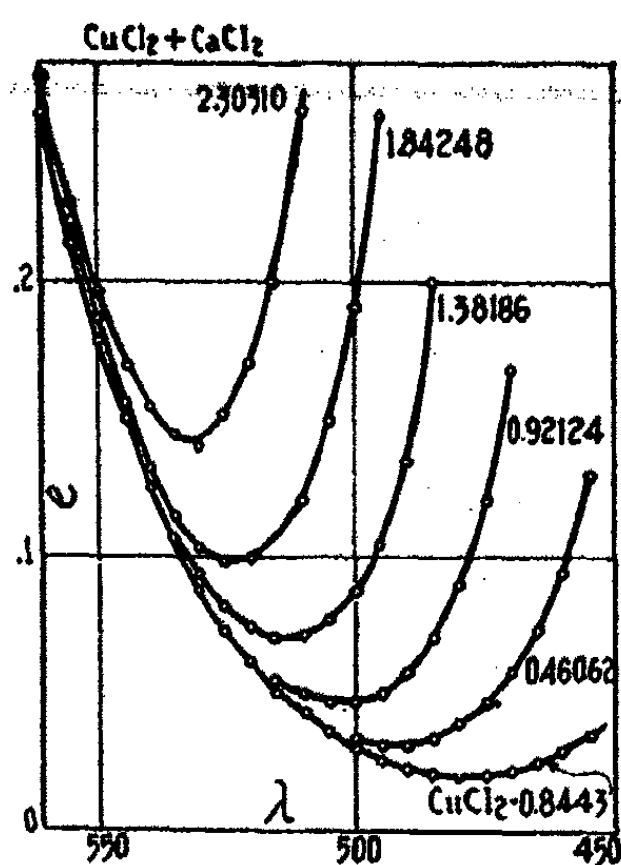


Fig. 5

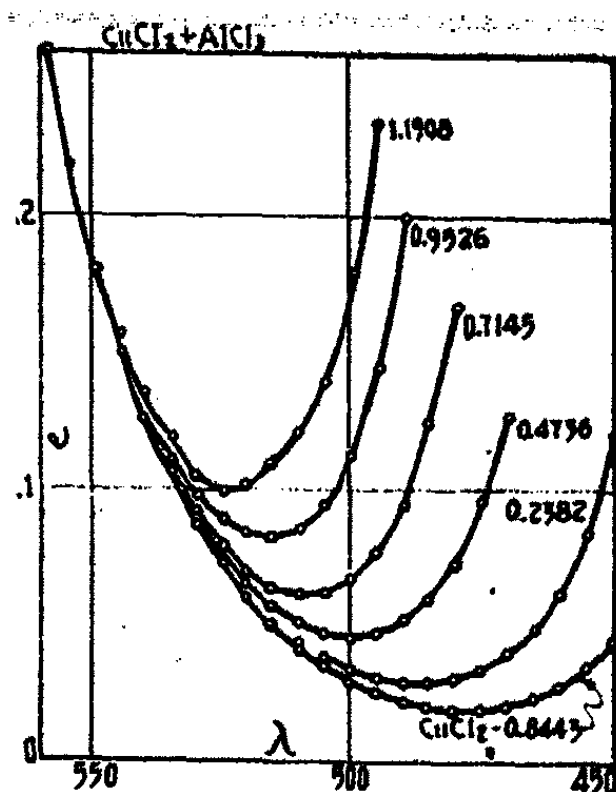


Fig. 6

cupric chloride to become either green or blue, depending upon the amount added. The difference in behavior between calcium chloride and zinc chloride in this respect is attributed by Donnan to the formation of double salts as suggested by Engels (*loc. cit.*): Thus, because of the tendency of zinc to enter complex negative groups, a double chloride,  $\text{Cu}(\text{ZnCl}_4)$ , which is blue in color, is assumed to be formed, whereas, calcium having an opposite tendency is assumed to form a green-colored double chloride,  $\text{Ca}(\text{CuCl}_4)$ .

If the wave-lengths corresponding to the minima in the

foregoing absorption curves are plotted as abscissas against the corresponding concentrations as ordinates, we obtain the curves shown in Fig. 8. These curves serve to bring out the relative influence of the different chlorides in displacing the absorption minimum of 0.8443 M cupric chloride. For example, the displacements, expressed in units of wave-length, produced by molar solutions of the six different chlorides studied are as follows:  $\text{ZnCl}_2$ ,  $9\mu\mu$ ,  $\text{KCl}$ ,  $17.5\mu\mu$ ,  $\text{LiCl}$ ,  $18\mu\mu$ ,  $\text{HCl}$ ,  $21.5\mu\mu$ ,  $\text{CaCl}_2$ ,  $27.5\mu\mu$  and  $\text{AlCl}_3$ ,  $41.5\mu\mu$ . It is

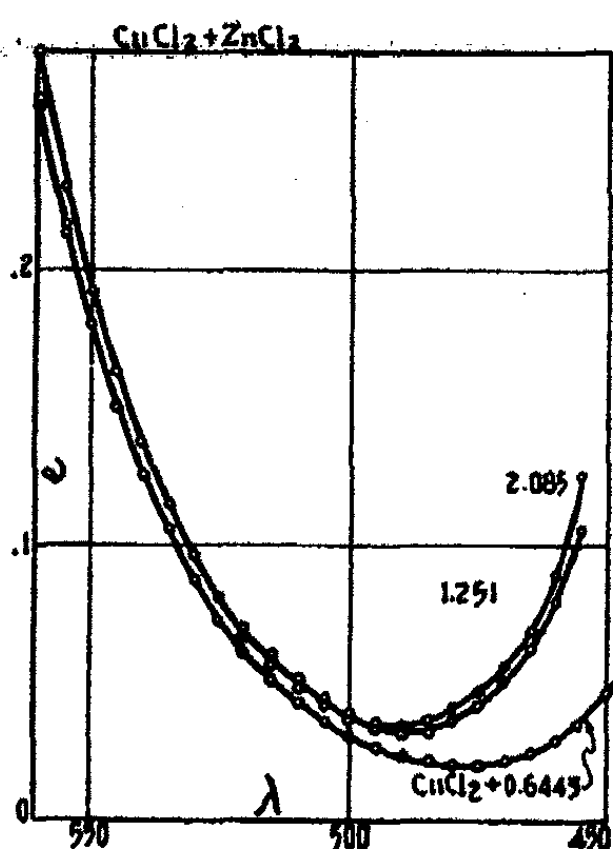


Fig. 7

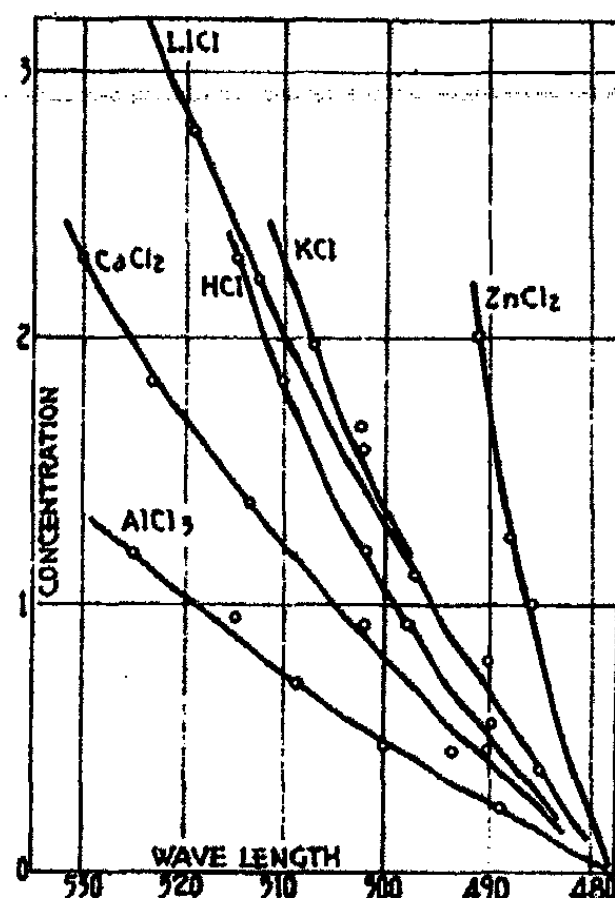


Fig. 8

important to note that potassium chloride, which possesses little or no dehydrating power, displaces the absorption minimum to a greater extent than zinc chloride, and nearly as much as lithium chloride, a salt having marked affinity for water. This somewhat anomalous behavior of potassium chloride, raises a doubt as to whether the power of certain chlorides to displace the absorption minimum of cupric chloride bears any relation to the tendency of these chlorides to combine with water.



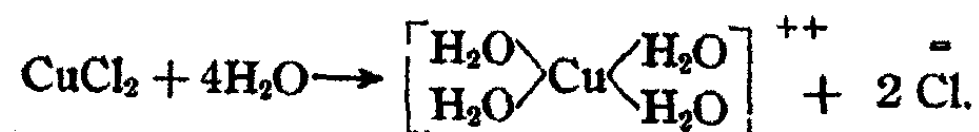
In reviewing the foregoing experimental evidence, the following facts appear to be thoroughly established:

(1) Complex anions containing copper exist in concentrated solutions of cupric chloride.

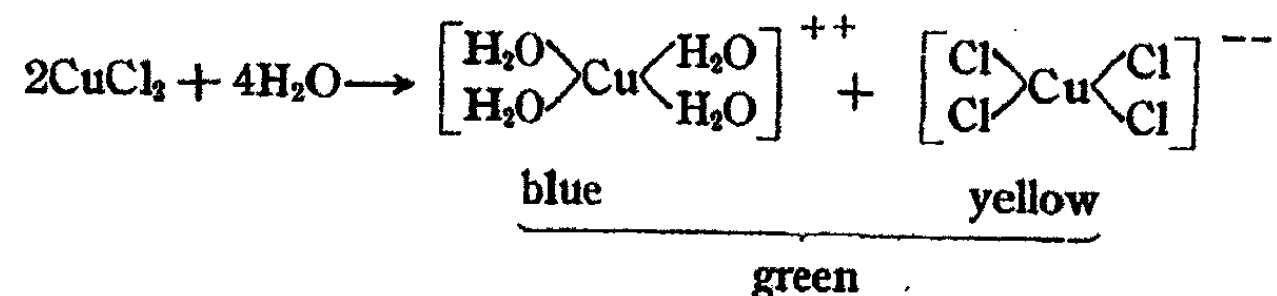
(2) The substitution of a chlorine atom for a water molecule in any complex ion, displaces the absorption toward the red end of the spectrum.

(3) Increase in concentration, rise in temperature or the addition of solutions of colorless chlorides, cause a displacement of the absorption minimum of cupric chloride toward the red end of the spectrum.

Of the various hypotheses which have been advanced in explanation of the change in color of cupric chloride solutions, that involving the assumption of complex ions seems to be in closest accord with all of the facts. Thus, in extremely dilute solutions, we may consider dissociation as taking place in the following manner:



On the other hand, in very concentrated solutions, the process of dissociation and complex formation may be formulated as follows:



In solutions of intermediate concentrations, other ions may exist in which the water groups of the fully hydrated copper ion are partially replaced by chlorine atoms. Not only is this hypothesis in agreement with the experimental facts, but also it is in accord with the law of mass action. As for Jones' criticisms of similar views advanced by Donnan and Bassett, it may be remarked that while complex ions probably break down with increase in temperature, it does not necessarily

follow that the absorption bands should become narrower. Furthermore, it is known that non-aqueous solutions of cupric chloride, although differing as to their absorption spectra, behave in other respects quite similarly to aqueous solutions. This fact would seem to meet the further criticism of the complex ion hypothesis, that the presence of complex ions renders it difficult to account for changes in the absorption spectrum occurring with change in solvent. For example, when cupric chloride is crystallized from its solution in pyridine, it separates as a blue salt having the formula,<sup>1</sup>  $\text{CuCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ , which will be seen to be the analogue of the salt  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , obtained from aqueous solution. It is more than probable, therefore, that complex ions containing pyridine exist in pyridine solutions which are entirely analogous to the hydrated ions occurring in aqueous solutions. In fact, if we accept Werner's view of the interdependence of dissociation and solvation, we must regard all cations in dilute salt solutions as consisting of metallic atoms combined with as many molecules of the solvent as correspond to the co-ordination number of the metal.

#### Summary

The results of the foregoing investigation may be briefly summarized as follows:

(1) The extinction coefficients of a series of solutions of cupric chloride have been determined over that portion of the visible spectrum which is included between  $460\mu\mu$  and  $560\mu\mu$ .

(2) The extinction coefficients of a series of binary mixtures of cupric chloride with six different colorless chlorides have also been determined over the same region of the spectrum; in each case the concentration of the copper salt was kept constant while the concentration of the added chloride was progressively increased.

(3) It has been shown that, in solutions of cupric chloride, Beer's law holds only in the region of the longer wave-lengths, and that in this region both ions and undissociated molecules may be assumed to possess nearly equal absorbing powers.

<sup>1</sup> Ber. deutsch. chem. Ges., 21, 1578 (1888).

(4) No apparent relation has been found to exist between absorption and dissociation; in fact, no satisfactory interpretation of the mechanism of the absorption of light by electrolytes seems to be possible, unless we adopt the view held by Hantzsch, that absorption is independent of dissociation.

(5) The absorption of light by solutions of cupric chloride has been attributed to the presence of complex ions, the composition of which is conditioned primarily by the concentration of the solution. In extremely dilute solutions, absorption is assumed to be due to the presence of copper atoms holding in combination as many molecules of solvent as correspond to the co-ordination number of the metal, which, in this case, is four. In extremely concentrated solutions, complex anions containing copper have been shown to be present, and to these the hypothetical formula,  $\text{CuCl}_4$ , has been assigned. Other complex ions, in which, one, two or three of the water molecules of the tetrahydrated copper ion have been replaced by chlorine atoms, are assumed to be present in solutions of intermediate concentrations.

(6) A study of the absorption spectra of the metalamines, has revealed the fact that substitution of a chlorine atom for a water molecule in a complex ion causes a displacement of the minimum in the absorption curve toward the red end of the spectrum.

(7) Increase in concentration, or the addition of colorless chlorides, has been shown to displace the absorption minimum of 0.8443 M cupric chloride toward the red end of the spectrum.

(8) The cause of the observed displacement of the absorption minimum in solutions of cupric chloride is believed to be the same as that in the case of the metalamines, viz., the successive replacement of water molecules by chlorine atoms in complex ions.

In conclusion, it is a pleasure to record my appreciation of the assistance rendered by Mr. Kenneth Tate, especially in connection with the spectrophotometric measurements.

*Stamford, Conn.*  
*Sept. 22, 1921*

THE MECHANISM OF THE DEHYDRATION OF CRYSTALLINE ALUMINUM HYDROXIDE AND OF THE ADSORPTION OF WATER BY THE RESULTING ALUMINA<sup>1</sup>

BY LOWELL H. MILLIGAN

1. Introduction

Ramsay<sup>2</sup> investigated the rate at which amorphous, ammonia-precipitated aluminum hydroxide loses water when heated to different temperatures, and concluded that under these conditions, either there are no definite hydrates, or a very large number exist, the vapor tensions of which are only slightly different from each other. Carnelley and Walker<sup>3</sup> worked with similarly prepared material and confirmed Ramsay's conclusions. J. M. van Bemmelen<sup>4</sup> investigated both the colloidal aluminum hydroxide and the crystalline deposit prepared from sodium aluminate solution. For the colloidal material he concluded that between 15° and 300° C the rate of water loss is uniform and hence no definite hydrates are formed. After drying at 300° C the remaining material had approximately the composition  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . However, the precipitate from an alkaline aluminate solution was found to be a true hydrate, a definitely micro-crystalline, chemical compound,  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . It remained practically unchanged in a stream of dry air at 160° C, but at higher temperatures it was decomposed. The results obtained by E. Martin<sup>5</sup> were very similar to those of the previous investigators and clearly indicated the difference between the amorphous, ammonia-precipitated, hydrated alumina, and the crystalline aluminum hydroxide prepared by the Bayer process.

<sup>1</sup> Contribution from the Research Bureau of the Aluminum Company of America, New Kensington, Pa.

<sup>2</sup> Jour. Chem. Soc., 32, 395 (1877).

<sup>3</sup> Ibid., 53, 59 (1888).

<sup>4</sup> Rec. Trav. chim. Pays-Bas, 7, 75 (1888).

<sup>5</sup> Mon. Sci., (5) 5, 225 (1915); through Chemical Abstracts, 10, 571 (1916).

Alumina prepared by the ignition of hydrated aluminum oxide at low temperature, has been used as a desiccating agent, and its relative value compared with other common desiccants has been studied by various authors.<sup>1</sup>

Hydrated ferric oxides, which are in many respects similar to the corresponding aluminum compounds, have recently been investigated by Posnjak and Merwin.<sup>2</sup> The conclusions which they drew were based chiefly on dehydration curves obtained for the original material and also for the dried or partially dried product which had been allowed to reabsorb water, each point on the curves representing the amount of water contained by the sample when dried to constant weight at a given temperature.

In the work described in the present paper this method was applied to the study of the mechanism of the dehydration of crystalline aluminum hydroxide, and of the adsorption of water by the resulting alumina; and the results have been plotted as equilibrium drying curves, between 20° and 275° C.

## 2. Experiments

The aluminum hydroxide used was prepared by the Bayer process, was washed thoroughly and dried. It consisted of white granular particles which would pass through a 100 mesh screen, the particles themselves being microscopic aggregates of anisotropic crystals. It had the following analysis:

Al(OH) <sub>3</sub> .....	99.82%
Fe <sub>2</sub> O <sub>3</sub> .....	0.09
SiO <sub>2</sub> .....	0.04
Na <sub>2</sub> O.....	0.05
TiO <sub>2</sub> .....	none.

A portion of this was heated in an electric muffle for 30 minutes at 810° C and then cooled in a desiccator over concentrated sulfuric acid, and marked alumina "A." A

<sup>1</sup> F. M. G. Johnson: *Jour. Am. Chem. Soc.*, 34, 911 (1912); Marden and Elliott: *Jour. Ind. Eng. Chem.*, 7, 320 (1915); Dover and Marden: *Jour. Am. Chem. Soc.*, 39, 1609 (1917).

<sup>2</sup> *Am. Jour. Sci.*, (4) 47, 311 (1919).

portion, heated for 1 hour at 985° C and similarly cooled, was marked alumina "B." A few experiments were made in order to show in a preliminary way that the water content of the alumina will come to equilibrium with the water vapor in the air at a given temperature. Check samples of alumina "A" were taken directly after the original ignition, and placed in an oven at 106° C, where they were allowed to come to practically constant weight. Under these conditions water was adsorbed, even though the temperature was above 100° C. The water in the samples was then determined by ignition. Check samples of alumina "A" in a thin layer were exposed to 50 percent saturated air at room temperature for two hours; and following this treatment, they were dried to constant weight at 106° C and determinations made of the water which was thus driven off and of the water still remaining. Two other samples were wet with water and then dried to constant weight at 106° C, and their water content determined after this treatment. The results are given in Table I.

TABLE I  
The Adsorption of Water by Alumina "A"

Procedure	H <sub>2</sub> O driven off at 106° C (%)	H <sub>2</sub> O retained at 106° C (%)
Alumina held at 106° C immediately after ignition.	0.00	2.22*
	0.00	2.39*
Alumina exposed to 50% saturated air and then dried at 106° C.	4.30	2.66
	4.43	2.61
Alumina wet with water and then dried at 106° C.	not determined	2.92
	not determined	2.89

These results show that alumina tends to come to equilibrium with water vapor at a given temperature, and that the point of equilibrium is roughly independent of the direction from which it is approached, whether it be reached by allowing the dry alumina to adsorb water at a given temperature, or by wetting the alumina and then drying it at that temperature. The fact that the adjustment at or near the equilibrium point

\* This represents water adsorbed by the sample at 106° C.

is very slow helps to account for the fact that these results are not identical.

The drying curves for the crystalline aluminum hydroxide and for the alumina prepared from it, were made by placing about 2-gram samples in weighing bottles,  $\frac{1}{8}$ " diameter 1.5" high, and allowing the water content of these to come practically to equilibrium with a slowly moving current of air of constant moisture content, at a given temperature. These were weighed at intervals after stoppering and cooling them in a desiccator, in order to determine the point of equilibrium. At the lower temperatures, the humidity of the air which was passed over the samples was controlled. The open weighing bottles were placed in a covered aluminum pan, which in turn was placed inside a Freas oven, the temperature of which could be maintained constant within at least 2° C. Through the pan was circulated a current of air brought to a known humidity outside the oven and heated to oven temperature by passing it through a small aluminum coil just before it was conveyed to the pan containing the samples. The temperature inside the pan was measured by a thermocouple inserted in an aluminum well in the pan lid. The humidity adjustments were obtained by passing the slow current of air through bottles containing either water, or 56% sulfuric acid (which gives 25% saturated air at room temperature), maintained at constant temperature. When air containing 51 mg of water vapor per liter (air saturated at 40° C), was used, the inlet tube between the saturator and the oven was electrically heated with nichrome wire to prevent condensation in it. At temperatures above 196° C the samples were placed directly in the oven and no attempt was made to control the humidity of the air. All the experiments were made at approximately atmospheric pressure.

Duplicate samples were run in each case. After the samples had been brought to equilibrium at 275° C, they were exposed for 54 hours in 50% saturated air at room temperature. This procedure served to "rehydrate" them, after which they were again brought to equilibrium at various temperatures.

Finally the samples were brushed as completely as possible into weighed, covered, platinum crucibles and ignited at about  $1100^{\circ}\text{C}$  to constant weight. The weight of the ignited alumina (when corrected for the amount which stuck in the weighing bottle and could not be removed—about 1 mg) was used in the case of the alumina samples as the basis for

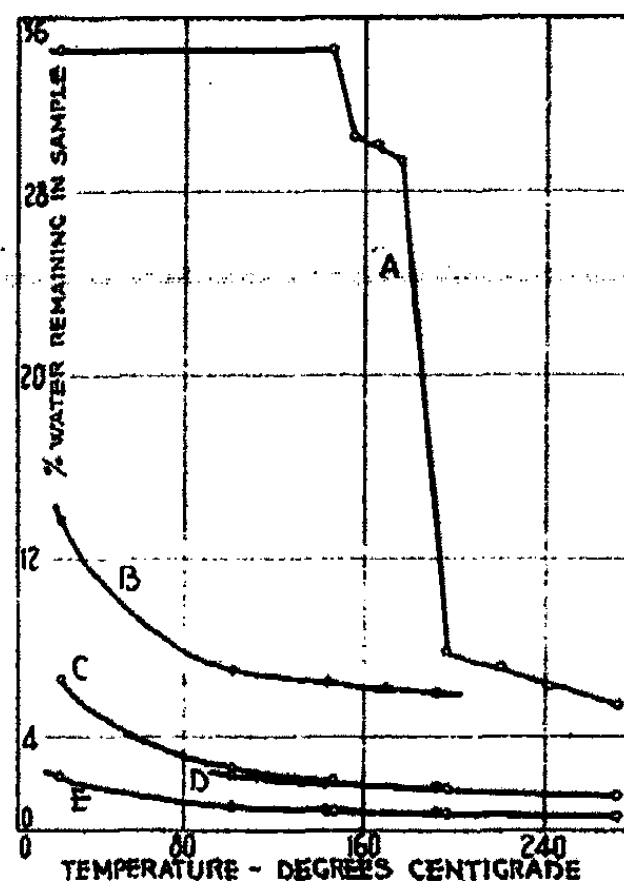


Fig. 1

Equilibrium Drying Curves in Air containing about 5 Milligrams of Water Vapor per Liter.

- (A). Crystalline Aluminum Hydroxide.
- (B). Crystalline Aluminum Hydroxide after drying at  $270^{\circ}\text{C}$  followed by Rehydration.
- (C). Alumina "A" (ignited at  $810^{\circ}\text{C}$  for 30 minutes).
- (D). Alumina "A" after drying at  $270^{\circ}\text{C}$  followed by Rehydration.
- (E). Alumina "B" (ignited at  $985^{\circ}\text{C}$  for 1 hour); and Alumina "B" after drying at  $275^{\circ}\text{C}$  followed by Rehydration.

the calculation of the final results. The hydrate samples, however, contained sufficient water even at the final drying temperature, to cause them to boil up when they were ignited, and consequently a small quantity of these samples was lost. Accordingly the theoretical figure of 34.60% water in  $\text{Al}(\text{OH})_3$  was used for the calculations in these cases.



The effect which a variable amount of water vapor in the air had on the point of equilibrium at constant temperature is best shown by the results at 100° C for alumina "A," which are given in Table II.

TABLE II  
Change in the Water Content of Alumina "A" at 100° C with Various Amounts of Water Vapor in the Air

Water vapor per liter of air (mg)	Water content of alumina at equilibrium (%)
3	2.69
17	2.72
51	2.92*

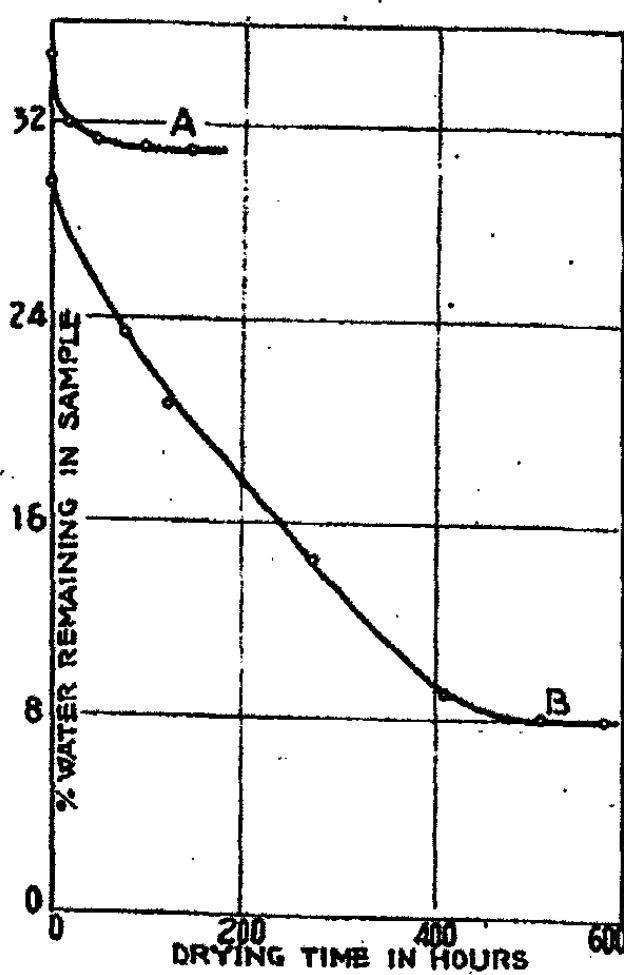


Fig. 2

Curves showing the Experimental Rate of Drying of Crystalline Aluminum Hydroxide in Air containing about 5 Milligrams of Water Vapor per Liter.

- (A). Temperature elevated from 145° C and maintained at 157° C.  
(B). Temperature elevated from 178° C and maintained at 196° C.

\* When the alumina was again brought to equilibrium in air containing 17 mg of H<sub>2</sub>O per liter, the water content dropped back to its former value.

The complete drying curves for the crystalline aluminum hydroxide and for the alumina samples (both before and after "rehydration") in air containing about 5 mg of water vapor per liter, are given in Fig. 1. Absolute equilibrium was not necessarily reached at each temperature, but the experiments were continued until the weight was approximately constant, and the curves of Fig. 2 will give an idea of the rate at which the drying of the hydroxide took place and the duration of the experiments at two given temperatures. As would be expected, the alumina reached equilibrium much more rapidly than did the hydroxide.

### 3. Conclusions

1. Crystalline aluminum hydroxide in air at ordinary atmospheric pressure and humidity, is not affected by temperatures below 145° C, and remains constant in composition as the trihydrate,  $\text{Al}(\text{OH})_3$ , up to this temperature. The decomposition and evolution of water starts just above 145° C, and as far as the evolution of the chemically combined water of the trihydrate is concerned, is practically complete at 200° C. (It is not known whether the slight irregularities in the drying curve between 145° C and 196° C have any particular significance, but it is thought that they are due to the very slow rate at which equilibrium is reached at these particular temperatures, and to the resultant experimental errors.) All the water is not driven off at 200° C, but an amount equal to about 8% of the original  $\text{Al}(\text{OH})_3$  is retained at this temperature, and is driven off slowly as the ignition temperature is increased, very much higher temperatures being required for complete dehydration. However, above 200° C the curve has the general form of an adsorption curve, as far as the experiments were carried, and the 8% of water which is retained at 200° C seems, therefore, to be practically adsorbed by the highly porous  $\text{Al}_2\text{O}_3$  resulting from the decomposition of the original  $\text{Al}(\text{OH})_3$ . The evidence does not show the existence of any series of hydrates formed by step-wise dehydration. The dehydration corresponding to a given

temperature, as found in this work, is somewhat greater than that obtained by previous investigators who did not continue their experiments for nearly so long a time at one temperature.

2. When alumina, produced by drying crystalline  $\text{Al}(\text{OH})_3$  at a temperature as low as even  $275^\circ \text{C}$ , is allowed to take up water, this water is simply adsorbed, and does not recombine chemically with the alumina. The drying curve after "rehydration" shows that this is the case, and bears no resemblance whatever to the original dehydration curve of the  $\text{Al}(\text{OH})_3$ . Hence, for a given sample of alumina the amount of water contained at equilibrium at any temperature will depend on the temperature and the amount of water vapor in the air (neglecting differences due to the sluggish equilibrium, and working at temperatures far enough away from the temperature at which the alumina was originally ignited, so that the original adsorptive capacity of the alumina is not altered). In general, the higher the ignition temperature, the smaller the amount of water which the alumina can adsorb under a given set of conditions.

No experiments were made with gelatinous, ammonia-precipitated, hydrated alumina. Previous investigations, however, have shown that this material is not a well-defined compound, but that its composition varies according to the conditions of precipitation; and it does not behave like a definite hydrate during drying. Should this material be ignited at a dull red heat and then "rehydrated," drying curves of the adsorption type, similar to those found in this work, would undoubtedly be obtained.

Prof. W. J. Mead of the University of Wisconsin, made an X-ray examination of the crystalline aluminum hydroxide of alumina prepared from it by ignition, and of this alumina after "rehydration." His results are in accord with the conclusions of this paper, and may be summarized as follows:

The X-ray pattern of the original crystalline aluminum hydroxide is identical with that of the mineral gibbsite, which is the trihydrate  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  (or  $\text{Al}(\text{OH})_3$ ), and is a definitely crystalline, chemical compound. Alumina, prepared by cal-

ination of the crystalline hydroxide at 325° C gives no trace of the original trihydrate structure; and it is similar, neither to the mineral diasporé which is crystalline mono-hydrate  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , nor to corundum which is crystalline anhydrous  $\text{Al}_2\text{O}_3$ . It does, however, show a distinct set of lines which are indicative of a crystalline condition. The adsorption of water does not alter its structure, and none of the trihydrate is produced. Alumina prepared by calcination at 600° shows a faint pattern similar to the preceding sample, but the bulk of the material is probably amorphous. When calcination temperatures somewhat above 1000° are employed, the product gives the pattern of corundum faintly, and still higher ignition temperatures increase the intensity of this pattern until it equals that of pure corundum.

# THE NATURE OF SECONDARY VALENCE

BY HOMER W. SMITH

## PART V. PARTITION COEFFICIENTS IN SYSTEMS CONTAINING WATER AS ONE COMPONENT WITH SPECIAL REFERENCE TO THE ABSOLUTE VALUES OF THE SERIES CONSTANTS

### 1. Introduction

We have thus far considered the behavior of various solutes in the systems:

Water : xylene  
Water : chloroform  
Water : ether  
Glycerine : acetone

By applying the equation:

$$\text{Log } 100\frac{C_1}{C_2} = V_m/60.00 \pm a$$

we have derived values for  $a$  which we have arbitrarily called series constants. The antilogs of these series constants for various solutes in each system have been shown to be related to each other by simple proportion. The series constants of the various systems containing water also appear to be similarly related. That is, if we denote the series constant for any given series in xylene by  $a_x$ , ether  $a_e$ , chloroform  $a_c$ , then:

Acids	Amines
$a_e = a_x + \log 15.00$	$a_x + \log 1.50 + 0.58840$
$a_c = a_x + \log 5.00$	$a_x + \log 5.0 + 0.58840$

In view of the simple proportion existing between these three systems, it seemed important to extend the investigation to a larger number of solvents, to see if this rule of simple proportionality is universally true.

It has been said that the behavior of a given solute in

two phase systems such as these is determined not only by the nature of the solute, but by the nature of the solvents, as well. Nearly all the acids, and a few of the amines, have been observed to change their relative behavior (or series number) in various systems. This uncertainty about the series number of a given solute in any system makes it essential to determine the partition coefficients for several solutes before the series constants for a given system can be safely evaluated. But when several series are represented in the experimental data, the series constants for any system can be determined with certainty because there are a limited number of series and they can be identified by their numerical inter-relationships.

Consequently the literature was carefully searched for material which would aid in obtaining the series constants for various solvents when used with water, other than the three already discussed (xylene, chloroform and ether). Such data as are available, together with some original data, are given in this paper.

## 2. The Corrected Series Constants

Before entering into the discussion of these other systems, it is necessary to point out that the series constants for the systems already discussed have been modified, in the light of subsequent information, with a view to increased accuracy.

In correcting them, I have been guided by several more or less obvious, but nevertheless assumptive, relationships. In the first place, the series constants for the amines appear to differ from the series constants of the acids by a constant amount (viz., 0.58840). This fact has not been previously mentioned and will be discussed later on. Secondly, in both xylene and ether, one amine series appears to extrapolate to a unit value at  $V_m=0$  (viz., for Series .6 in xylene and .4 in ether,  $a = \pm 0.00000$ ). Thirdly, the series constants of the acids in the cases of xylene, chloroform and ether, as I have already pointed out, are apparently related to each other by pure integrals (viz.,  $\log 1.0 : \log 5.0 : \log 15.0$ ).

I have assumed that these relationships actually did exist. Thus it has been possible to correlate the values derived in all three systems, and to evaluate the series constants with much greater accuracy. If these assumptions are correct, and if the simple numerical relationships exist between the various series in any system as we suppose, it is evident that the series constants for the integral series, at least, can be directly evaluated with ultimate accuracy to any degree.

The series constants in the system water : xylene, as originally given, were derived from the experimental data by a cut-and-try process, since here there is no series which on extrapolation approximates any unit value at  $V_m = 0$ ; the constant difference law between the acids and amines was not at that time recognized. Consequently it occasioned some surprise when, on reworking the data, I found that these values were fairly accurate to the fourth decimal place.

That the foregoing assumptions, by which I have been guided in revising the series constants, are correct is borne out by the study of other solvents presented in this paper.

In theory, since all series in any system, and since all systems as well, are related to each other by simple proportion it is only necessary to know one series constant to obtain the series constant for any series in any system. But for the sake of clarity, I have chosen the series constants for the system water : xylene for presentation. One might suppose that an infinite number of series could exist; but the evidence indicates that the number of series in each system is limited. It is impossible to be sure about this at the present time, but since some method of numbering the various series is necessary, a purely arbitrary designation has been adopted. They have already been numbered by integers from 1 to 10; that series having the highest value of  $a$  in any system has now been designated with an integer, and the succeeding series by decimation. This aids in their identification since they repeat themselves after every decrease of ten times in the partition coefficient. I have chosen Series 4 as a beginning in the

following table because it is the highest one so far observed among the acids or amines.<sup>1</sup>

In résumé, it may be said that these series comprise the recognized possible values of  $\mathfrak{P}$ ; the partition coefficients in several series are in the same proportion to each other as either the respective series numbers, or the antilogs of the respective series constants,  $a$ .

TABLE I  
The Corrected Series Constants for the  
Acids in the System Water : Xylene

Series number	$a$	Series number	$a$
4.	+0.23551	.4	-0.76449
3.	+0.11057	.3	-0.88943
2.	-0.06552	.2	-1.06552
1.414	-0.21610	.1414	-1.21610
1.	-0.36655	.1	-1.36655
.8	-0.46346	.08	-1.46346
.7	-0.52145	.07	-1.52145
.6	-0.58840	.006	-2.58840
.5	-0.66758	.005	-2.66758

etc.

### 3. The Series Constants of Various Systems in which Water is One Component

Instead of tabulating the data as actually found, I have presented the "pure" or theoretical values indicated, and then calculated the values of  $\mathfrak{P}$  on the basis of these "pure" values. Thus I have ascertained that the series constant for toluene is  $a_x + \log 0.0000$  (still an assumption, of course) and used this "pure" relationship in calculating the desired values of  $\mathfrak{P}$ . This enables us to avoid in discussion the errors arising in the experimental work, and presents the data in a final form. The degree of agreement between  $\mathfrak{P}$  obs. and  $\mathfrak{P}$  calc. indicates the degree to which the assumption of simple

<sup>1</sup> In comparing two systems in this manner we have each series characterized; there will be a Series 1.0 in each system, a Series .1, etc. That these series are chemically identical, or rather chemically related, is evident from the facts that one compound (such as diethylamine) will appear in the same series in all systems, and that the various systems are related, through any one series, by simple proportion.



proportionality is borne out. The figures given under the caption  $C_2$  show the concentration in the second solvent to which interpolation is made to obtain  $\beta$ .

TABLE II  
Water: Toluene  
Acids.  $a_1 = a_x \pm 0.00000$

Series number	$a$	$V_m$	$C_2$	$\beta$ obs.	$\beta$ calc.
14.14	+0.78390				
	Phenol	101.9	1000.0	2.75 <sup>1</sup>	3.03
.8	-0.46346				
	Chloroacetic acid	78.0	1000.0	0.07 <sup>1</sup>	0.069
.6	-0.58840				
	sec-Butyric acid	107.3	1.0	0.16	0.1585
.3	-0.88943				
	Chloroacetic acid	78.0	100.0	0.028 <sup>1</sup>	0.0257
.2	-1.06552				
	Acetic acid	64.0	1.0	0.0101 <sup>1</sup>	0.010
Amines. $a_1 = a_x + 0.58840$					
4.0	+0.82391				
	Pyridine	89.5	100.0	2.06 <sup>1</sup>	2.07
1.0	+0.22185				
	Trimethylamine	88.0	100.0	0.43 <sup>1</sup>	0.488

TABLE III  
Water: Benzene  
Acids.  $a_b = a_x + \log 1.25$

Series number	$a$	$V_m$	$C_2$	$\beta$ obs.	$\beta$ calc.
6.0	+0.50851				
	Benzoic acid	126.9	10.0	4.20	4.23
2.0	+0.03139				
	Benzoic acid		1.0	1.45	1.41
1.0	-0.26964				
	Acetone	76.6	1000.0	0.98	1.00
.8	-0.36655				
	Acetic acid	64.0	100.0	0.054 <sup>1</sup>	0.050
.6	-0.49149				
	sec-Butyric acid	107.3	1.0	0.202	0.198
.1	-1.26964				
	Picric acid	172.0	100.0	4.0	3.95
.04	-1.66758				
	Picric acid		10.0	1.55	1.582

TABLE III (Continued)

Amines. $a_b = a_x + \log 1.25 + 0.58840$					
4.0	+0.92082				
	Pyridine	89.5	100.0	2.6 <sup>1</sup>	2.565
.8	+0.22185				
	Trimethylamine	88.0	100.0	0.50 <sup>1</sup>	0.488
.4	-0.07918				
	Diethylamine	109.3	1.0	0.560	0.553

TABLE IV

Water : Carbon Tetrachloride  
Acids.  $a_a = a_x + \log 1.414$

Series number	$a$	$V_m$	$C_2$	# obs.	# calc.
8.	+0.68705				
	Phenol	101.9	1000.0	2.45 <sup>1</sup>	2.429
5.	+0.48293				
	Acetone	76.6	1000.0	0.61	0.575
4.0	+0.38602				
	Acetone	76.6	100.0	0.450 <sup>1</sup>	0.460
1.414	-0.06559				
	Acetic acid	64.0	1000.0	0.10 <sup>1</sup>	0.100
.5	-0.51707				
	Acetic acid	64.0	100.0	0.0365 <sup>1</sup>	0.0354
	Chloroacetic acid	78.0	1000.0	0.06 <sup>1</sup>	0.0606
.3	-0.73892				
	sec-Butyric acid	107.3	1.0	0.104	0.112
.1	-1.21604				
	Chloroacetic acid	78.0	100.0	0.0115 <sup>1</sup>	0.0121
Amines. $a_a = a_x + \log 1.414 + 0.58840$					
.4	-0.02558				
	Diethylamine	109.3	1.0	0.615	0.625
.007	-1.78254				
	Ammonia	26.9	10.0	0.0047	0.0046

Nearly nine-tenths of the data incorporated in the foregoing tables have been obtained from the literature. Moreover everything available that could possibly be utilized has been used. It is indeed remarkable that such satisfactory agreement should be secured from the experimental work of so many investigators.

TABLE V  
Water: Amyl Alcohol  
Acids.  $a_a = a_x + \log 5.00$

Series number	$a$	$V_m$	$C_x$	$\bar{\mu}$ obs.	$\bar{\mu}$ calc.
14.14	+1.48287				
	Phenol	101.9	100.0	15.7	15.18
4.0	+1.93448				
	Acetic acid	64.0	1000.0	0.921	1.00
.5	+1.03149				
	Picric acid	172.0	10.0	7.4	7.91
.4	+0.93448				
	Picric acid		100.0	6.7	6.325
.1	+0.33242				
	Oxalic acid	75.6	100.0	0.40	0.422
.08	+0.23551				
	Oxalic acid		10.0	0.295	0.313
.03	-0.19046				
	Succinic acid	120.0	100.0	0.675	0.6324
<i>Amines. <math>a_a = a_x + \log 5.00 + 0.58840</math></i>					
1.0	+0.92082				
	Triethylamine	152.6	100.0	26.0	29.1
.8	+0.82391				
	Methylamine	43.0	100.0	0.335	0.347
.6	+0.69897				
	Ammonia	26.9	100.0	0.146	0.140
.4	+0.52288				
	Diethylamine	109.3	1.0	2.22	2.21

The primary motive in presenting these data is to show that a simple proportion exists between solvents, as well as between solutes. That all the proportions are not simple, or integral, is not a matter to concern us greatly at the present time. It may be remarked that they have been determined with sufficient accuracy to warrant careful consideration. Consider, for example, carbon tetrachloride; here,

$$a_a = a_x + \log 1.414$$

With the exception of two instances, the data given for this system were determined by Herz and Lewy. The mean algebraic variation between the observed and calculated values is +0.013. The maximum variation is +0.075

in the case of diethylamine, one of my own determinations. The existence of series corresponding to 1.414 has already been discussed and it was pointed out that this value was chosen because it is the square-root of two.<sup>1</sup>

TABLE VI  
Water : Bromoform  
Acids.  $a_{br} = a_x + \log 5.0$

Series number	$a$	$V_m$	$C_s$	$\bar{\mu}$ obs.	$\bar{\mu}$ calc.
4.0	+0.93448				
	Phenol	101.9	1000.0	4.3 <sup>2</sup>	4.294
.6	+0.11057				
	Acetic acid	64.0	1000.0	0.148 <sup>2</sup>	0.1502
.2	-0.36655				
	Chloroacetic acid	78.0	1000.0	0.094 <sup>2</sup>	0.108
.1	-0.66758				
	Picric acid	172.0	100.0	1.6 <sup>2</sup>	1.582
<i>Amines. <math>a_{br} = a_x + \log 5.0 + 0.58840</math></i>					
.01414	-0.92873				
	Ammonia	26.9	100.0	0.0292	0.033

#### 4. The Use of Diethylamine in Determining the Series Constants in Various Systems

If we could be sure that a given compound would never shift from one series to another, it would only be necessary to study that one compound in order to obtain the series constants for any system.

It was noticed, however, in the first three water-containing systems studied that the acids were likely to occur in different series in each system. The amines nearly always appeared in the same series in every system. This regular behavior of the amines persists in the systems studied above, though there are exceptions.

Diethylamine is one compound which has always appeared

<sup>1</sup> Jour. Phys. Chem., 25, 611 (1921).

<sup>2</sup> For the derivation of these values see Section I of Part II of this series. Jour. Phys. Chem., 25, 204 (1921). For all other values see the following experimental section.

in the same series (i. e., Series .4) and for this reason it has been studied in a number of systems where only a small quantity of the organic solvent was available or where time prohibited extensive work. The results are listed below. It cannot be said definitely that diethylamine has not changed its series number in any of these systems, but from its previous behavior I believe this to be unlikely. On this assumption we then have this simple relationship between xylene and the unevaluated solvent,  $r$ :

$$\frac{\text{Antilog } a_r}{\text{Antilog } a_x} = \frac{\mathfrak{P}_r}{\mathfrak{P}_x}$$

That is, the series constants of the two systems bear the same proportion as do the partition coefficients of diethylamine. Of course  $\mathfrak{P}$  must be obtained from equal values of  $C_2$ . These data are all based upon determinations of  $\mathfrak{P}$  when  $C_2$  is 1 m/L.

TABLE VII  
The Behavior of Diethylamine in Various Systems

	$P_r(C_2=1 \text{ m/L})$	Observed ratio <sup>1</sup> $P_r/P_x$	Pure ratio $P_r/P_x$
Paraffin Oil	0.185	0.419	.4?
Petroleum (C <sub>9</sub> -)	0.277	0.627	.625?
Trichlorobenzene	0.333	0.754	.75
<i>iso</i> -Amylphenyl ether	0.435	0.985	1.00
Bromobenzene	0.556	1.26	1.25
<i>o</i> -Dichlorobenzene	0.650	1.47	1.50
<i>n</i> -Butylbromide	0.65	1.47	1.50
<i>n</i> -Butyl ether	0.65	1.47	1.50
Ethylene chloride	0.884	2.00	2.00
<i>sec</i> -Octyl alcohol	1.11	2.52	2.50
<i>n</i> -Butyl alcohol	2.20	4.98	5.00
<i>iso</i> -Butyl alcohol	2.20	4.98	5.00

We now have the series constants for twenty systems containing water. Eight of these have been determined from data based on several solutes (these are marked with an asterisk in the following table). The remaining twelve are based on diethylamine alone.

<sup>1</sup>  $P_x = 0.442$

TABLE VIII  
Summary of Series Constants

Water and	$a$ (Acids)	$a$ (Amines)
Paraffin Oil	$a_s + \log 0.40$	+0.58840
Petroleum	$a_s + \log 0.625$	+0.58840
Trichlorobenzene	$a_s + \log 0.75$	+0.58840
Xylene*	given as $a_s$	+0.58840
<i>iso</i> -Amylphenyl ether	$a_s + \log 0.00$	+0.58840
Toluene*	$a_s + \log 0.00$	+0.58840
Benzene*	$a_s + \log 1.25$	+0.58840
Bromobenzene*	$a_s + \log 1.25$	+0.58840
Carbon tetrachloride*	$a_s + \log 1.414$	+0.58840
Dichlorobenzene	$a_s + \log 1.50$	+0.58840
<i>n</i> -Butylbromide	$a_s + \log 1.50$	+0.58840
<i>n</i> -Butyl ether	$a_s + \log 1.50$	+0.58840
Ether <sup>1</sup> *	$a_s + \log 15.00$	+1.58840
Ethylene chloride	$a_s + \log 2.00$	+0.58840
<i>sec</i> -Octyl alcohol	$a_s + \log 2.50$	+0.58840
<i>n</i> -Butyl alcohol	$a_s + \log 5.00$	+0.58840
<i>iso</i> -Butyl alcohol	$a_s + \log 5.00$	+0.58840
Amyl alcohol*	$a_s + \log 5.00$	+0.58840
Chloroform*	$a_s + \log 5.00$	+0.58840
Bromoform*	$a_s + \log 5.00$	+0.58840
Glycerine : acetone	$a_s + 1.66758$	$\approx 0.00000$

### 5. The Behavior of Acids and Amines

A very interesting point brought out in the above table is the fact that the series constants of the amines and the acids differ by a constant amount (+0.58840) in those systems which contain water, while there is no difference in the system glycerine: acetone.

I was led to wonder while preparing the data on xylene and chloroform why the amines should behave differently, so far as the absolute values of the series constants are concerned, from the acids; it now appears that this difference is

<sup>1</sup> Note that the anomaly in the system water : ether appears to rest with the acids, the series constants of which are ten times as great as the series constants of the amines. In so far as the amines are concerned, this system ( $a_s + \log 1.50$ ) falls into a position relative to the other systems which is in agreement with its general physical properties. This suggests that other systems (*n*-butyl ether, etc.) might show a similar discrepancy if studied with the acids as well as the amines, but at the time of writing it has been impossible to cover these points.

to be attributed to the presence of water in the system, for the difference disappears in a water-free system. No satisfactory explanation of this important relationship has occurred to me as yet, but it may be worth while to make this comment: The value  $+0.58840$  corresponds to an increase in molecular volume of 35.14 units. This is approximately the volume of two molecules of water at  $25^\circ$  ( $18.03 \times 2 = 36.06$ ). The molecular volumes of the amines have been figured on the basis of unhydrated molecules; that is, as  $\text{RNH}_2$ , etc., and not  $\text{RNH}_2\text{OH}$ . In comparing the amines with the acids there is no doubt but that this chemically combined molecule of water should be included in the calculation of the volume.

But why another molecule of water should be involved is not so easily explained, unless we assume that all amines possess in aqueous solution one molecule of water of hydration. Such an assumption is favored by a great number of facts indicating that the amines are hydrated to a much greater extent than the acids or other compounds, but that this water of hydration is constant in amount and equal to one molecule is not so easily believed.

#### Summary

1. The series constants for eight systems in which water is one component have been derived from data in large part quoted from the literature.

2. In each of these systems, the series constants for the various *solutes* studied are related to each other by simple proportion.

3. The series constants for twelve systems in which water is one component have been tentatively formulated through the study of diethylamine.

4. In all twenty of the systems studied, the series constants for the various *systems* are related to each other by simple proportion.

5. In every system in which water is one component, the amines differ from the acids in the value of their series constants by a constant amount.

6. It is concluded that the intermolecular forces concerned in the solvent powers of various molecular species differ in intensity by discrete and simply related amounts. The bearing of the foregoing data on the structure of the atom and on the quantum theory will be discussed in the next communication.

## EXPERIMENTAL

$C_1$  : Concentration in Water Layer.

$C_2$  : Concentration in Other Layer.

The figures given in the last column show the concentration of  $C_2$  to which interpolation for  $\mu$  is made. All concentrations in millimols per liter.

		$C_1$	$C_2$	$C_1/C_2$	$\mu$
<i>Amyl alcohol</i>					
Acetic acid	20°	1326.0	1208.0	0.911	H. and F.
		1024.5	948.1	0.925	
		794.4	729.6	0.918	
		351.5	330.4	0.941	1000
		88.88	80.34	0.909	0.921
Ammonia	20°	1970.0	287.4	0.146	H. and F.
		1016.5	154.9	0.151	
		579.5	84.22	0.145	
		364.06	54.55	0.149	
		240.83	34.61	0.144	100
		89.17	12.24	0.137	0.146
Diethylamine	25°	4.95	20.00	4.04	S
		2.875	10.625	3.70	
		1.675	5.450	3.26	
		1.05	2.9625	2.82	1
		0.65	0.625	2.52	2.22
Methylamine	25°	1061.3	397.4	0.374	H. and F.
		812.6	298.1	0.367	
		642.9	231.5	0.360	
		505.4	175.9	0.348	
		303.6	107.0	0.352	100
		115.5	38.04	0.330	0.335
Oxalic acid	20°	1002.9	430.0	0.47	H. and F.
		827.9	340.0	0.47	
		669.9	255.0	0.43	100
		459.9	171.7	0.43	0.40
		236.4	72.33	0.38	
		127.5	32.73	0.34	10
		68.06	14.51	0.31	0.295
Phenol	25°	390.0	5630.0	14.4	H. and F.
		383.0	5410.0	14.1	



## EXPERIMENTAL (Continued)

	$C_1$	$C_2$	$C_1/C_2$	$\beta$
	16.0	260.0	16.2	
	7.0	110.0	15.7	100
	4.7	75.0	16.0	15.7
Picric acid 25°	64.23	254.9	6.50	H. and F.
	44.71	163.8	6.65	
	31.61	107.9	6.90	100
	18.69	51.82	6.82	6.7
	9.203	18.50	7.10	10
	5.531	9.296	10.07	7.4
Succinic acid 20°	1155.5	711.9	0.616	H. and F.
	809.9	519.95	0.642	
	404.95	271.47	0.670	
	103.73	70.77	0.682	100
	26.84	18.80	0.703	0.675
Triethylamine 25°	27.74	741.8	26.0	H. and F.
	16.64	440.8	26.5	100
	8.75	227.3	26.0	26.0
<i>iso</i> -Amylphenyl ether				
Diethylamine 25°	9.50	3.90	0.411	S.
	5.775	2.55	0.442	
	3.30	1.35	0.410	I
	1.85	0.815	0.440	0.435
Benzene				
Acetone 25°	2216.7	2394.7	1.080	H. and F.
	1936.7	2071.7	1.070	
	1208.3	1204.5	0.997	
	918.5	896.7	0.976	
	608.9	575.7	0.945	1000
	220.0	206.5	0.938	0.980
Benzoic acid 25°	4.00	19.75	4.93	S.
	2.80	11.90	4.25	
	1.725	5.50	3.19	10
	1.300	3.45	2.57	4.20
	0.925	1.95	2.11	I
	0.8725	1.525	1.75	1.45
<i>sec</i> -Butyric acid 25°	18.90	5.0	0.264	S.
	9.60	2.20	0.230	
	3.75	0.7125	0.190	I
	2.55	0.410	0.170	0.202
Diethylamine 25°	22.30	18.30	0.822	S.
	11.95	9.05	0.756	
	6.575	4.35	0.662	
	3.875	2.475	0.638	I
	2.1375	1.2375	0.578	0.560
Picric acid	26.09	94.01	3.60	K.

## EXPERIMENTAL (Continued)

		20.80	77.90	3.74	100
		18.82	61.84	3.28	4.0
		13.20	35.90	2.72	10
		9.73	19.77	2.03	1.5
<i>Bromobenzene</i>					
<i>Diethylamine</i>	25°	7.15	4.05	0.567	S.
		3.825	2.075	0.542	
		3.40	1.70	0.50	
		2.1875	1.1375	0.520	
		2.0875	1.225	0.587	
		1.4625	0.8875	0.607	(mean)
		1.100	0.625	0.5680	0.556
<i>Bromoform</i>					
<i>Ammonia</i>	25°	8530.0	417.0	0.0489	H. and L.
		8050.0	362.0	0.0449	
		6300.0	235.0	0.0370	
		4180.0	131.0	0.0132	100
		2590.0	70.0	0.0272	0.0292
<i>n-Butyl alcohol</i>					
<i>Diethylamine</i>	25°	2.50	6.8	2.72	S.
		1.35	3.175	2.35	
		0.675	1.540	2.30	1
		0.275	0.575	2.09	2.2
<i>iso-Butyl alcohol</i>					
<i>Diethylamine</i>	25°	1.0875	2.6125	2.4	S.
		0.650	1.500	2.3	
		0.550	1.225	2.22	1
		0.300	0.625	2.08	2.20
<i>n-Butyl bromide</i>					
<i>Diethylamine</i>	25°	6.60	4.00	0.606	S.
		3.475	2.20	0.633	
		2.10	1.3375	0.637 <sup>1</sup>	
		1.10	0.725	0.660	0.65
<i>n-Butyl ether</i>					
<i>Diethylamine</i>	25°	7.75	4.55	0.587	S.
		4.05	2.45	0.605	
		2.1625	1.375	0.632	1
		0.925	0.625	0.676	0.65
<i>Carbon tetrachloride</i>					
<i>Acetone</i>	25°	2870.0	2100.0	0.733	H. and L.
		1660.0	997.0	0.601	1000
		1010.0	514.0	0.511	0.61
		322.0	146.0	0.454	100
		186.0	83.3	0.449	0.45
<i>Ammonia</i>	25°	8590.0	73.5	0.00856	H. and L.
		6860.0	46.4	0.00676	

## EXPERIMENTAL (Continued)

	C <sub>1</sub>	C <sub>2</sub>	C <sub>1</sub> /C <sub>2</sub>	$\bar{R}$
	5700.0	35.7	0.00626	
	2350.0	11.8	0.00502	<i>I</i>
	1730.0	7.87	0.00455	0.0047
<i>sec</i> -Butyric acid 25°	17.50	2.70	0.154	S.
	13.80	1.725	0.125	
	9.25	1.05	0.1135	
	7.10	0.595	0.0838	<i>I</i>
Diethylamine 25°	4.775	0.305	0.0639	0.104
	7.80	7.00	0.897	S.
	5.075	4.00	0.788	
	2.525	1.9375	0.700	<i>I</i>
	1.425	0.850	0.597	0.615
<i>o</i> -Dichlorobenzene				
Diethylamine 25°	11.70	7.15	0.61	S.
	5.50	3.30	0.60	
	3.175	2.325	0.732	
	1.55	1.075	0.693	(mean)
	1.475	0.95	0.643	0.650
Ethylene chloride				
Diethylamine 25°	4.475	4.075	0.910	S.
	2.15	1.925	0.886	
	1.1875	1.05	0.886	<i>I</i>
	0.95	0.835	0.880	0.884
<i>sec</i> -Octyl alcohol				
Diethylamine 25°	2.10	2.50	1.19	S.
	1.75	2.01	1.16	
	1.05	1.20	1.14	<i>I</i>
	0.475	0.50	1.05	1.11
Paraffin oil				
Diethylamine 25°	16.10	3.00	0.186	S.
	8.80	1.50	0.170	
	8.70	1.40	0.161	
	5.25	1.025	0.192	
	3.35	0.650	0.194	
	3.30	0.650	0.1955	
	3.20	0.575	0.180	(mean)
	1.475	0.300	0.204	0.185
Petroleum (B. P. 145° -155° (Nonane))				
Diethylamine 25°	11.35	3.25	0.287	S.
	7.25	2.05	0.283	
	4.825	1.425	0.295	
	4.50	1.30	0.289	
	4.175	1.275	0.305	
	2.7125	0.850	0.313	

## EXPERIMENTAL (Continued)

	1.9725	0.450	0.228	(mean)
	1.6375	0.3625	0.222	0.277
<i>Toluene</i>				
<i>sec-Butyric acid 25°</i>	15.70	5.50	0.350	S.
	8.90	1.65	0.185	
	3.60	0.50	0.139	I
	1.975	0.2025	0.1025	0.160
<i>1,3,4-Trichlorobenzene</i>				
<i>Diethylamine 25°</i>	9.45	4.05	0.43	S.
	4.95	1.925	0.403	
	3.325	1.125	0.346	I
	1.4375	0.4125	0.287	0.333

H. and F.—Herz and Fischer: Ber. deutsch. chem. Ges., 37, 4746 (1909); 38, 1138 (1905).

H. and L.—Herz and Lewy: Zeit. Elektrochemie, 11, 818 (1905); Sitzungsber. schles. Ges. vaterländische Kultur. Natur-Wissenschaftl. Sektion, 1906. Most of these data are also given by Herz; Sammlung Chemischer und chemisch-technischer Vorträge, 15, 1 (1910-11).

K.—Kuriloff: Zeit. phys. Chem., 25, 418 (1898).

S.—Original.

*Johns Hopkins University  
School of Hygiene and Public Health  
Department of Physiology  
Baltimore*

*and  
Lilly Research Laboratories  
Eli Lilly and Company  
Indianapolis*

3-1824

## CATALYTIC PREPARATION OF ANILINE. II

BY O. W. BROWN AND C. O. HENKE

### Introduction

In a previous paper we have given the results of some studies on the reduction of nitrobenzene to aniline by hydrogen in the presence of nickel and copper catalysts. In this paper we shall give the results of some studies on the effect of different catalysts on this reduction. The apparatus used, the method of procedure and the analysis was the same as in our previous paper, where it was fully described.<sup>1</sup> Each catalyst was used in a new iron tube which had been previously cleaned by heating in a current of hydrogen to about 535°.

### Silver

Silver carbonate was prepared by precipitation from a solution of silver nitrate by ammonium carbonate. The precipitate was thoroughly washed with distilled water and dried, a part of the carbonate being thus converted to the oxide. Twenty grams of the dried material was then put in the furnace and reduced and heated in hydrogen at 280° for about an hour. The results of experiments carried out at different temperatures are given in Table I.

TABLE I

Catalyst—Silver.

Rate of flow of hydrogen—17 liters per hour.

Rate of flow of nitrobenzene—3.9 grams per hour.

Excess of hydrogen—710%.

Temperature of catalyst, °C	Material yield in % of theory	Temperature of catalyst, °C	Material yield in % of theory
200	25.5	280	98.4
215	35.4	300	98.7
235	60.1	320	96.2
260	97.1	340	90.2

<sup>1</sup> Brown and Henke: Jour. Phys. Chem., 26, 161 (1921).

The results of Table I are plotted in curve Ag of Figure 1. The curve is very similar to the curve for copper which is redrawn from the graph of the previous paper. The best

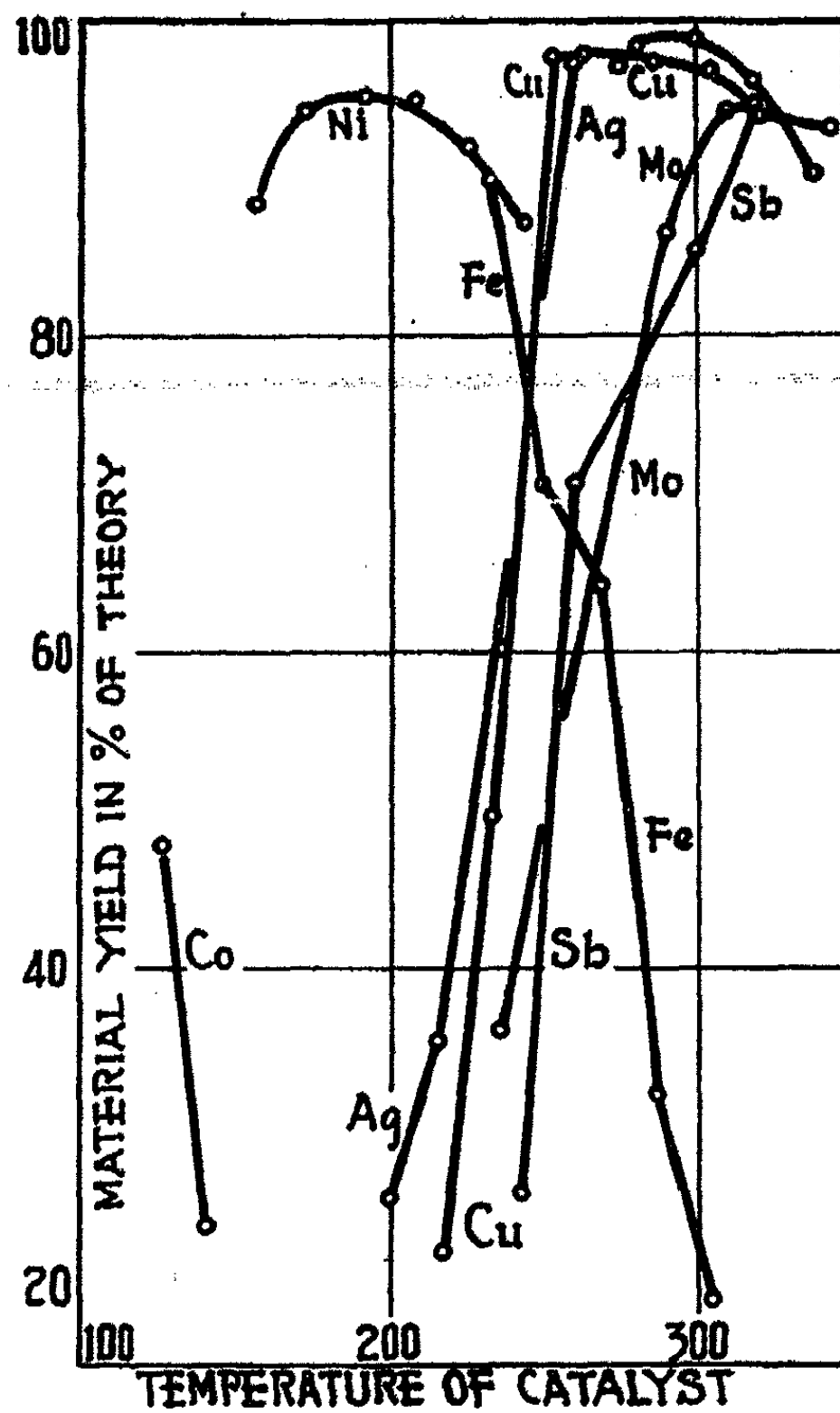


Fig. 1

temperature for carrying out the reduction with silver as catalyst is seen to be from 280° to 300°.

This catalyst was then used to study the effect of the rates of flow of the hydrogen and nitrobenzene. The results

with different rates of flow of nitrobenzene are given in Table II.

TABLE II

Catalyst—Silver.  
Temperature of catalyst—300°.  
Rate of flow of hydrogen—17 liters per hour.

Nitrobenzene in grams per hour	Excess of hydrogen in %	Material yield in % of theory
15.5	100	59.2
10.7	190	77.1
9.7	220	90.2
6.3	400	93.1
3.9	710	98.7

The results of Table II are plotted in curve Ag of Figure 2. For purposes of comparison the curves for nickel and copper are redrawn from the data of the previous paper.

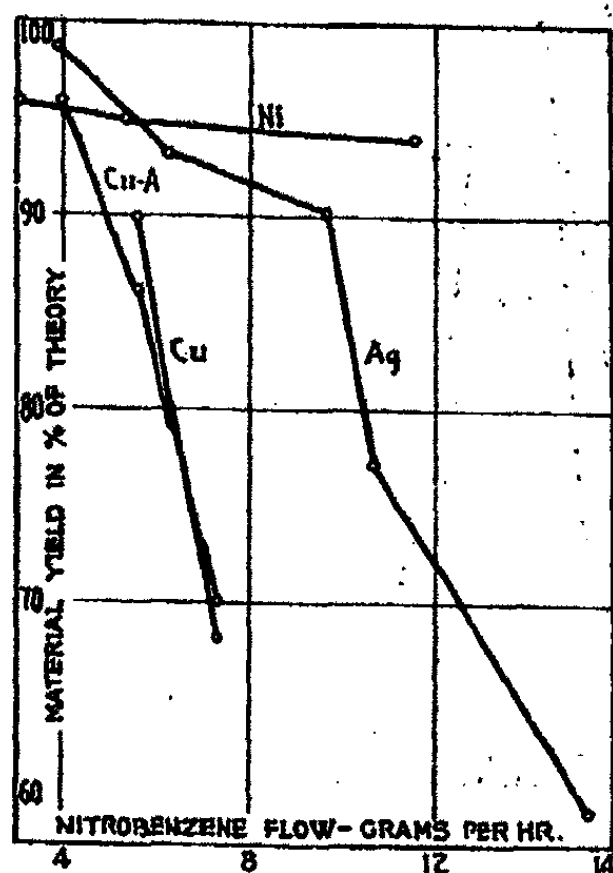


Fig. 2

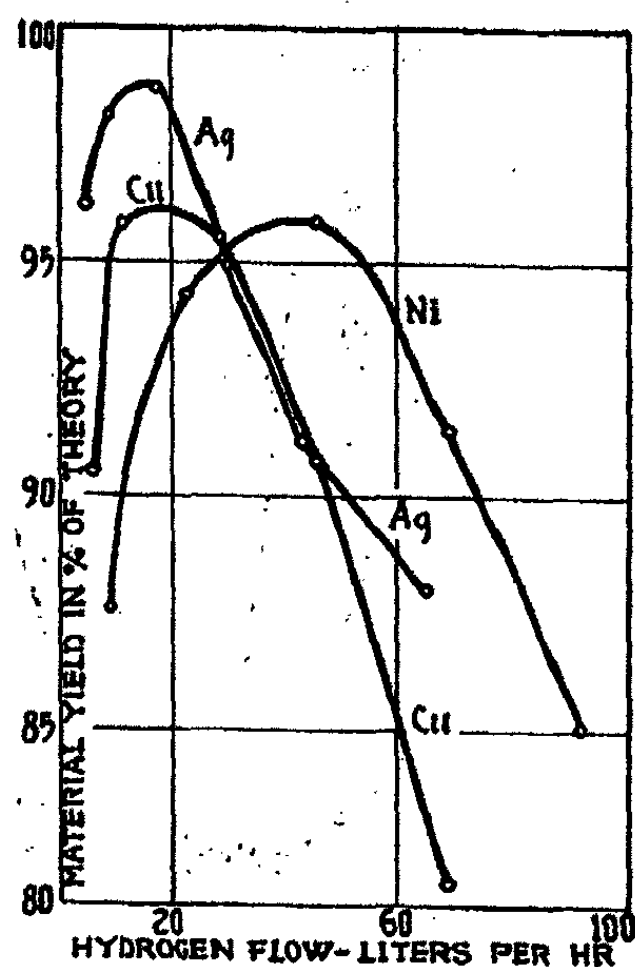


Fig. 3

In curve Cu-A the rate of flow of hydrogen was 11.4 liters per hour while in all the other curves it was 17 liters per hour. The graph shows that with nickel the speed of reduction of

nitrobenzene is greatest and with copper the least. Silver, though not equal to nickel has a far greater speed of reduction than copper. The temperatures of the different catalysts were not the same, but each one was used at the temperature where it had given the highest yield of aniline with the rate of flow of nitrobenzene at 3.9 to 4 grams per hour and the rate of hydrogen at 17 liters per hour. Since silver is like copper in that it does not attack the aromatic ring it appears that it would be a better catalyst to use than copper in cases where the action of the nickel was too violent, for the silver can be used at a much greater rate than the copper catalyst.

The results of experiments with different rates of flow of hydrogen are given in Table III.

TABLE III

Catalyst—Silver.

Temperature of catalyst—300°.

Rate of flow of nitrobenzene—3.9 grams per hour.

Hydrogen in liters per hour	Excess of hydrogen in %	Material yield in % of theory
4.3	100	96.2
8.5	300	98.1
17	710	98.7
30	1310	94.9
43.5	1940	91.2
65.5	2970	88.0

The results of Table III are plotted in curve Ag of Figure 3. The curves for nickel and copper are redrawn from the previous paper for purposes of comparison. The temperatures of the different catalysts are the same as in Figure 2. Here again the nickel is capable of effecting the reduction at the greatest rate with silver second and copper last, although the difference between silver and copper is not so great as in Figure 2.

An experiment in which the hydrogen was bubbled through water at 50° before being passed into the furnace gave the same result as when it was not bubbled through the water. Likewise passing the hydrogen through an approximately 1/2% ammonia solution did not affect the yield of aniline appreciably.



## Cobalt

The cobalt catalyst was prepared by ignition of the nitrate and subsequent reduction of the oxide. The nitrate used contained 0.003% Fe, 0.51% Ni and 0.001% SO<sub>3</sub>. The nitrate with the addition of nitric acid was ignited at 445° in a small porcelain evaporating dish in an electrically heated muffle, the temperature being measured by a thermocouple in the dish just above the cobalt oxide. Twenty six grams of the ignited oxide were put in the furnace and reduced and heated in hydrogen to 400°. This temperature of ignition and reduction was found to give the highest yields of aniline when nickel was used as catalyst. Since cobalt is similar to nickel, although supposed to be less active than nickel, it was thought that these temperatures would likewise be the best for cobalt. The results for experiments carried out at different temperatures are given in Table IV.

TABLE IV

Catalyst—Cobalt.

Rate of flow of hydrogen—17 liters per hour.

Rate of flow of nitrobenzene—3.9 grams per hour.

Excess of hydrogen—710%.

Temperature of catalyst, °C	Material yield in % of theory	Temperature of catalyst, °C	Material yield in % of theory
305	0.6	153	12.6
232	5.4	140	23.6
170	5.0	125	47.6

The last two results of Table IV are plotted in curve Co of Figure 1. The curve for Ni is redrawn from the graph of the previous paper for purposes of comparison. It is seen that with Co the highest yield of aniline is obtained at a lower temperature than with Ni. With Co, the lower the temperature the higher the yield of aniline until 125° is reached, below which it was practically impossible to work.

From the work of Sabatier this is exactly what one would not expect for he found Ni to be more active than Co in other hydrogenations. The low yields of aniline with Co were not due to incomplete reduction of the nitrobenzene but to the fact that the Co was carrying on the reduction too far; which

was shown by the fact that the odor of ammonia was strong and at the higher temperatures there was only a small amount of condensate which indicated that the cobalt was reducing some of the nitrobenzene even to methane. This variance from Sabatier's results may however be due to the fact that he very carefully freed his nickel from cobalt and his cobalt from nickel, while the cobalt nitrate that we used contained 0.51% nickel and the nickel nitrate contained 0.386% cobalt. Also Sabatier used a glass tube while we have used these catalysts in an iron pipe.

#### Iron

The iron catalyst was prepared from ferric nitrate, which had been repeatedly boiled down with nitric acid to free it from chlorine. Ferric oxide was precipitated from the ferric nitrate solution by ammonium hydroxide, and then dried in an oven at about 110°. Twenty six grams of the oxide were used. This was heated in hydrogen to 415° and kept at that temperature for 30 minutes. It was then used in the experiments recorded in Table V, which show the effect of different temperatures on the yield of aniline secured.

TABLE V

Catalyst—Iron.

Rate of flow of hydrogen—17 liters per hour.

Rate of flow of nitrobenzene—3.9 grams per hour.

Excess of hydrogen—710%.

Experiment number	Temperature of catalyst, °C	Material yield in % of theory
6L1	305	19.4
7L1	305	19.7
8L1	305	17.8
9L1	286	32.0
10L1	268	64.2
11L1	250	70.5
25L1*	232	89.9
17L1**	250	44.2
18L1**	250	13.8

\* Prior to experiment 25L1 the catalyst was heated in hydrogen at 415° for 30 minutes.

\*\* For experiments 17L1 and 18L1 the rate of flow of nitrobenzene was 4.9 grams per hour.

The first seven results of Table V are plotted in curve Fe of Figure 1. The graph indicates that iron has a high activity. The low results at the higher temperatures are not due to incomplete reduction of the nitrobenzene but to the fact that the iron carried on the reduction too far, as shown by the fact that the product was colorless and there was a very strong odor of ammonia. Even in experiment 25L,1 which was carried out at 232° the product was colorless and contained no nitrobenzene indicating that even at this low temperature the iron has reduced a part of the nitrobenzene farther than the aniline stage. However at the lower temperatures the iron quickly lost its activity as is illustrated by experiments 17L,1 and 18L,1 which were made under duplicate conditions, one following the other. The second one is about 30% lower than the first. However merely heating in hydrogen at 415° for 30 minutes completely restores the activity of the iron. This indicates that at 250° metallic iron partially reduces the nitrobenzene and is converted to the oxide. Then at this low temperature the oxide is not reducible by hydrogen or is only very slowly reduced by hydrogen and as a result the iron is soon converted to the oxide and the catalyst has lost its activity simply because it is no longer metallic iron but iron oxide. Then by heating at 415° the catalyst regains its activity because the iron oxide is reduced and we again have metallic iron as catalyst.

Sabatier<sup>1</sup> states that the iron oxide is reduced with difficulty at 400° to 450°. He claims that it takes 6 or 7 hours to completely reduce it with hydrogen at this temperature.

#### Antimony

The antimony catalyst was prepared by reducing 35 grams of the trioxide, which was c. p. material from Kahlbaum, and then heating in hydrogen to 435°. The results of experiments carried out at different temperatures with this catalyst are given in Table VI.

<sup>1</sup> Sabatier: "La Catalyse," 1st Ed., Paris, 1913, p. 106.

TABLE VI

Catalyst—Antimony.  
Rate of flow of hydrogen—17 liters per hour.  
Rate of flow of nitrobenzene—3.9 grams per hour.  
Excess of hydrogen—710%.

Experiment number	Temperature of catalyst, °C	Material yield in % of theory
1E1	242	25.8
5E1*	300	85.4
6E1	300	68.7
7E1	300	58.3
8E1	300	20.8
9E1**	300	76.9
10E1**	320	95.2
11E1	320	93.3
12E1	320	95.2
13E1**	260	70.6

The results of Table VI are plotted in curve Sb of Figure 1. It will be noted that at 320° the antimony catalyst did not lose its activity while at 300° its activity decreased steadily with use as the data in the table indicates. However, its activity was restored by merely heating in hydrogen at 450° for about 25 minutes. This indicates that at 300° the metallic antimony partially reduces the nitrobenzene and is converted to the oxide which then is not reduced by the hydrogen at that temperature. However at a higher temperature it is reduced and the catalyst then regains its former activity. The results of the table indicate that at 320° the antimony catalyst, at the indicated rates of nitrobenzene and hydrogen, does not lose its activity. This action of antimony was very similar to the action of iron except that the metallic iron was a much more vigorous catalyst. (With antimony at 300° the product was colored indicating the presence of azoxybenzene or azobenzene while with iron at this temperature the reduction was carried on farther than the aniline stage.)

\* Prior to experiment 5E1 the catalyst was heated in hydrogen at 470° for 30 minutes.

\*\* Prior to each one of these experiments the catalyst was heated in hydrogen at 450° for about 25 minutes.

Both would indicate that the nitrobenzene oxidizes the metal which in turn is reduced by the hydrogen.

In experiments 9E1 and 13E1 a small amount of azobenzene was formed. Other catalysts that yielded considerable amounts of azobenzene were lead and bismuth and since the formation of azobenzene with these two catalysts is so marked and peculiar, the results will be given in a separate paper in a later number of this journal.

#### Molybdenum Oxide

The molybdic acid that was used for this catalyst contained 88.03% MoO<sub>3</sub>, a trace of phosphorus, a trace of insoluble residue and ammonia. No arsenic or copper was present. This was heated in hydrogen at 405° for about two hours, a few experiments carried out and then after heating in hydrogen at 405° for another hour the experiments of Table VII were carried out.

TABLE VII

Catalyst—Molybdenum Oxide.  
Rate of flow of hydrogen—17 liters per hour.  
Rate of flow of nitrobenzene—3.9 grams per hour.  
Excess of hydrogen—710%.

Experiment number	Temperature of catalyst, °C	Material yield in % of theory
11J1	235	36.0
12J1	252	26.0
7J1	290	86.5
8J1	310	94.3
17J1	345	93.1

The results of Table VII are plotted in Figure 1. The result of experiment 12J1 is not shown in the curve. It will be noted that 12J1 has a lower aniline yield than 11J1 although 12J1 was carried out at the higher temperature. This indicates that this catalyst loses its activity when used at the lower temperatures similar to the iron and antimony catalysts. The catalyst in the case of molybdenum is probably a lower oxide and not the metal itself. It appears that the lower oxide, besides acting as a catalyst to cause the reduction by

hydrogen, may also remove oxygen from the nitrobenzene and be oxidized to a higher oxide, which in turn is reduced to the lower oxide by hydrogen. When the temperature is too low the lower oxide may partially reduce the nitrobenzene, but it in turn may not be reduced by the hydrogen and hence its activity may decrease.

From this it would appear that when an oxide catalyst is used for reduction it would work best at that temperature at which the higher oxide is both easily formed from the lower oxide and also easily reduced to the lower oxide by hydrogen. On the other hand when this same catalyst is used for oxidation it should work best at that temperature at which the lower oxide is easily oxidized to the higher oxide, and the latter in turn is easily reduced to the lower oxide. Thus red lead<sup>1</sup> is rapidly formed from litharge at about 450°. At higher temperatures the red lead begins to decompose into oxygen and litharge. So red lead when used as an oxidizing catalyst should act best at about 450°. Then it would be suitable for all those oxidations which would take place best at about 450°, but probably would not be so good a catalyst for oxidations that require a higher or lower temperature.

#### Manganese

The manganese catalyst was prepared by precipitating the hydroxide from a solution of the nitrate by ammonium

TABLE VIII

Catalyst—Manganese.

Rate of flow of hydrogen—17 liters per hour.

Rate of flow of nitrobenzene—4 grams per hour.

Excess of hydrogen—680%.

Temperature of catalyst, °C	Material yield in % of theory
360	84.0
340	85.5
320	83.1
300	79.6
280	67.5
260	28.2

<sup>1</sup> Brown and Nees: Jour. Ind. Eng. Chemistry, 4, 867 (1912).

hydroxide. The hydroxide was then dried at about  $110^{\circ}$  and of course became oxidized to the sesquioxide. Twenty-seven grams of the dry sesquioxide were put in the furnace and reduced and heated in hydrogen to  $435^{\circ}$  and kept at that temperature for 30 minutes. The results of experiments carried out at different temperatures are given in Table VIII.

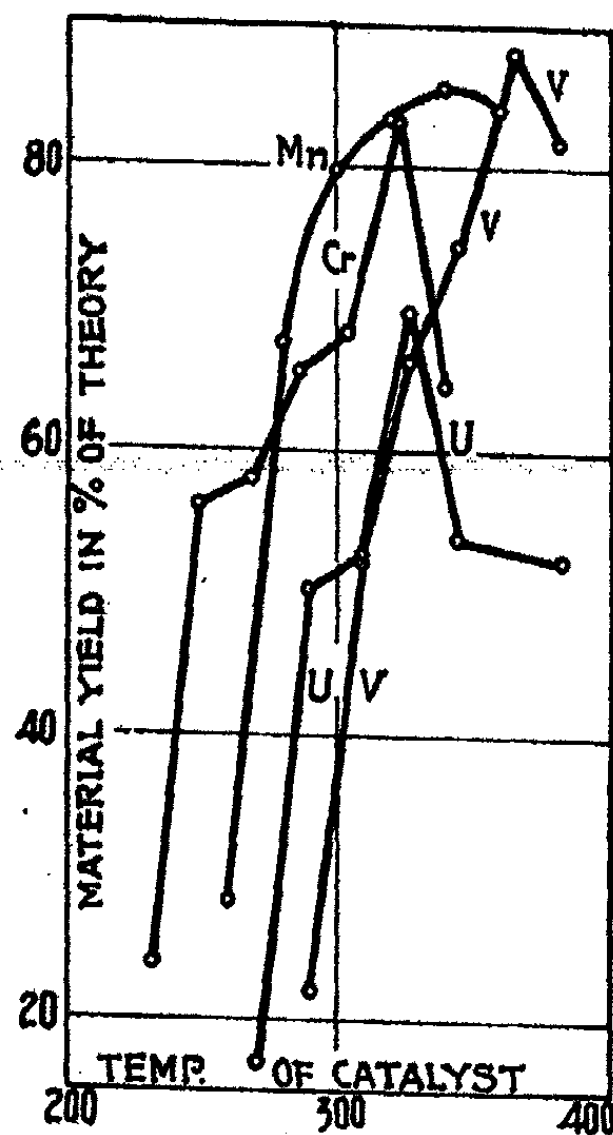


Fig. 4

The results of Table VIII are plotted in curve Mn of Figure 4. From the curve the best temperature with manganese as catalyst is seen to be about  $340^{\circ}$ .

#### Chromium

The chromium catalyst was prepared by precipitating the hydroxide from a solution of the nitrate by ammonium hydroxide. Ten grams of the dried oxide were put in the furnace and reduced and heated

in hydrogen at  $415^{\circ}$  for about an hour. The results of experiments at different temperatures are given in Table IX.

The results of Table IX are plotted in curve Cr of Figure 4. The shape of this curve is quite different from those of the other catalysts. The most favorable temperature falls within narrow limits and the decrease with the higher temperatures is very great. Possibly with slower rates of hydrogen and nitrobenzene the optimum temperature range would not have been so narrow and the percentage yield would have been greater.

TABLE IX

Catalyst—Chromium.

Rate of flow of hydrogen—17 liters per hour.

Rate of flow of nitrobenzene—4 grams per hour.

Excess of hydrogen—680%.

Experiment number	Temperature of catalyst, °C	Material yield in % of theory
201	340	64.5
301	323	83.0
401	304	68.3
501	286	65.5
601	268	58.0
701	250	56.7
801*	250	56.1
901	232	23.8
1001	214	9.4

**Vanadium Oxide**

The vanadium oxide catalyst consisted of 10.5 grams of ammonium metavanadate. This was heated in hydrogen at 420° for one hour. The results with this catalyst at different temperatures are given in Table X.

TABLE X

Catalyst—Vanadium Oxide.

Rate of flow of hydrogen—17 liters per hour.

Rate of flow of nitrobenzene—4.1 grams per hour.

Excess of hydrogen—660%.

Experiment number	Temperature of catalyst, °C	Material yield in % of theory
2P1	345	74.3
3P1	327	66.1
4P1	310	52.0
5P1	290	21.9
6P1	270	14.4
7P1	252	5.6
8P1	382	81.8
9P1	365	88.0
10P1	345	74.3

The results of Table X (except 6P1 and 7P1) are plotted in curve V of Figure 4. The curve is similar to the one for chromium, the most favorable temperature range being like-

\* In experiment 801 a small amount of azobenzene was formed.



wise very narrow. The catalyst in this case is probably a lower oxide of vanadium.

#### Uranium Oxide

The uranium oxide catalyst was prepared by precipitating the hydroxide from a solution of the acetate by ammonia. Twenty-seven grams of the dried hydroxide were put in the furnace and heated in hydrogen at 420° for one hour. The results with this catalyst at different temperatures are given in Table XI.

TABLE XI

Catalyst—Uranium Oxide.

Rate of flow of hydrogen—17 liters per hour.

Rate of flow of nitrobenzene—4.1 grams per hour.

Excess of hydrogen—660%.

Experiment number	Temperature of catalyst, °C	Material yield in % of theory
8N1	310	33.5
9N1	310	52.6
10N1	290	50.1
11N1	270	16.9
12N1	252	7.5
13N1	235	2.5
14N1*	345	49.8
15N1	345	53.9
16N1	327	69.6
17N1	310	55.1
18N1	382	52.3

The results of Table XI are shown in curve U of Figure 4. It will be noted that each time after heating in hydrogen the first experiment is lower than the second. It thus increases in activity with use. This same behavior was also noted with copper as catalyst. In the graph the results of experiments 9N1 and 15N1 are plotted instead of the results of 8N1 and 14N1. The curve for uranium is very similar to those for chromium and vanadium. In fact these three are very similar and are different from the others which are also similar in shape.

\* Prior to experiment 14N1 the catalyst was heated in hydrogen at 420° for one hour.

### Other Catalysts

Twenty grams tungstic acid were put in the furnace and heated in hydrogen to 420° and kept at that temperature for about two hours. Experiments carried out at 310° with 4 grams nitrobenzene per hour and 17 liters hydrogen per hour gave 50.1% yields of aniline. It was not used at higher temperatures, although the yield of aniline would probably have increased with increase in temperature.

Commercial cerium oxalate was also used as catalyst after heating in hydrogen at 420° for one hour. The cerium oxalate contained some lanthanum and the didymiums. An experiment at 358 with 3.9 grams nitrobenzene per hour and 17 liters hydrogen per hour gave a yield of 49.5% aniline.

Calcium and barium oxides were also tried but results were not appreciably higher than those given by the empty iron pipe alone. Commercial tellurium likewise had no appreciable activity. Silica which had been precipitated from a sodium silicate solution with HCl and then treated repeatedly with HNO<sub>3</sub> and evaporated with HNO<sub>3</sub> showed no appreciable activity. With these catalysts the yields obtained were not appreciably more than with the empty iron pipe alone, the results of which were given in the previous paper.

An alumina catalyst, prepared by the method described by Johnson,<sup>1</sup> was used in a glass combustion tube instead of in an iron pipe. Glass is a poorer conductor of heat than iron and as a result the end of the glass combustion tube which extends in the condenser was not kept hot enough to keep the products from condensing in it. So the end of the glass tube was surrounded by an electric heating jacket about 4<sup>3</sup>/<sub>4</sub> inches long and 3<sup>1</sup>/<sub>2</sub> inches in diameter. This kept the temperature in the tube near 200° and prevented the products from condensing in the tube. All the other details of the furnace remained the same. Thirteen grams of the alumina were used. The results are given in Table XII.

<sup>1</sup> Johnson: Jour. Am. Chem. Soc., 34, 911 (1912).

TABLE XII

Catalyst—Alumina.

Rate of flow of hydrogen—17 liters per hour.

Rate of flow of nitrobenzene—3.9 grams per hour.

Excess of hydrogen—710%.

Temperature of catalyst, °C	Material yield in % of theory
290	2.8
327	5.0
364	13.2

Thus alumina in a glass tube showed some catalytic activity. Its action may be looked upon as one of dehydration, since water is one of the products of the reaction and alumina is known to be a good dehydrating catalyst.

#### Summary of Results

1. For the reduction of nitrobenzene cobalt was found to be active at a lower temperature than nickel. However the cobalt contained a little nickel and the nickel a little cobalt.
2. Iron was found to carry the reduction farther than copper but cannot be used below about 300° and at this temperature its action is too vigorous, the reduction being carried on too far.
3. Silver was found to be an excellent catalyst, even better than copper prepared by ignition of the nitrate, because it can be used at a much higher rate of flow of nitrobenzene.
4. Antimony, manganese and chromium were also found to act as catalysts in the reduction of nitrobenzene.
5. The lower oxides of molybdenum, vanadium, uranium, tungsten and cerium also acted as catalysts in the reduction. The activity of the oxides of molybdenum and vanadium was greater than that of the other three.
6. Alumina was found to possess a little activity. Its activity is probably that of a dehydrating catalyst as water is one of the products of the reaction.
7. Commercial tellurium and the oxides of calcium, barium and silicon were not found to possess appreciable activity.

8. It was pointed out that with iron and antimony a part of the reduction was due to the direct action of the metal, an oxide being formed.

9. When antimony was used at a low temperature the catalyst lost its activity, which was restored by heating to 450° in hydrogen. When however antimony was used at about 320° it did not lose its activity with use.

10. In choosing a catalyst for any particular reaction that catalyst should be chosen which works best at the temperature at which the reaction takes place.

*Laboratory of Physical Chemistry  
Indiana University  
Bloomington*

32. 9/6

## THE EFFECT OF LIGHT ON FIBRES DYED WITH A MIXTURE OF CHRYSANILINE AND FUCHSINE

BY W. W. PADDON

Stobbe<sup>1</sup> states that a mixture of chrysaniline and fuchsine fades faster than either dye by itself. An attempt to verify this statement led to an entirely different conclusion.

One gram samples of wool were dyed from the following baths. The total volume of the bath was in every case 250 cc. The wool was entered cold into the boiling bath, removed hot after 45 minutes' boil, rinsed in cold water, and dried in the open room. The following samples were dyed.

TABLE I

No. of sample	Conc. of original bath mg dye per 250 cc	No. of sample	Conc. of original bath mg dye per 250 cc
1	30 mg chrysaniline	4	30 mg fuchsine
2	75 mg "	5	75 mg "
3	150 mg "	6	150 mg "
Dyed in separate baths, first with chrysaniline and then with fuchsine		Dyed in separate baths, first with fuchsine and then with chrysaniline	
7	75 mg chrysaniline 30 mg fuchsine	11	30 mg fuchsine 75 mg chrysaniline
8	30 mg chrysaniline 75 mg fuchsine	12	75 mg fuchsine 30 mg chrysaniline
9	30 mg chrysaniline 150 mg fuchsine	13	150 mg fuchsine 30 mg chrysaniline
10	150 mg chrysaniline 30 mg fuchsine	14	30 mg fuchsine 150 mg chrysaniline
Dyed from one bath, the bath containing both dyes as specified			
15	75 mg chrysaniline 30 mg fuchsine	17	30 mg chrysaniline 150 mg fuchsine
16	30 mg fuchsine 75 mg chrysaniline	18	150 mg chrysaniline 30 mg fuchsine

<sup>1</sup> Zeit. Elektrochemie, 14, 481 (1908).

When the samples that were first dyed in fuchsine were placed in the chrysaniline baths, they bled to a marked degree, showing that to some extent chrysaniline replaces the fuchsine on the fibre. The samples, Nos. 11, 12, 13, 14, had adsorbed less fuchsine than Nos. 4, 5, 6 and 6, respectively, although dyed from baths of the same original concentrations.

These dyed fibres were now exposed to the light from the violet carbon arc of a "Fade-ometer." Three hours' exposure to this light is equivalent to five hours' exposure to Arizona sunlight.<sup>1</sup>

In Table II are given the samples which had shown noticeable fading at the end of the given number of hours.

TABLE II

Exposure	Samples showing noticeable fading
3 hrs.	1-3
6 hrs.	1-3, 14, 15, 18
17 hrs.	1-3, 14, 15, 18
31 hrs.	1-3, 10, 11, 14, 15, 18
100 hrs.	1-3, 10, 11, 14, 15, 18
131 hrs.	1-3, 7, 10, 11, 14, 15, 18
205 hrs.	1-3, 7, 10, 18
	Unfaded, 4-6, 8, 9

The data in Table II show at once that chrysaniline alone on the fibre is more fugitive than any of the mixtures of the two dyes tried. Furthermore the mixed colors fading first are those in which the minimum amount of fuchsine used is present. The samples dyed with fuchsine alone or with mixtures containing an excess of fuchsine over chrysaniline, the fuchsine being applied last, had not faded at the end of 205 hours when the test was concluded.

These results indicate that the fuchsine, which was in itself shown to be relatively fast to light, exerts a protective action against light on mixtures of fuchsine and chrysaniline. A further verification lies in the fact that sample No. 14, which was dyed first in fuchsine and then in chrysaniline, started to fade 25 hours before sample No. 10, on which the fuchsine

<sup>1</sup> Gordon: *Textile Colorist*, Jan., 1921, p. 29.

was applied last. Sample No. 11, dyed last in chrysaniline, faded 100 hours before No. 7 which had been dyed under the same conditions, except that the fuchsine was applied last.

The absorption spectra of solutions of varying concentrations of fuchsine were compared with the absorption spectra of solutions of chrysaniline of the same concentrations and thicknesses. The absorption band for fuchsine solutions extends from the extreme violet end of the visible spectrum into the blue or green depending on the concentration, but in every case except the most extreme dilution the fuchsine band was broader than the broadest chrysaniline absorption band. Since it has been shown that fuchsine alone is relatively fast to light it is safe to say that it protects the chrysaniline and hence a mixture of chrysaniline and fuchsine where the fuchsine is applied last; for it absorbs the light that would be absorbed by the chrysaniline and which would therefore tend to fade the chrysaniline.

Experiments were also carried out on water solutions of the dyes. Solutions of chrysaniline alone and fuchsine alone and of mixtures of the two were exposed to the light of the "Fade-ometer." The chrysaniline solutions alone faded in ten hours while the fuchsine solutions and the mixtures containing fuchsine showed no fading at the end of thirty hours. 5 cc of 3% hydrogen peroxide were now added to each solution (volume originally 10 cc) and the samples again exposed to light. In 5 hours the chrysaniline had not faded further appreciably, but the fuchsine solutions were completely bleached, and the solutions containing fuchsine and chrysaniline had assumed a yellow color, which became less and less pronounced as the exposure to light continued, and which was undoubtedly due to the chrysaniline of the mixture. Chrysaniline is not bleached, under the conditions of the experiments, by hydrogen peroxide while fuchsine is. The hydrogen peroxide first removes the protecting fuchsine and the chrysaniline is then faded by the light.

Exposure to light of samples of wool dyed with both fuchsine and chrysaniline, and of water solutions of the two

dyes demonstrate conclusively the protective action toward light of fuchsine on chrysaniline. The surprising thing about these results is the relative stability of fuchsine. It was supposed that this dye would be much more fugitive than it has turned out to be under these conditions.

This work has been carried out under the direction of Professor Bancroft and was made possible by a grant from the Chemical Foundation.

*Cornell University*

BY THE UNIVERSITY OF MICHIGAN LIBRARY



## NEW BOOKS

*Soil Conditions and Plant Growth.* By Edward J. Russell. Fourth edition. 22 X 14 cm; pp. ix + 406. New York and London: Longmans, Green and Co., 1921. Price: \$5.00. The previous edition was reviewed less than four years ago (20, 525.)—The subject has since grown so much that there are now to be a series of monographs called "The Rothamsted Monographs on Agricultural Science," of which this is the first.

The importance of team work is recognized explicitly by the author, p. 28. "At the Rothamsted Experimental Station, instead of a number of isolated individuals, there is a body of workers investigating the subject, each from his own special point of view, but each fully cognizant of the work of others, and periodically submitting his results to discussion by them. Separate workers investigate, respectively, the bacteria, protozoa, fungi, algae, helminths, and insects of the soil; in addition physical and organic chemists are studying the soil conditions, while others are concerned in the study of the growing plant. A body of workers by harmonious co-operation is able to make advances that would be impossible for any single individual, however brilliant."

There is a very good presentation, pp. 57-77, of the effect of some of the plant foods. With barley grown in sand cultures, the effect of nitrogen supply on the grain is very marked. When nitrogenous food is wholly withheld, the grain formed is only two-thirds of the normal weight per individual. "The first addition of nitrate causes a marked rise in the weight per grain and the proportion of grain to total produce, but successive additions cause no further rise. Indeed other experiments prove that excess of nitrogenous food causes the proportion of grain to fall off somewhat. The leaf and the general character of growth are affected to a much greater extent. Nitrogen starvation causes yellowing of the leaf, especially in cold spring weather, absence of growth, and a poor starved appearance generally: a moderate supply of nitrogen leads to more rapid growth, very useful in cold weather or in case of attacks of insect pests. Abundance of nitrogen, on the other hand, leads to the development of large dark green leaves which are often crinkled, and usually soft, sappy, and liable to insect and fungoid pests (apparently because of the thinning of the walls and some change in composition of sap) and to retarded ripening: the effects resemble those produced by abundant water supply. A series of plants receiving varying amounts of nitrate are thus at somewhat different stages of their development at any given time, even though they were all sown on the same day, those supplied with large quantities of nitrate being less advanced than the rest. If they could all be kept under constant conditions till they had ripened this difference might finally disappear, but in crop production it is not possible much to delay the harvest owing to the fear of damage by autumn frosts, so that the retardation is of great practical importance. Seed crops like barley that are cut dead ripe are not supplied with much nitrate, but oats, which are cut before being quite ripe, can receive large quantities. All cereal crops, however, produce too much straw if the nitrate supply is excessive, and the straw does not commonly stand up well, but is beaten down or 'logged' by wind and rain. Swede and

potato crops also produce more leaf, but not proportionally more root or tuber, as the nitrogen supply increases; no doubt the increased root would follow, but the whole process is sooner or later stopped by the advancing season—the increased root does, in fact, follow in the case of the late-growing mangold. Tomatoes, again, produce too much leaf and too little fruit if they receive excess of nitrate. At the Cheshunt Experiment Station the omission of nitrogen compounds from the fertilizer mixture has caused the yield of fruit to increase 11 percent. On the other hand crops grown solely for the sake of their leaves are wholly improved by increased nitrate supply: growers of cabbages have learned that they can not only improve the size of their crops by judicious applications of nitrates, but they can also impart the tenderness and bright green colour desired by purchasers. Unfortunately the softness of the tissues prevents the cabbage standing the rough handling of the market. These qualitative differences are of great importance in agriculture and horticulture."

The effect of a phosphate on the crop is two-fold. In the early stages of growth it promotes root formation in a remarkable way. "Dressing of phosphates are particularly effective wherever greater root development is required than the soil conditions normally bring about. They are invaluable on clay soils, where roots do not naturally form well, but, on the other hand, they are less needed on sands, because great root growth takes place on these soils in any case. They are used for all root crops like swedes, turnips, and mangolds; in their absence swedes and turnip roots will not swell but remain permanently dwarfed like radishes: the introduction of superphosphate as a fertilizer revolutionized agriculture on some of the heavier soils by allowing better growth of these crops. Phosphates are needed also for shallow-rooted crops with a short period of growth, like barley. Further, they are beneficial wherever drought is likely to set in, because they induce the young roots to grow rapidly into the moister layers of soil below the surface; probably, as Hall has suggested, this explains the marked effect of superphosphate on wheat in the dry regions of Australia.

"Later on in the life of the plant phosphates hasten the ripening processes, thus producing the same effect as a deficiency of water, but to a less extent; for this reason they are applied to the wheat crop in some of the northern districts of England, and the oat crop in the west, to bring on the harvest a few days earlier and obviate risk of loss by bad weather. The northern limit of growth of several crops may in like manner be extended. This ripening effect is well shown on the barley plots at Rothamsted; crops receiving phosphates are golden yellow in colour while the others are still green."

"The effect of potassium compounds is more localized than that of phosphates, so that potash starvation can be more readily detected. The colour of the leaf becomes abnormal; the potash-starved grass plots at Rothamsted have a poor, dull colour, as have also the mangold plots; the leaves also tend to die early at the tips. The stem is weaker, so that the plant does not stand up well. The most striking effect, however, is the loss of efficiency in making starch; either photosynthesis or translocation—it is not yet clear which—is so dependent on potassium salts that the whole process comes abruptly to an end without them. Mangold, sugar beets, potatoes, and other sugar- and starch-forming crops reduce their production of sugar with decreasing potassium supply even before the leaf area has been diminished."

Next to the sugar-producing plants, the leguminosae seem to stand most in need of potassium salts. The potash-starved grass plots at Rothamsted contain notably less clover than those fully manured, the actual depression fluctuating according to the season. Some of the weeds, especially the sorrel, require a good supply of potash. There is some controversy as to whether potassium plays any important part in protein synthesis in plants. In the absence of potassium salts, mitotic cell division does not go to completion; Reed observed that the cell and nucleus both elongate, but actual division does not occur.

"It is not at present possible to say whether all these phenomena are different manifestations of one and the same specific action of potassium in the plant, or whether there are several different causes at work. Zwaardemaker puts forward the interesting suggestion that the potassium ion (which is somewhat radioactive) may be replaced by any other radioactive element, light or heavy, or by free radioactive radiation, provided the doses are equi-radioactive.

"Sodium does not appear to be essential even to salt-marsh plants, although *salicornia* grew better in presence of salt than in its absence. It can partially, but not completely, replace potassium as a plant nutrient; it thus delays the setting in of potash starvation, but will not keep it off altogether. Hellriegel found that sodium salts always gave increases in crop even when potassium salts were present in quantity."

Forbes recognizes three classes of peat in Ireland, p. 135:

1. Mountain peat, corresponding with the wet peat lowland moss of the British Committee, which originates wherever the conditions are too sterile or the subsoil too impervious or water-logged to allow deep-rooted vegetation to flourish, and where, therefore, shallow rooted plants come in and, on dying, form a layer of organic matter on which sphagnum, cotton grass, etc., begin to develop. This occurs above the 800 feet level in most parts of Ireland, but in the west it often covers the entire surface down to the sea-level.

2. Marsh peat, corresponding with the British fen, which arises from reeds, sedges, rushes, etc., and which, so long as the water contains lime and nutrient salts, is as favourable a medium for plant growth as ordinary soil, though it affords no root-hold for trees, so that they are liable to be overturned in strong gales. This kind of peat forms the basis of all the low-land bogs in Ireland and of many of the small bogs in mountain districts.

3. This marsh peat finally becomes so consolidated with time and pressure that it loses connection with the water table, and a surface swamp forms on which a sphagnum bog of the "mountain type" arises. This, therefore, becomes similar in character to the first group: it differs, however, in its uniformity of growth, being higher in the centre than at the margins where soil water can get in and where, therefore, decomposition is more rapid.

A sandy soil may, without any change in type, be a dry and barren heath, if underlain near the surface with rock or gravel; a highly fertile fruit or market-garden soil if sufficiently deep; or a stagnant marsh giving rise to peat, if so situated that water accumulates and cannot drain away, p. 302.

The simplest case of a calcareous soil is presented by soils where the calcium carbonate exceeds about ten percent and dominates every other constituent, becoming the controlling factor in determining the soil properties, p. 304. "The conditions here seem to be extraordinarily well suited to plant

and animal life. Bacteria are numerous and active, rapidly oxidising organic matter. Hosts of animals, wireworms, earthworms, and others live in the grass land, and even get into the arable land, honeycombing the soil with their passages, puffing it up or 'lightening' it considerably, and encouraging the multiplication of moles. Rabbits abound in dry places. Vegetation is restricted on thin exposed soils, but becomes astonishingly varied where there is sufficient depth of soil and shelter to maintain an adequate water supply. Ash is the characteristic tree in the north and west, and beech in the south of England, and there is a great profusion of shrubs—buck thorn, spindle, guelder rose, dogwood, hawthorn, hazel, maple; and especially of flowering plants—scabious (*S. Columbaria*), the bedstraws, vetches, ragwort, yellow wort (*Chlora perfoliata*), salad burnet (*Poterium sanguisorba*), lady's fingers (*Anthyllis*), *Linum catharticum*, *Bromus erectus*. Still more remarkable, perhaps, is the fact that a few plants—the so-called calcifuges—do not occur. Where the amount of calcium carbonate is too high plants tend to become chlorotic; Chauzit showed that vines suffered badly when 35 percent, or more was present, but not when the amounts fell to 3 percent. Mazé attributes part of the action to the rendering insoluble of zinc, manganese, etc., necessary for complete growth.

"Investigations in Porto Rico, where a considerable portion of the arable land is sufficiently calcareous to produce nutritional disturbances in crops, show that bush beans (*Phaseolus mungus*) and radishes are unaffected by even 35 percent of  $\text{CaCO}_3$ ; sunflowers, soy beans, and sugar canes are somewhat depressed; while sweet cassava (*Manihot palmata*), rice and pineapples were considerably depressed by this amount. The amount of nitrogen, potash, and phosphoric acid in the various crops was apparently unaffected by the carbonate, but the iron was notably depressed." *Wilder D. Bancroft*

**Animal Proteins.** By Hugh Garner Bennett. 21 × 14 cm; pp. xiii + 287. New York: D. Van Nostrand Company, 1921. Price: \$3.75.—The title is a bit ambitious because the author really discusses leather and glue. The subject is presented under six heads: hides for heavy leather; skins for light leather; chrome leathers; miscellaneous tannages; gelatine and glue; miscellaneous proteins and by-products.

The author classifies proteins, on the basis of their behavior towards water, into albumins, keratins, and gelatins, p. 3. "Cold water dissolves the albumins, does not affect the keratins, and only swells the gelatins. The behaviour in hot water confirms and elaborates the classification. When heated in water, the albumins coagulate at temperatures of 70–75° C, the gelatins (if swollen) dissolve readily, whilst the keratins only dissolve at temperatures above 100° C. Albumins and keratins may be distinguished also from gelatins by adding acetic acid and potassium ferrocyanide to their aqueous solutions. Albumins and keratins give a precipitate, gelatins do not. Another distinguishing reaction is to boil with alcohol, wash with ether, and heat with hydrochloric acid (S.G. 1.2). Albumins give a violet colour, keratins and gelatins do not."

While one will agree with the author that tanning is a problem of colloid chemistry, it does seem as though the theory of vegetable tanning could be stated more clearly. The reviewer fears that neither the tanner nor the colloid chemist will get very much from the author's description, p. 41. "Vegetable

tannage is a phenomenon of colloid chemistry. The old arguments as to whether tanning was a chemical or a physical process have been rendered obsolete by the advent of a new set of explanations, which, though shedding light on many obscure points, have enormously increased the complexity of the problem. In vegetable tannage an emulsoid gel (pelt) is immersed in a complex emulsoid sol (tan liquor), which immersion results, not in simple action or change, but in a series of changes.

"One of these changes is *adsorption*. Pelt is a gel which possesses a great development of surface. It not only exhibits like gelatine the phenomenon of imbibition and dehydration to a very marked extent, but also possesses a very fine fibrous structure due to its organic origin; thus pelt possesses an enormous specific surface, further intensified by the preparation processes previously discussed, which split up the hide fibres into smaller bundles and into much finer constituent fibrils. Tannins, on the other hand, are hydrophile colloids which in water form emulsified sols, and which may thus be expected to exhibit the phenomenon of adsorption. A tan liquor usually contains several tannins in addition to other closely similar substances, also in colloidal solution, and is therefore a sol of considerable complexity. The immersion of pelt into a tan liquor results in an adsorption, which consists essentially in an inequality of concentration in the sol, the greater concentration being at the interface. This inequality between the surface concentration and the volume concentration of the sol, is due primarily to considerations of surface tension and surface energy, and exists before the immersion of the pelt. The surface layer having excess over the volume concentration, any considerable extension of surface in a fixed volume of sol must produce a very considerable decrease in the volume concentration. This is what occurs when pelt is immersed in a tan liquor, the immersion being the considerable extension of surface. It should be especially remembered that the inequality of concentration is in the sol, on the liquid side of the interface. In adsorption, the substance adsorbed, i. e., the excess at the surface, is too frequently regarded as bound to the solid immersed. This is because the excess is in the layer which wets the solid and remains wetting it when the solid is removed. Thus the immersion of pelt produces primarily only a change in the distribution of the tannins in the liquor. It follows from this that the adsorption is an equilibrium and that if the sol be diluted, the equilibrium will become the same as it would have been by immersing the pelt directly into the dilute solution. Thus, if pelt be first immersed in one tan liquor and then into a weaker one it will yield tan to the latter solution."

"In addition to adsorption, there is another phenomenon of colloid chemistry in operation, viz., the *mutual precipitation* of the solid in the liquid by the gels in the hide. In most sols the disperse phase is electrically charged. The sol therefore possesses electric conductivity, and migration occurs in the electric field to the cathode or anode according to the nature of the charge. Oppositely charged sols precipitate one another, the precipitate containing both colloids. The maximum precipitation occurs when the + charge of one sol exactly equals and neutralizes the - charge of the other. There is thus an electrical equivalence; an amount of sol which is equivalent to a given amount of the other. This is not a chemical equivalence, however, and the precipitate is not a chemical compound in spite of its fairly constant composition. The composition of the

precipitate, indeed, is not quite constant, for the optimum precipitation may not correspond exactly with the electrical equivalence, being influenced by the number of particles required, their size (dispersity), the rate of mixture, and the relative concentrations of the sols. This mutual precipitation is exhibited by emulsoids as well as suspensoids, but the charge (+ or -) on an emulsoid is in many instances largely an accidental matter, being determined by the medium in which it happens to be, its normal condition being electrical neutrality. Gelatin and pelt are such emulsoids, and a positively charged gelatin sol has been observed to precipitate a negatively charged gelatin sol. It is thought, however, that gelatin is primarily a positive sol. Pelt (whether delimed or not) is rapidly acidified by the quickly penetrating and strongly adsorbed organic acids of the old tan liquors and becomes positively charged before the tannins are adsorbed. The positive charge increases with the acidity of the liquor. Other emulsoids are not electrically neutral, but are electrically charged and exhibit considerable conductivity. Into this class fall the tannins, and in tanning it is thought that there is a mutual precipitation of the negative tanning sol with the positive hide gel, the precipitation of the negative sol being favoured by the acid condition of the liquor. The effect of increasing acidity soon falls off, however, as a saturation limit is soon reached. This mutual precipitation of colloids in tanning is in reality but an extension of the adsorption theory, which explains the predominant effect of  $H^+$ , and  $OH^-$  on the electric charge by stating that these ions are more readily adsorbed than other ions, and that as  $OH^-$  is more readily adsorbed than  $H^+$  most sols are negative to water.

"In addition to the adsorption phenomena described, there are in vegetable tannage *secondary changes* which are slow and 'irreversible.' These changes are obscure and are difficult to investigate. Oxidation, dehydration and polymerization have all been suggested but there is little direct evidence. Certain it is, however, that time renders the tannage more permanent. It perhaps should be pointed out that in the very strongest tan liquors the viscosity of the tannin sol is so great that adhesion would be a better term than adsorption. There is no abrupt division between the two phenomena."

The same remarks hold for the theory of chrome tannage, p. 129. "As to the theory of chrome tanning there is still considerable difference of opinion and much room for experiment. Some leather chemists regard the tannage as differing essentially from the vegetable tannages. Mr. J. A. Wilson has even suggested that the proteid molecule is in time partly hydrolyzed with the formation of a chromic salt with the acid groups. The author, however, strongly favours the view that in chrome tanning changes take place which are closely analogous to those which occur in vegetable tannage, the differences being mainly of degree. Thus the hide gel is immersed into a lyophile sol—the chrome liquor—and there follows lyotrope influence, adsorption, gelation of the tanning sol, as well as diffusion into the gel, and finally also, probably, precipitation of the tanning sol at this interface.

"In chrome tannage the lyotrope influence is much more prominent than in vegetable tannage, but the effect is in the same sense, viz., to reduce the imbibition of the hide gel. Thus the potassium sulphate in a chrome alum liquor has its own specific action of this kind and contributes to the leather formation.



Unhydrolyzed chromium sulphate and the sodium sulphate formed in 'making basic' act also in the same sense.

"The tanning sol is probably chromium hydrate, formed by the hydrolysis of chromium sulphate: it is a lyophile or emulsoid sol and is in consequence very strongly adsorbed by the hide gel. This adsorption, involving a concentration of lyophile sol, is the first stage in gelation, which occupies a relatively more prominent place in chrome than in vegetable tannage. Some diffusion into the gel occurs, and both the gelatin and diffusion of the sol are affected by lyotrope influence, but to a greater extent than in the vegetable tannage. Thus far the analogy is almost complete.

"There remains the question of the precipitation of the tanning colloid at the interface. This is a point which has not yet been thoroughly investigated, and which offers considerable difficulty to a clear understanding, but the matter may be probably summarized thus: the adsorbed chromium hydrate is precipitated at the interface of gel and sol to some extent, chiefly through the neutralization of its charge by the oppositely charged ions of the electrolytes present, but possibly also—in the last stages of manufacture by the mutual precipitation of oppositely charged gel and sol."

On p. 203, the author states that "On this view, we must regard a gelatine gel as a continuous network of water under great compression, and in this network are zones of still greater compression, which surround the particles of the disperse phase—the gelatine itself, and zones of less compression which in a weak gel, at any rate, have a compression equal to or much the same as the normal state of compression in water."

"However these things may be, the fact of water compression determines the rigidity of the gel, and the changes in this compression of the continuous phase determine the surface tension resultant which hinders swelling, and which is one of the two main factors fixing both the rate at which gelatine swells in water, and the final volume attained by the gel."

"Before leaving this point, it is desirable to note the effect on the swelling of gelatine of the extremes of this lyotrope influence. Substances like iodides, thiocyanates and urea prevent a gelatine sol from setting to a gel at all, and a piece of gelatine in such solutions swells rapidly until it solates. On the other hand, sulphates, tartrates, etc., make a stiffer gel on account of the enhanced compression. Gelatine in such solutions may swell, but at a much slower rate than in water and with a decreased maximum extent. A gelatine gel may in such solutions not only fail to swell at all, but actually contract and in some cases, indeed, be practically dehydrated. If a gel be in a very concentrated solution of such a substance, it may be that the lyotrope compression in the external solution is greater than the compression in the dispersion medium of the gel; in which case the surface tension effect is reversed, and the external solution tends to increase in volume and the gel to contract. Hence we find that the saturated solutions of such substances as ammonium sulphate and potassium carbonate will dehydrate a gel almost completely, and will also, by a similar action on pelt, make a kind of white leather. It is important to remember this contractile effect of strong solutions of salts, because it is very easy to confuse this effect with a similar result produced in another manner, viz., by a reduction of the force tending to swell."

It will be obvious from these quotations that the author has made a brave attempt to present the subject of leather and glue from the view-point of colloid chemistry. Unfortunately, he is like most of us in thinking that a new word is in itself an explanation. Also, he takes himself very seriously and his colloid chemistry is a bit rigid. He probably would not admit that chromic oxide can adsorb ferric oxide, because they are both positively charged colloids. On p. 210 he says that "a very important feature of the colloid state is that the particles of the disperse phase appear to possess an electric charge, and, if this charge be removed, a colloid sol no longer remains such, but precipitates, flocculates, coagulates, etc." This is perfectly true for a colloidal solution stabilized by adsorption of an ion; but it is not true when the colloid is peptized by a liquid. It is difficult, for instance, to see how the author's view-point could be applied to colloidal solutions of cellulose nitrate in amyl acetate or acetone.

The book is eminently praiseworthy as being the first attempt to present the subject from a common-sense point of view. That the effort is not more of a success is not entirely the author's fault. We are very much up in the air on the subject of jellies in general and of gelatine in particular. It is to be hoped that the author will rewrite this book when our knowledge of the subject has increased. Even if circumstances prevent this, he will always deserve credit as the pioneer in this line.

*Wilder D. Bancroft*

*Soaps and Proteins.* By Martin H. Fischer. 23 × 15 cm; pp. ix + 272. New York: John Wiley and Sons, 1921. Price: \$4.00.—The author states quite frankly in the preface that *Science* and *The Chemical Engineer* were the only scientific journals willing to publish any portions of the fragments of which the book is composed. We are not told whether these two are now wiser.

The subject is treated under three main heads: the colloid chemistry of soaps; the colloid chemistry of soap manufacture; the analogies in the colloid chemistry of soaps, protein derivatives, and tissues. On p. 19 we read that "sodium caprate yields a solid gel if 500 cc of water are present to the mol of soap. As we mount in the acid series, the water-holding capacity grows tremendously. One mol of sodium laurate will hold four liters of water; the same amount of sodium myristate, twelve liters; of sodium palmitate, 20 liters; of sodium margarate, twenty-four liters; of sodium stearate, twenty-seven liters; and of sodium arachidate, the enormous value of thirty-seven liters." This quotation shows the author's dramatic skill, the enormous value corresponding to a little under a one percent solution.

On p. 49 is the impressive and italicized statement that, when sodium linolate, sodium oleate, and sodium stearate are dissolved in different alcohols, the soap dissolves first in the lower members of the alcohol series and last in the uppermost, while, upon lowering the temperature, the gels formed first in the upper alcohols and last in the lowest members of the series. Most people would have said that the solubility (or peptization) decreases with increasing carbon content of the alcohol. On p. 69 the author says: "We are not unaware that the concept 'solution' needs itself to be defined. While the field of 'solution' constitutes slippery ground, we accept, for pragmatic reasons, as characteristic of the 'true' solution, the teachings of Wolfgang Ostwald and P. P. von Weimarn, who define such solutions as dispersions of A in B with the degree of subdivision



measurable in molecular or smaller values. To express the matter in the terms of A. P. Mathews, we may say that A is dissolved in B or *vice versa* when the solvent has overcome the cohesive forces of the dissolved substances. As Mathews has shown, the forces of cohesion operate within molecular dimensions."

There is a characteristic paragraph on p. 75. "Some years ago we showed in the case of gelatin, that the 'swelling' of this substance and its 'liquefaction' are not identical processes, and that the latter is not a mere continuation of the former. When ordinary gelatin is thrown into water, it swells up somewhat; but the amount of this swelling is enormously increased if a little acid is added to the water. If liquefaction were a mere continuation of this swelling, then the addition of a little acid to a gelatin near its gelatin point ought to make it set. As a matter of fact, not only does this not happen, but the addition of such acid to a previously solid gelatin makes it liquefy. As maintained at that time, an increased 'swelling' was declared to be an increased capacity for taking up the solvent; an increased tendency to liquefy, the expression of an increase in the degree of dispersion of the colloid material."

At first the reviewer thought that this must be a typographical error; but the author repeats elsewhere the extraordinary statement that if liquefaction is a continuation of swelling, addition of acid to a gelatine solution should make it set. The setting-up and knocking-down of straw men is hardly a legitimate scientific occupation. The curious thing about it all is that apparently some people are still impressed by the author, though the number is decreasing steadily.

The book is padded thoroughly with tables, graphs, and half-tones. Some of the half-tones are very good; but most of them show practically nothing.

*Wilder D. Bancroft*

*Flüssige Kristalle und ihr scheinbares Leben.* By O. Lehmann. 23 X 16 cm; pp. 72. Leipzig: Leopold Voss, 1921. Price: paper, 30 marks.—By means of about one hundred and sixty cuts the author brings out the variety of forms which liquid crystals can adopt under different conditions of stress. Many of these are so like the forms of living matter that Haeckel at one time was inclined to believe that these were actually living crystals. The author points out that in the living organisms we find a number of these materials which form liquid crystals, such as oleates, compounds of cholesterol, lecithin, phrenosin, cholin, etc.

On p. 12 there is brought out the very interesting fact that it is possible to make crystals of ammonium nitrate which are plastic like lead or yellow phosphorus and which can be bent into a ring shape. When one of these rings is examined under crossed nicols, it appears that the bending has caused no change in the structure and is not due to the breaking down of the crystals. On p. 14 we learn that the thrust given by crystals of *p*-azophenetol in changing from one modification to the other may be sufficient to shatter the glass tube in which they are, even though the new modification occupies a lesser actual volume than the one from which it is formed.

The author has taken moving picture photographs of all his results and it is possible in Germany to obtain a film showing the changes. It must be a very interesting one and should be of distinct interest to the universities.

*Wilder D. Bancroft*

# THE PRESSURE-VOLUME RELATION OF SUPERHEATED LIQUIDS

BY K. L. WISMER

## 1. Introduction

The phenomenon of superheating is often observed in the laboratory in the bumping that occurs when a liquid is heated in a clean test tube or beaker. Closely related to this phenomenon is the "mechanical stretching" of liquids which has been investigated by Berthelot,<sup>1</sup> Worthington,<sup>2</sup> Dixon,<sup>3</sup> and J. Meyer,<sup>4</sup> the latter having succeeded in subjecting ether to a stretching, or negative pressure, of 72 atmospheres. But the extent to which liquids can be superheated at atmospheric pressure has not received much consideration. Conditions corresponding to the minimum point of van der Waals' P-V curve have been attained by J. Meyer<sup>5</sup> in the case of ether, by reducing the pressure on the liquid to zero at 115°, but he states that he was not able to reach zero pressure above 115°. No serious attempts have been made to reduce the pressure of the liquid below the minimum point of van der Waals' curve.

The present research is an attempt to obtain actual P-V curves at high temperatures to see whether the curve shows any tendency to bend more sharply as the limit of superheating is approached; to find what degree of superheating may be attained; and, if possible, to discover what initiates the explosion.

From the equation  $(P + a/V^2)(V - b) = RT$ , by obtaining the relation between  $T$  and  $V$  for the condition of the minimum point, and selecting a number of volumes, a projection of the trough of van der Waals' P-T-V surface on the P-T plane

<sup>1</sup> Ann. Chimie, 30, 232 (1850).

<sup>2</sup> Phil. Trans., 183, 355 (1892).

<sup>3</sup> Proc. Roy. Dublin Soc., (2) 12, 60 (1909-10).

<sup>4</sup> "Zur Kenntnis des negativen Druckes in Flüssigkeiten" (1911).

<sup>5</sup> Zeit. Elektrochemie, 18, 709 (1912).

can be drawn. Taking the data for ether, for which most of the measurements were made, a curve was drawn in this way, Fig. 1, Curve II. The values for the constants  $a$  and  $b$  were calculated from Ramsay and Young's values for the critical temperature and pressure according to the relationships:

$$a = \frac{27 T_c^3}{64 R^2 P_c}; \quad b = \frac{T_c}{8 R P_c} \quad \text{Using } T_c = 194.4 \text{ C.,}$$

$$P_c = 35.61, \text{ and } R = 0.003764, \text{ then } a = 0.03668 \text{ and } b = 0.006177.$$

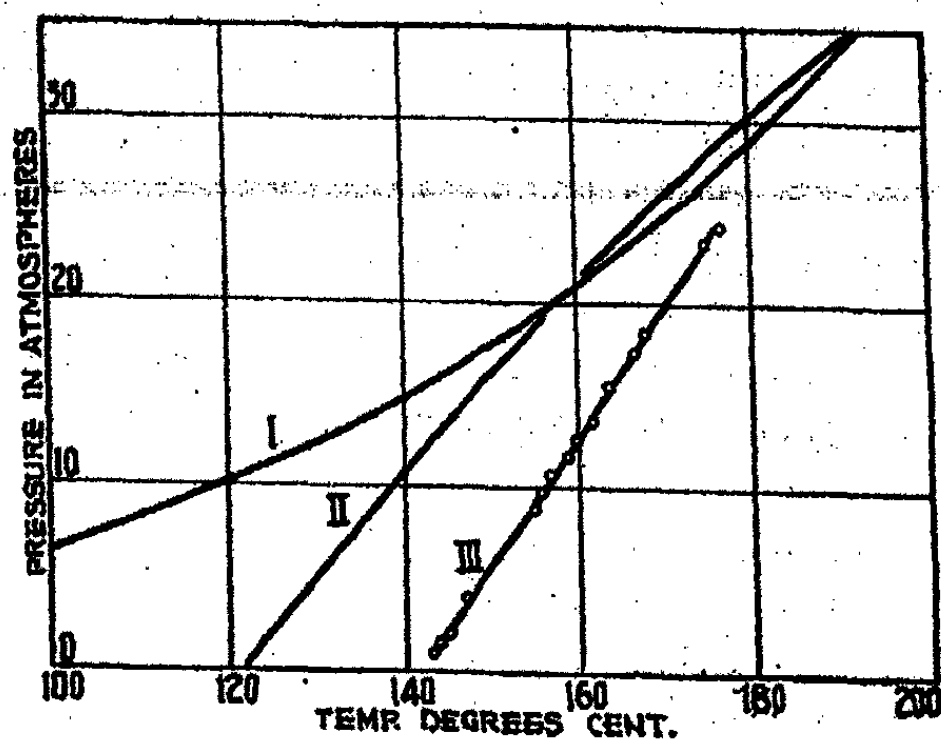


Fig. 1

- I Vapour Pressure Curve
- II Minimum-point Curve
- III Lowest Pressures reached experimentally

From this graph it will be noticed that on the basis of van der Waals' equation, the highest temperature for liquid ether at one atmosphere pressure is  $123^\circ$ . This was remarked by J. Meyer (see above) who, however, by using different values for his constants calculated  $115^\circ$  as the maximum temperature for zero pressure (corresponding to  $117^\circ$  at 1 atmosphere).

## 2. Preliminary Experiments

Ether, ethyl chloride and isopentane were chosen for study because of their low boiling points and because their critical temperatures and pressures are comparatively low.

A few preliminary experiments were carried out to find the highest temperatures to which each of these liquids could be heated at atmospheric pressure; and to find also the length of time they could be kept under atmospheric pressure at different temperatures, so that a temperature could be chosen at which there was a reasonable probability of the liquid holding for a sufficient time to make quantitative measurements.

The ether used throughout the experiments was Kahlbaum's, "über Natrium destilliert." This was again distilled over sodium to free it from all traces of water, and was kept in a number of small glass-stoppered bottles. Immediately before being used it was boiled to drive out absorbed gases.

The ethyl chloride was Hedley's C. P. "For general anaesthesia." Sp. Gr. 0.920.

The isopentane was Kahlbaum's, B. P. 29°.

*Apparatus.*—The form of apparatus used is illustrated in Fig. 2. Pressures up to 50 atmospheres are obtained by

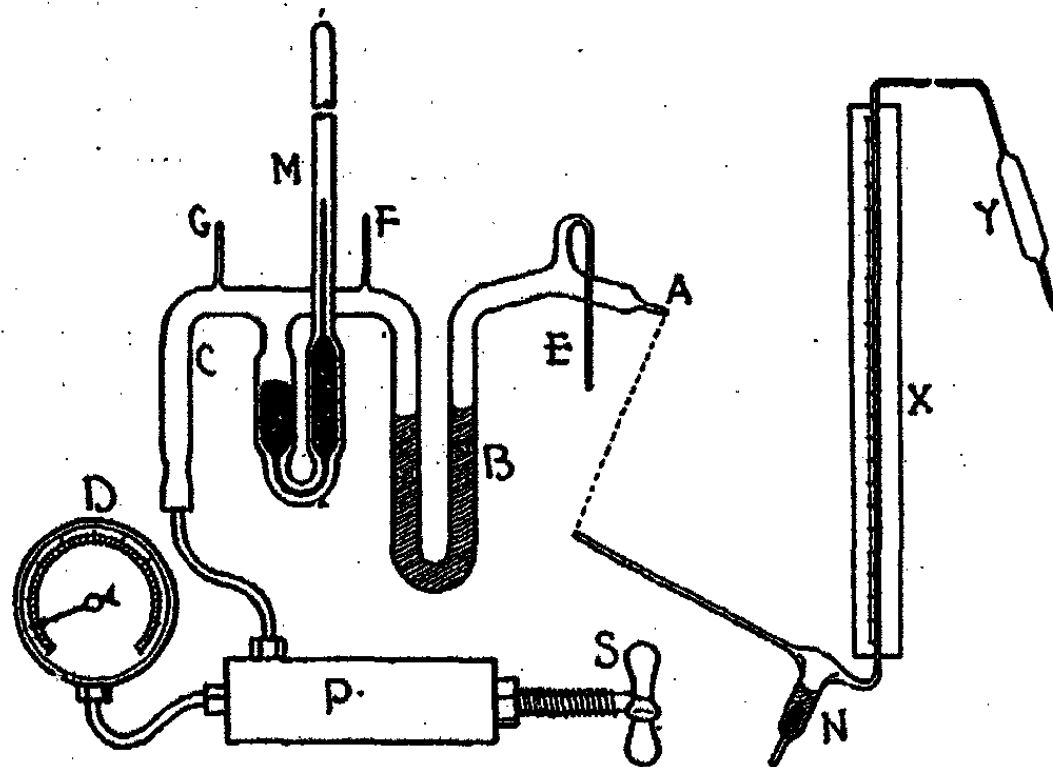


Fig. 2

means of a Fritz Köhler pressure machine, in which a steel rod, S, screws into a cylinder, P, filled with Russian paraffin oil. The pressure is transmitted to the glass part of the

apparatus by a coil of small bore copper tubing. Another coil of copper tubing connects with the pressure gauge D. The liquid under investigation is contained in a capillary U-tube attached at A (not shown in figure). This is separated from the oil in C by a trap of coloured water in the U-tube B. An air-manometer, M, is necessary to indicate atmospheric pressure since the gauge D has a large zero error. E, F and G are tubes used in filling the apparatus with oil, water and the liquid being studied. A tin vessel of 2 liters capacity, covered with two layers of asbestos paper and filled with Russian paraffin oil, served as a thermostat. It was stirred by a motor, and the temperature was kept constant to within  $1/10^\circ$  by a gas thermo-regulator.

Ether and isopentane were introduced into the capillary U-tube by dipping the turned-down tip into a dish of the liquid, and applying suction at E. Both open tips were then sealed off with a blow-pipe with the liquid as close to the end of the tube as possible, so that the imprisoned gas was for the most part vapour from the liquid, and thus easily compressible to liquid again. To fill with ethyl chloride, which boils at  $12.5^\circ$ , the filling-tip E was replaced by a thistle tube into which a few cc. of the liquid were poured and allowed to run down into the capillary by gravity, the tube being kept cold by running tap-water. After breaking off the capillary neck of the thistle tube, the open tips were sealed by touching with the molten end of a glass rod. With every filling the strength of the seal was tested by applying 50 atmospheres pressure.

*Qualitative Results.*—Ether was the first liquid investigated. The capillary U-tube was immersed in the thermostat at  $120^\circ$ , under pressure of 20 atmospheres. The pressure was then quickly reduced to 1 atmosphere; the ether exploded in 5 secs., the time being noted with a stop-watch. With this apparatus the same filling of liquid may be used time after time, the formation of vapour in the U-tube merely sending up the mercury column of the manometer until the vapour-pressure is approximately reached. A number of trials were made with increasing temperatures, and it was

soon observed that while the first attempt at 120° resulted in an explosion after 5 secs., after repeated trials at 125° it was possible to keep the liquid phase at 120° and atmospheric pressure for as long as 60 secs. This led to the installation of a second higher temperature thermostat for the purpose of "training up" the tube or ether, or whatever it is that favourably influences the time-period and temperature of superheating. Finally after a great number of attempts, by a previous heating to 175° under 30 atmospheres pressure, it was possible to maintain the liquid state for 15 secs., at a temperature of 140° and atmospheric pressure. The highest temperature reached in the course of the whole research was 143° for 1 second.

Subsequent work seemed to indicate that the same favourable conditions were obtained simply by a long heating of from 2 to 3 hours, and that a greater superheating under pressure was not essential. Glass tubing particularly free from inclusions of long drawn-out air bubbles as a general rule gave the best results; and it was invariably noticed that a tube which had not had a strong heating to redness prior to filling with liquid could not be depended upon. Also, a number of experiments point to a gradual deterioration, either in the tube or the ether, after 20 or 30 explosions.

However, the very erratic behavior of the tubes makes it difficult to draw more than the above few conclusions from the large number of experiments performed. Moreover, this aspect of the problem is the subject of a special investigation by Mr. Gilbert in this laboratory.

TABLE I

Substance	B. P.	Highest temp. reached at 1 atmosphere	Press. for min. pt. at highest temp.*	Vap. press. at highest temp.
Ether	35° C.	143° C.	12.5 atm.	15.4 atm.
Isopentane	29°	136°	11.0	14.3
Ethyl chloride	12.5°	126°	14.0	20.0

\* Determined from Curve II, Fig. 1, and from similar curves for isopentane and ethyl chloride.

The highest temperatures reached with ether, isopentane and ethyl chloride, together with the vapour-pressures and the pressures at the minimum points of van der Waals' curve at these temperatures, are given in Table I.

A few experiments were made with ether to determine the lowest pressures that could be reached at temperatures above 143° without immediate explosion occurring. The results are shown in Curve III, Fig. 1. The points are almost on a straight line pointing to the critical point in one direction and very nearly to the -72 atmosphere point of Meyer, at ordinary temperature. Although the latter must be more or less a fluke, the general position of the points in relation to the vapour-pressure curve (I, Fig. 1) can be accounted for by a simple assumption as to the size of the nuclei which are visible both in liquids and on the glass walls under the ultra-microscope, and round which the initial bubbles may be assumed to form. This, however, is also the subject of another investigation in this laboratory.

### 3. Quantitative Measurements of Volume

The liquids for which P-V curves were obtained were ethyl ether and ethyl chloride. The limited supply of isopentane gave out before a successful result was obtained.

Ether was again the first liquid to be investigated quantitatively, and the details of the method will be described for this substance. In making measurements of volume to secure data for a P-V curve, the ether was heated in a thick-walled tube or bulb connected to a fine capillary tube. The obvious method of measuring the volume of the heated ether by separating it from the oil of the pressure machine by a column of mercury, or other insoluble liquid, could not be used because the extent of superheating was much reduced by contact with both mercury and water. After a number of unsuccessful attempts to isolate a quantity of ether by various means and to determine its volume at atmospheric pressure, the following method was adopted in which the contact point between mercury and ether was *outside* the thermostat. With the contact

point at room temperature, there was no greater probability of an explosion than if the capillary were filled only with ether.

*Method.*—The method can best be explained by an example. At  $133.8^{\circ}$  and 20 atmospheres, the heated portion of ether occupies that part of the bulb and tube between  $c$  and  $d$ , shown diagrammatically in Fig. 3.  $bc$  is a length of very fine capillary tube extending out from the thermostat two or three inches, in which there is a temperature gradation from  $133.8^{\circ}$  at  $c$  to  $20$  at  $b$ . The end of the mercury thread



Fig. 3

stands at  $a$ , while  $ab$  is a section of capillary tube containing ether at room temperature. When the pressure is reduced to 1 atmosphere, a small amount of ether issues from the bulb, and the mercury stands at  $a'$ . The volume  $aa'$ , when corrected to the temperature of the thermostat, represents the volume increment for 19 atmospheres. The application of this method involves a number of corrections which will be dealt with later.

*Apparatus.*—For the quantitative measurements, the pressure machine and manometer were the same as already described. The bulb Y, Fig. 2, is made of heavy glass tubing, about 5 cm. long, with inside and outside diameters of 5 mm. and 8 mm., respectively. This is connected by fine-bore capillary tubing to a section of fairly uniform tubing, X, of about 1 mm. bore and 2 mm. outside diameter, to which a mm. scale is attached, and into which mercury is introduced for taking readings. This in turn is connected to the U-tube B by a flexible capillary, AN, about one meter long. During the process of "training up" the bulb, the mercury is kept in a side-tube, N, with a layer of water separating it from the ether, which now fills the bulb and the whole length of tube to the water-trap B. In this way a number of explosions



may be allowed to occur without churning up the mercury meniscus, and without allowing ether to touch the mercury and tarnish its surface before the actual readings are made. When the behavior of the bulb indicates a good chance of the explosion holding off long enough to secure a reading at atmospheric pressure, the temperature of the bulb is raised about  $10^{\circ}$  while the pressure is kept at 25 atmospheres, and the side-tube N is pulled forward and upwards (the flexibility and torsion of the capillary line allows this), until the mercury runs down into the bend of the tube, and closes off a portion of ether in the tube and bulb. On cooling the bulb again to the temperature of the thermostat, the mercury is drawn up into the capillary X in readiness for readings. Starting with, say, 50 atmospheres, the position of the mercury column is noted at intervals of 5 atmospheres. One or two explosions after the introduction of the mercury usually rendered the apparatus unfit for further use, and the tubes and bulbs had to be remade and refilled.

It may be mentioned that while no bulbs ever burst during the experiments, a bulb purposely broken in the thermostat scattered the oil for about 6 feet in all directions, and badly distorted the tin vessel. As a protection to the experimenter, the thermostats were housed in a case of wire-reinforced plate glass, with a slot at the side through which the bulbs could be manipulated.

*Measurements and Corrections.*—At the conclusion of a set of readings, the volume of the bulb (*c* to *d*, Fig. 3) was calculated from the weight of mercury filling it when at the temperature of the bath, and thus the correction for the thermal expansion of the glass becomes unnecessary. The tube X in which readings were taken was calibrated by means of a thread of mercury.

Employing the foregoing method, corrections must be made for:

(1) *Enlargement of bulb due to pressure:* The bulb and part of the graduated stem were filled with mercury, and placed in the thermostat. The apparent compression, less the known

compression of mercury, gave the expansion of the glass due to pressure. This correction, at most, amounts to 0.07%.

(2) *Expansion of volume on reducing pressure:* This portion of ether was at room temperature, and the correction was easily made from Amagat's compressibility coefficients.<sup>1</sup> It is at most 0.05% of the total volume, and therefore practically negligible.

(3) *Temperature correction for volume aa':* Since no thermal expansion data were available for the high temperature and low pressure conditions of this research, use was made of the values for the volume of one gram of ether at high temperatures and the corresponding vapour-pressures determined by S. Young.<sup>2</sup> For ethyl chloride a special experiment was made at the vapour-pressure. Thus at only one pressure does the correction hold strictly true, the corrected values of the volume aa' being slightly too large for pressures above the vapour-pressure, and slightly too small below the vapour-pressure.

(4) *Temperature change on adiabatic expansion:* This correction is required only in the last pressure reductions where the liquid is in an unstable state and there is no time to wait for temperature equalization between bulb and bath. To determine the temperature change on adiabatic expansion, a long thin-walled glass bulb with fine capillary to serve as an air-thermometer was sealed into a larger bulb which was attached to the pressure machine and filled with ether. A short thread of oil was inserted in the thermometer capillary to register temperature changes. A rise or fall in pressure of 20 atmospheres gave a sharp displacement of the oil of 2 mm., which slowly returned to its original position after 50 secs. This displacement corresponded to a temperature change of 0.6°. This value, along with the thermal expansion coefficient of ether, calculated from Young's data (see above), were used to make the adiabatic volume correction. Unfortunately conditions have not permitted a similar deter-

<sup>1</sup> Ann. Chim. Phys., 11, 530 (1877); 29, 505 (1893).

<sup>2</sup> Proc. Roy. Dublin Soc., (2) 12, 374 (1909-10).

mination for ethyl chloride, and consequently only those measurements could be made for which there was sufficient time to allow temperature equalization to take place.

Applying these corrections, if  $T$  = temperature of the thermostat, and  $P_1$  = one of a succession of pressures, the volume at a temperature,  $T$ , and a pressure,  $P_1$ , becomes:

$$V + (\text{expansion of glass bulb for } P_1 \text{ atms.}) + (\text{vol. } aa') \\ (1 + \alpha_{T_0} \Delta T) - (\text{vol. } ab) \beta_0 \Delta P + V \alpha_T \Delta T,$$

where  $V$  = vol. of bulb at temp.  $T$  and atmospheric pressure.

$\Delta T$  =  $T$  - room temperature.

$\Delta P$  =  $P_0 - P_1$ .

$P_0$  = initial pressure.

$\Delta T$  = adiabatic temp. change.

$\alpha$  = coeff. of thermal expansion of the liquid.

$\beta$  = coeff. of compressibility of the liquid.

For example, at  $133.8^\circ$  and 48.4 atms., the vol. of ether =  $0.96299 + 0.00067 \dots \dots \dots 0.96366$  cc.

At  $133.8^\circ$  and 19.3 atms., volume =  $0.96299 + 0.00035 + 0.02085 (1 + 0.00261 \times 114) - 0.0448 \times 176 \times 10^{-6} \times 29.1 = 0.99014$  cc.

At  $133.8^\circ$  and 1 atm., volume =

$$0.96299 + 0.03493(1 + 0.00261 \times 114) - 0.0448 \times 176 \times 10^{-6} \times 47.4 + 0.96299 \times 0.00356 \times 0.6 = 1.00997 \text{ cc.}$$

In addition to the above easily made corrections, the following are more difficult to take into account, but their omission does not appreciably affect the accuracy:

(1)  $\alpha$  is probably not independent of pressure in correction (3) above. Since the total correction amounts to only about 1% of the volume of the liquid, a slight error in the value of  $\alpha$  will obviously be negligible. A rapid turning of the lower end of the  $133.8^\circ$  curve for ether might cause a considerable change in  $\alpha$ , but the plotted results show that this is not the case, and there is therefore no appreciable error in the use of  $\alpha$  determined at the vapour-pressure.

(2) The volume  $bc$ , in which there is a temperature gradation from the temperature of the thermostat to room

temperature, is not more than  $\frac{1}{10}$  the volume of  $ab$ , and a compressibility correction is therefore unnecessary.

(3) There is a lag in the flow of liquid through the capillary  $bc$ . This introduces the largest source of error, but affects only the last readings in the experiments with ether. All that can be said is that there is a possible maximum error of about 7% in the last volume increment, or 0.3% on the whole volume.

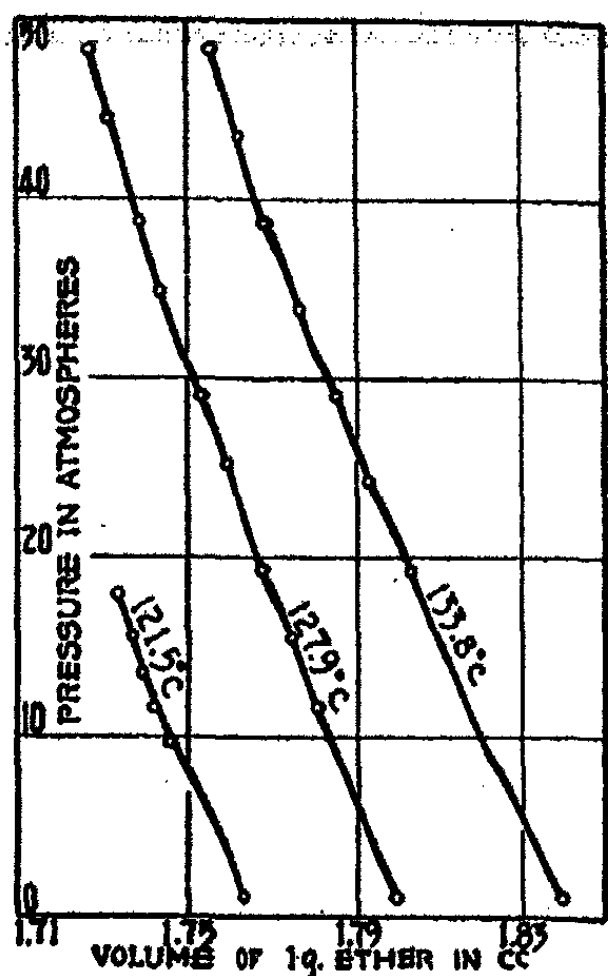


Fig. 4

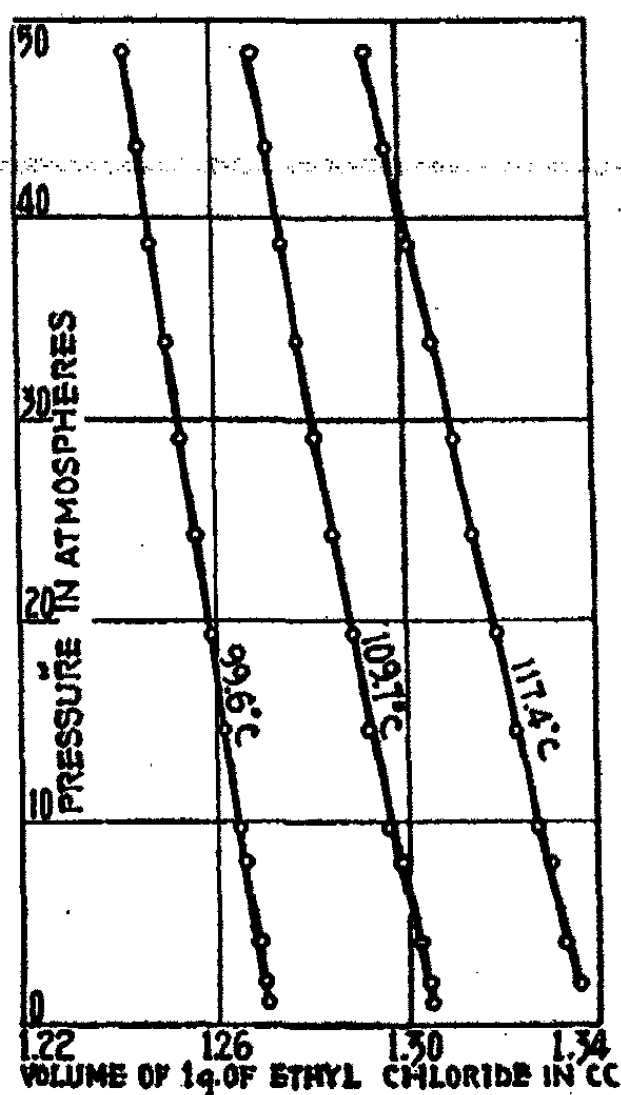


Fig. 5

*Results.*—The results for ether at 121.5°, 127.9° and 133.8°, and for ethyl chloride at 99.6°, 109.7° and 117.4° C. are given in Tables II and III. In the columns under the head of "time" are given the times in seconds which were allowed after each pressure reduction before taking the reading. The volumes, with all the corrections applied (Column VI) were converted to the basis of the volumes of 1 gram (Column

VII)\* and are represented graphically in Figures 4 and 5.

These curves show no unusual tendency to curve sharply in the low pressure regions, although the 1 atmosphere point on the ether curve at 133.8° is 7½ atmospheres below van der Waals' minimum point, and 13 atmospheres below the vapour-pressure. The very great divergence of actual pressure-volume relations from van der Waals' theoretical curve is very strikingly shown in Fig. 6, in which the unit of volume

TABLE II—Ether

I Press. atms.	II Temp. deg. C.	III Time secs.	IV Scale reading	V Vol. aa' uncorrected	VI Volume in cc.	VII Volume of 1 g.
17.9	121.5	—	10	0	1.59421	1.7334
15.5	121.5	—	20	0.00250	1.59671	1.7368
13.5	121.5	—	31	0.00443	1.59864	1.7394
11.6	121.5	—	47	0.00668	1.60089	1.7424
9.7	121.5	—	73	0.00957	1.60378	1.7464
1.0	121.5	10	228	0.02184	1.61605	1.7630
48.4	127.9	—	35.5	0	1.66574	1.7267
44.5	127.9	—	42	0.00343	1.67008	1.7312
38.7	127.9	—	63.5	0.00957	1.67780	1.7392
34.8	127.9	—	82	0.01322	1.68238	1.7440
29.0	127.9	—	118	0.01992	1.69080	1.7527
25.2	127.9	—	142	0.02435	1.69637	1.7585
19.3	127.9	—	192	0.03176	1.70568	1.7681
15.5	127.9	—	233	0.03653	1.71168	1.7743
11.6	127.9	—	287	0.04147	1.71789	1.7808
1.0	127.9	—	386	0.05473	1.73597	1.7995
48.4	133.8	30	—3	0	0.96366	1.7550
43.5	133.8	30	6.5	0.00310	0.96759	1.7622
38.7	133.7	30	20	0.00600	0.97126	1.7689
33.9	133.7	30	41	0.00934	0.97550	1.7766
29.0	133.7	30	72	0.01310	0.98029	1.7853
24.2	133.7	30	107	0.01650	0.98461	1.7932
19.3	133.7	30	157	0.02085	0.99014	1.8033
1.0	133.8	moment	296	0.03493	1.00997	1.8394

\* For ether the conversion was made with S. Young's data at the vapour-pressure. In the case of ethyl chloride the conversion is dependent on the special experiment referred to on page 309, which was not done accurately. The numbers in Col. VII, Table III, may therefore have a constant error of as much as 1% throughout.

TABLE III—Ethyl chloride

I Press. atms.	II Temp. deg. C.	III Time secs.	IV Scale readings	V Vol. <i>aa'</i> uncorrected	VI Volume in cc.	VII Volume* of 1 g.
48.4	99.6	—	174	0.0	0.51757	1.2426
43.5	99.6	—	181	0.00101	0.51861	1.2451
38.7	99.6	—	187.5	0.00198	0.51963	1.2475
33.9	99.6	—	195	0.00310	0.52078	1.2503
29.0	99.6	—	203	0.00432	0.52205	1.2533
24.2	99.6	—	210	0.00540	0.52318	1.2561
19.3	99.6	—	218	0.00662	0.52445	1.2591
14.5	99.6	—	225	0.00778	0.52566	1.2620
9.7	99.6	—	233	0.00908	0.52703	1.2653
8.0	99.6	—	235.5	0.00950	0.52757	1.2664
4.0	99.6	15	241	0.01042	0.52844	1.2687
2.0	99.6	15	244	0.01095	0.52898	1.2700
1.0	99.6	30	245	0.01110	0.52913	1.2703
48.4	109.7	30	241	0.0	0.51757	1.2688
43.5	109.7	30	248.5	0.00123	0.51887	1.2720
38.7	109.7	30	255.5	0.00245	0.52018	1.2752
33.9	109.7	30	263	0.00375	0.52156	1.2786
29.0	109.7	30	270.5	0.00512	0.52303	1.2822
24.2	109.7	30	278	0.00640	0.52440	1.2856
19.3	109.7	30	286	0.00794	0.52609	1.2897
14.5	109.7	30	293	0.00920	0.52741	1.2930
9.7	109.7	30	300.5	0.01066	0.52898	1.2967
8.0	109.7	45	305	0.01155	0.52997	1.2992
4.0	109.7	45	311	0.01273	0.53125	1.3024
2.0	109.7	45	314	0.01331	0.53185	1.3038
1.0	109.7	50	315.5	0.01362	0.53219	1.3046
48.4	117.3	90	290	0.0	0.51757	1.2941
43.5	117.35	40	297.5	0.00138	0.51909	1.2978
38.7	117.35	40	304.3	0.00268	0.52052	1.3014
33.9	117.35	40	312	0.00420	0.52225	1.3058
29.0	117.4	40	320.5	0.00590	0.52409	1.3103
24.2	117.5	40	328	0.00740	0.52577	1.3145
19.3	117.5	40	336	0.00906	0.52761	1.3192
14.5	117.45	40	343	0.01060	0.52932	1.3234
9.7	117.45	40	350.5	0.01225	0.53115	1.3280
8.0	117.45	20	354	0.01302	0.53224	1.3307
4.0	117.5	20	358.3	0.01397	0.53349	1.3338
2.0	117.5	10	360.5	0.01445	0.53442	1.3362

\* See footnote, page 312.

in van der Waals' curve is so chosen that it corresponds with the actual volume of 1 gram of liquid ether at 50 atmospheres.

The high degree of superheating, and the great uncertainty of explosions, imposed unusual conditions on the experiments, and the occurrence of a great many failures explains the restriction of the investigation to two liquids.

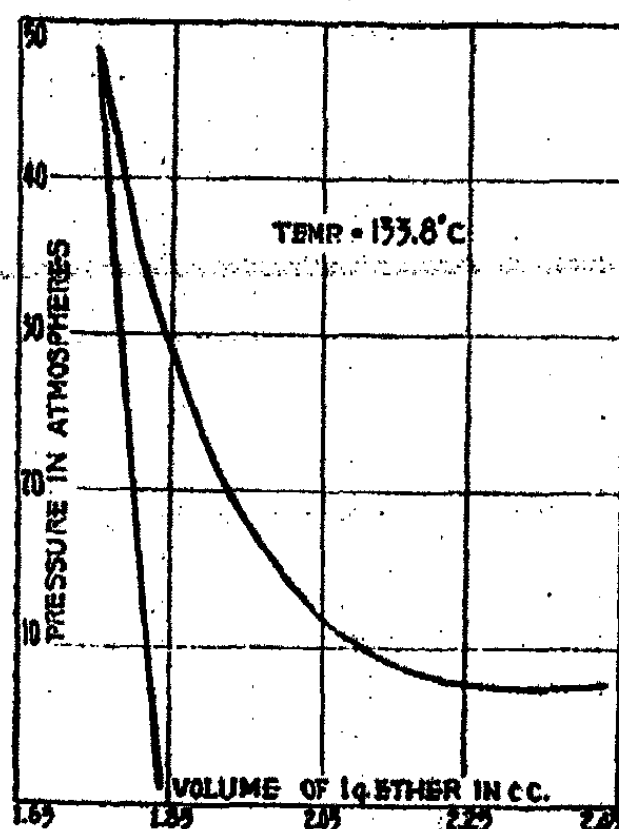


Fig. 6

#### 4. Summary

(1) The highest temperatures of superheating at atmospheric pressure were: ethyl ether, 143°; isopentane, 136°; ethyl chloride, 126°.

(2) The minimum pressures which can be reached with liquid ether at temperatures above, 143° increase with the temperature, the points lying approximately on a straight line joining the critical point with the -72 atmospheres point of J. Meyer.

(3) The pressure-volume relation was determined experimentally for liquid ethyl ether at 121.5°, 127.9° and 133.8°, and for liquid ethyl chloride at 99.6°, 109.7° and 117.4° at pressures down to 1 atmosphere.

(4) The pressure-volume relation under these conditions was almost linear. There was no tendency shown by the P-V curves to bend more sharply at low pressures as the limit of superheating was approached. Actual experiments showed a marked departure from van der Waals' curve.

This research was carried out at the suggestion and under the direction of Prof. F. B. Kenrick.

*University of Toronto  
Department of Chemistry  
June, 1921*



16-410

## STUDIES ON THE ELECTRO-DEPOSITION OF LEAD FROM MATHERS' PERCHLORATE BATH. I. THE STRUCTURE OF THE DEPOSIT

BY W. E. HUGHES

F. C. Mathers' solution, patented in 1909,<sup>1</sup> is one of the best of the baths available for the purpose of depositing lead. Its composition and other features have been fully described by the inventor himself.<sup>2</sup> He describes the lead deposited from it as "smooth and coherent," or, again, as "solid, smooth, finely crystalline."<sup>3</sup> Its density is given as 11.36.<sup>4</sup> Such descriptions relate to the macroscopic aspect of the deposit; its microscopic structure does not appear to have been investigated. The object of the present paper is to record some observations made during such an investigation.

### METHOD OF INVESTIGATION

#### I. Etching

The usual methods of preparing metal surfaces for study under the microscope are well known to be difficult to carry out successfully in the case of lead. No success was attained with them in the present instance. It was, therefore, decided to etch, by electrolytic means, the, in many cases, extremely smooth surface of the deposit. In this way no question of alteration of structure in consequence of polishing could arise; there was no opportunity for re-crystallization to occur. A disadvantage was that no sections of the metal lying in a plane parallel to the normal direction of grain growth could be examined; and such a disadvantage is of importance for many purposes.<sup>5</sup> In the present case, however, the exami-

<sup>1</sup> U. S. P., 931,944, Aug. 4 (1909).

<sup>2</sup> Trans. Am. Electrochem. Soc., 17, 261 (1910).

<sup>3</sup> Ibid., at p. 266.

<sup>4</sup> The density of lead deposited from A. G. Betts' silicofluoride solution varies from 11.29 to 11.36. Trans. Am. Electrochem. Soc., 36, 266 (1919).

<sup>5</sup> Cf. K. Debebke and M. V. Schwarz: Zeit. Metallkunde, 12, 505.

nation of the natural surface of the metal (after etching and without polishing) which lay in a plane at right angles to the direction of grain growth yielded some interesting results. After etching, the surfaces were washed, first, in tap water, and then, with distilled water, absolute alcohol and ether; they were then carefully dried between filter papers.

#### Conditions of Etching

These were as follows. *Solution*: 30 cc (Kahlbaum's) perchloric acid (spec. grav., 1.20—about 30 percent acid, that is); 270 cc distilled water. *Cathode*: 10-gauge copper wire; *Current density*: 9 to 10 amp./ $\text{dcm}^2$ ; *E. M. F.*: 1.5 volts at 0.8 cm electrode distance; *Temperature*: 18°/19° C; *Time*: varying, as shown in the table (infra).

#### Phenomena Observed

The phenomena observed at the anode are, for convenience of reference and comparison, as well as for brevity, put into tabular form. The progress of the etching was, in each case, carefully watched throughout the whole period, since continuous observation of the phenomena was considered necessary.

#### Remarks

(1) *The condition of the etched surface at the end of the period of etching was as follows—First sample*: The surface was much worn: it was cindery and dull, and light grey in colour. Examination with a pocket lens disclosed no sign of crystallization. *Second sample*: The surface was, for the most part, dark and patchy, and it was smeared with a dark, powdery substance; but in places, for example, near the surface of the solution, the surface of the anode had a sparkling (as though crystalline) appearance, when examined through a lens. *Third sample*: The remarks made about the first sample apply to this one also.

(2) *The formation of the skin-like substance*—Where the surface that was next the base metal on which the deposit was formed is presented to the cathode (as in 1), the skin

TABLE

Sample	Time of etch mins.		Phenomena observed at the anode
A piece of sheet lead deposited by the author from Mathers' bath	30	The <i>inside</i> surface of the deposit faced the cathode. The surface was very smooth, shiny and iridescent	A very few (adherent) bubbles seen form on the anode. After 10 minutes a very thin "skin" peeled away from the surface. This, when doubled upon itself, appeared to be brownish in colour, and broke into pieces when removed from the anode surface by a glass rod. After removal of the "skin," the anode was clean, matt and grey. During the remainder of the time of etching small pieces of "skin" came away from the anode surface on tapping the anode holder
A piece of a cathode supplied by Mathers	30	The lead could not be detached from its copper base. The <i>outside</i> surface had, therefore, to be exposed to etching	A few adherent bubbles form on the anode. During the first 20 minutes, tapping the anode caused dislodgement of small pieces of "skin." After 25 minutes, a large piece of "skin" fell away from the anode surface
As in 1	50	The <i>outside</i> surface of the deposit was in this case directed to the cathode. The original surface had upon it some tiny lumps, which caused it to feel slightly rough	During the first 15 minutes, the anode surface darkened and appeared to become covered with a blackish powder. No gas was observed. After 30 minutes, threads of a skin-like substance became detached, of themselves, from the edges of the anode. After 40 minutes, a dark curtain of "skin" had formed upon the anode surface: tapping detached this. At the end of the period of etch, there were numerous small pieces of "skin" floating about in the solution

forms early on in the etch period, and it consists of one piece covering the whole, or nearly the whole, of the exposed area; thereafter, after detachment of this, the skin-like substance is detached in small fragments. On the other hand, where the *outside* of the deposit faced the cathode (as in 2 and 3) the skin-like substance becomes detached in small fragments during the major part of the period of etch: in this latter case, a complete, one-piece, skin-like cover forms *towards the end* of the etch period, but it does not exceed a size greater than some two-thirds that of the exposed anode area. It may be mentioned that similar phenomena were noticed while etching several other samples; those given are typical of many cases. Three minutes was the shortest period of time in which the one-piece "skin" covering the whole of the exposed anode area was seen to form, using a current density of 9 to 10 amperes per square decimeter.

## II. Examination under Microscope

Examination of the etched surface of Sample 1 (of the table) at a magnification of 125 diameters and with normal illumination disclosed a curious structure. The deposit appeared to consist of cells of various sizes and of irregular outline. The cell walls were bright—even, lustrous, and they were slightly yellowish in colour. The interior of each cell appeared to be made up of a mosaic of very small, bright (like the walls) and dark particles. The centres of the cells were re-entrant: it was necessary to focus down from the plane of the focus of the cell walls in order to bring the interiors into a clear definition. Such was the structure seen, not only in the case of Sample 1, but also in all the other samples examined.

## Discussion

In this paper the author's intention is to state the facts observed, and to offer some suggestions as to the deductions that these facts seem to support. It is hoped to consider at a later time the general subject of the effect of colloids on deposited metal. The deductions which, it is suggested,

can be drawn from the observed facts are contained in paragraphs 1, 2 and 3, which follow.

1. *The lead deposited from Mathers' perchlorate bath has a structure.*—That this is a fact, and that the structure is definite and, perhaps, characteristic, may be said to be clear from the description given above. Moreover, it is a compound structure. It consists of a cellular or honeycomb framework and, within the cells, a mesh-work of very tiny particles. It would be easy to enter upon a strained argument as to the inferences that can be drawn from these facts, but the only deduction which it is wished to make is this:—*The arrangement of the atoms of the deposited metal is ordered; the structure is not amorphous, and, therefore, directive forces were at work other than, but in addition to, those ranged under the term 'cohesion.'* This is not to say that the directive forces are those to which the name "crystallization forces" has been given.<sup>1</sup> There is some evidence, as, for instance, in the case of Sample 2, that such forces may have operated; but the facts observed in these experiments would not justify a definite assertion regarding the matter. Insistence is placed upon the deduction here made, because metals deposited from solutions containing colloids or substances that give rise to the same results as colloids, namely, such as aluminium sulphate in solutions of zinc sulphate, ferric sulphate in cadmium sulphate baths,<sup>2</sup> and many others, are often (and always on little or no evidence) said to be *amorphous*.<sup>3</sup>

2. *The effect of the colloid on the depositing lead.*—This appears to be to prevent the building of any such structure as one usually finds when examining deposited metal. Without the colloid, the solution gives a crys-

<sup>1</sup> G. Wolff: *Zeit. f. Krystallographie*, 34, 449 (1901). W. Vernardiks (*Bull. de l'Acad. des Sciences de St. Petersburg*, 1908, p. 215) classifies the forces which operate during crystallization.

<sup>2</sup> A. Hollard: "La théorie des ions," p. 184. See also W. D. Bancroft (*Trans. Am. Electrochem. Soc.*, 1912); approving, apparently, M. Schlötter's view ("*Galvanostegie*," 1910, 1 Teil, pp. 38 and 51) that "the action of aluminium sulphate is clearly that of a colloid."

<sup>3</sup> E. F. Kern (*Trans. Am. Electrochem. Soc.*, 15, 473 (1909)) speaks of deposits formed from baths containing *addition agents* as being "less crystalline."

talline deposit, which, in no long time, becomes a mass of loosely adherent skeleton crystals. The experiments show that the surface change caused by the introduction of the colloid (peptone) is concurrent with a complete change of internal structure. The minuteness of the grains of the mesh within the cells of the frame-work shows that diminution of grain-size is one effect produced by the colloid;<sup>1</sup> the examination of the deposited lead gives, therefore, ocular demonstration of the fact. But diminution of grain-size is not the sole effect brought about by the colloid. So far as the microscope shows there is not, except in the intracellular areas, an aggregation of separate grains that meet to occasion lines of division. There are no such lines of division as usually occur between the grains of deposited metal: they are replaced by a separating substance that partitions the granular contents of one cell from the contents of the cells around it, similarly as the wax cell-wall of a honey-comb separates the contents of one cell from the honey contained in the cells around it. The deduction made from the observed facts is, therefore, that *the mode of growth of the lead deposited from Mathers' perchlorate bath is, or, under some conditions, may be, essentially different from that of deposited metal in general.* This statement may be opposite to the effect produced by colloids during the deposition of other metals—it may, in other words, have a general application. But the author's immediate concern is with a particular metal deposited from a particular bath.

3. *The forms of the separated colloid.*—It is well known that colloidal substances, present in a solution, are carried over into the deposited metal.<sup>2</sup> Mathers states that in the perchlorate bath the colloid-peptone becomes "used up," and it is necessary to add quantities of it periodically, the quantities being roughly proportional to the amounts of lead deposited. The separation, in the above experiments, of

<sup>1</sup> Cf. W. D. Bancroft: Chem. Met. Eng., 23, 454 (1920).

<sup>2</sup> Cf. S. A. Tucker and E. G. Thommsen: Trans. Am. Electrochem. Soc., 15, 477 (1909), and S. A. Tucker in the discussion on Kern's paper (op. cit., at p. 475).

large pieces of skin-like substance during the etching shows that this must exist in the deposit in the form of one or more layers, and there is here, therefore, a structure something similar to that observed by G. Grube and V. Reuss in their examination of copper deposited from solutions containing gelatin.<sup>1</sup> It seems to the author inconceivable that a layer of the skin-like substance, having an area as large or almost as large as that of the cathode, could have become separated in consequence of the etching, unless it existed in the metal as a layer formed somehow during the process of deposition. And especially does this seem true when it is considered that no special care was taken and a high current density (which may be considered as equivalent to rough treatment) was employed. The mode of formation of such layers as these found by Grube and Reuss and by the author is a matter of the greatest interest; but it is one that deserves to be treated with respect. Hurriedly built theories based upon an altogether insufficient foundation of facts are not likely to be other than confusing.<sup>2</sup> The only deduction that the author feels justified in drawing from the facts is that *the separation of colloid is not haphazard. The separation of the colloid occurs in such a way that it is able to form one or more continuous layers in the deposit, instead of being contained in this in the form of a number of very small pieces caught up by the metal and, thus, by chance, as it were, enclosed in it during its formation.* The examination with the microscope has led the author to the belief that, as a matter of fact, small particles of colloid are contained in the deposit, but not through chance separation. Small particles of colloid appear to a part of the content of the cells. It is an observed fact that, where the external surface of the deposit faces the cathode during etching, small particles of colloid separate during the first and greater part

<sup>1</sup> Zeit. Elektrochemie, 27, 45 (1921).

<sup>2</sup> Grube and Reuss, working with copper sulphate containing gelatin, obtained different results from those gotten by A. Sieverts and W. Wippelmann, from baths of like composition. Naturally, therefore, the explanations vary. G. Grube: Zeit. Elektrochemie, 27, 15 (1921), Sieverts and Wippelmann: Zeit. anorg. Chem., 91, 1 (1915).



of the etch period. On the other hand, where the internal surface faces the cathode, the continuous "skin" is first formed, and, subsequently, the colloid separates as small particles. These facts suggest that in both cases the small particles come from the contents of the cells.

4. *The number of continuous layers of colloid.*—The observations made during the experiments point to the existence of only *one* continuous layer of colloid in the deposit, and they indicate, further, that this is formed very near the cathode surface. The deposit of Samples 1 and 3 (of the table) was 0.018 inches thick, so that it would seem that in a deposit of that thickness or less only one continuous layer is formed. The author abstains from drawing any theoretical deductions from the facts just mentioned; a study of the cathode phenomena during the deposition is being pursued, and this, it is hoped, will throw some light upon the way in which the continuous layer comes to be formed.

#### Summary

The twofold structure of the lead deposited from Mathers' perchlorate bath is described; and certain deductions are stated which are based (1) upon the observations made during the disclosure of the structure by electrolytic etching, and (2) upon the study of the structure itself.

The author wishes to express his indebtedness and thanks to Professor F. C. Mathers for kindly sending him several samples of lead deposited from the perchlorate bath, and also for information of a general kind respecting it.

*Imperial College  
Royal School of Mines  
London, November, 1921*



24-485

## CATALYTIC PREPARATION OF AZOBENZENE AND ANILINE

BY C. O. HENKE AND O. W. BROWN

### Introduction

In two previous papers we have given the results of some studies on the reduction of nitrobenzene to aniline by hydrogen in the presence of several different catalysts and have determined several of the factors affecting the activity of the nickel and copper catalysts as measured by the yields of aniline produced.<sup>1</sup> In this paper we shall give the results of some studies on the reduction of nitrobenzene to azobenzene and aniline in the presence of lead and bismuth catalysts and the effect of the physical condition of the catalyst on its activity.

### Experimental Details

The apparatus used was the same as that described in our first paper. The azobenzene condensed to some extent in the end of the catalyst tube. In order to prevent this it was surrounded by an electric heating jacket about  $4\frac{3}{4}$  inches long and  $3\frac{1}{2}$  inches in diameter. This kept the temperature in the tube near  $200^{\circ}$  and prevented the products from condensing in the tube. The azobenzene is solid and clogs up the glass tube between the condenser and the flask. To avoid this difficulty the glass tube was taken off the condenser which was then turned around so that the short side-tube would stick upward instead of downward. To aid in condensing the products the condenser was kept about a fourth full of water. The solid azobenzene was washed out of the condenser, filtered out, allowed to dry and weighed. When an experiment was carried out under conditions where there was incomplete reduction some of the azobenzene was dissolved by the undissolved azoxybenzene and nitrobenzene. However these conditions are unfavorable both for the production of aniline and of

<sup>1</sup> Brown and Henke: Jour. Phys. Chem., 26, 161, 272 (1921).

azobenzene so that the error introduced here is immaterial. The aniline was left in the filtrate from the azobenzene. This was transferred to a graduated liter flask and the amount of aniline determined by titration with tenth-molar sodium nitrite as described in our first paper.

#### Experimental Results with Lead as Catalyst

The catalyst used to determine the best temperature for the reduction with lead as catalyst was prepared by reducing orange mineral in hydrogen at 270° for about an hour. Orange mineral is an extremely finely divided red lead which is made by roasting sublimed litharge. Thirty-two grams of this material were used, the catalyst tube being an iron pipe. The results of several experiments at different temperatures are given in Table I. The experiments are given in the order in which

TABLE I

Catalyst—lead from orange mineral.  
Rate of flow of hydrogen—17 liters per hour.  
Rate of flow of nitrobenzene—4 grams per hour.  
Excess of hydrogen—680%.

Temperature of catalyst °C	Material yield of azobenzene in % of theory	Material yield of aniline in % of theory	Total material yield in % of theory
270	20.3	27.1	47.4
270	....	14.5	14.5
270	....	35.6	35.6
290	29.5	54.8	84.3
290	33.8	35.0	68.8
290	32.0	61.7	93.7
290	29.6	67.5	97.1
290	32.1	54.9	87.0
290	20.8	78.2	99.0
290	7.2	88.0	95.2
290	12.5	74.4	86.9
290	15.1	71.6	86.7
308	4.0	92.7	96.7

they were carried out. In the blank spaces in Table I (as in all the other tables also) the yield of azobenzene was small and was not determined.

The results of Table I are not at all regular and do not

check. However with each increase in temperature there is an increase in yield of aniline. At 308°, which is the highest temperature used with this catalyst, the aniline yield is 92.7% and the azobenzene yield is 4%, making a total material yield of 96.7%. This high total material yield compares very favorably with that secured with the nickel, copper and silver catalysts. The azobenzene yield is highest at 290°; increasing the temperature to 308° decreased the azobenzene yield materially, while at 270° it decreased to practically nothing in the second experiment. This indicates that 308° is too high a temperature for the production of azobenzene and 270° is too low. Several of the experiments at 290° gave good yields of azobenzene but the yields seemed to decrease with use, although not so rapidly as at 270°. It will be noted that each time (except in the third experiment at 270°) the yield of azobenzene increases the aniline yield decreases and vice versa.

The effect of the method of preparation of the catalyst on its activity when used in an iron tube is shown by the results of Table II. Catalyst C2b consisted of 27 grams of sublimed litharge with an apparent density of 11.7.<sup>1</sup> Sublimed litharge is made by volatilizing lead and then allowing the fumes to burn to the oxide which produces a very finely divided material. Catalyst C2a consisted of 38 grams of red litharge with an apparent density of 26.0. Red litharge is made by allowing molten litharge to solidify slowly. The solidified mass is then ground to a fine powder. Catalyst C10 consisted of 55 grams of yellow litharge with an apparent density of 32.9. The yellow litharge<sup>2</sup> was also molten in one stage of its manufacture but, instead of allowing the molten mass to solidify slowly by slow cooling, it is dropped onto cold iron plates and cooled quickly, after which it is ground to a fine powder. Catalysts C2a and C10 were heated in hydrogen at 290° for about an hour before being used in the experiments listed in the table,

<sup>1</sup> As determined by Dr. Schaeffer's modification of the Scott volumeter.

<sup>2</sup> The yellow, red and sublimed litharges, the orange mineral and several of the other catalysts used in this work were furnished by Dr. Schaeffer of the Eagle-Picher Lead Co.

while catalyst C2b was heated for 6 hours in hydrogen at that temperature before use. In each case the catalyst tube was an iron pipe.

TABLE II

Rate of flow of hydrogen—17 liters per hour.  
Rate of flow of nitrobenzene—3.9 grams per hour.  
Excess of hydrogen—710%.

Experiment number	Temperature of catalyst °C	Material yield of azobenzene in % of theory	Material yield of aniline in % of theory	Total material yield in % of theory
5C2b (Sub. L.)	290	45.1	53.6	98.7
6C2b	290	40.6	41.4	82.0
7C2b	290	40.0	26.3	66.3
8C2b	290	39.3	27.9	67.2
1C2a (Red L.)	290	.....	53.6	53.6
2C2a	310	.....	28.8	28.8
129C10 (Yel. L.)	290	35.3	54.2	89.5
130C10	290	39.5	45.7	85.2
131C10	290	32.8	61.6	94.4
132C10	290	40.0	47.0	87.0
133C10 <sup>1</sup>	310	20.7	71.3	92.0
135C10 <sup>1</sup>	290	33.4	59.9	93.3
140C10	290	15.1	73.0	88.1
143C10	290	7.4	74.6	82.0
144C10	310	1.0	80.5	81.5
145C10	310	.....	84.6	84.6
146C10	290	0.5	85.2	85.7

The catalysts from sublimed litharge and yellow litharge are much better than the one from red litharge, the latter giving but small amounts of azobenzene in both experiments while both of the former gave considerable amounts of azobenzene in several experiments. Also the catalyst from red litharge, after the first experiment gave very low aniline yields, the experiment at 310° giving but 28.8% while the experiment with the catalyst from yellow litharge at 310° gave 71.3% aniline. The azobenzene yields with the catalyst from sublimed litharge at 290° were a little higher than those with the catalyst from the yellow litharge. However with both catalysts the azobenzene yield decreased with use. Also in ex-

<sup>1</sup> The experiments not listed were carried out with different rates of hydrogen and nitrobenzene and are not comparable to those in the table.

periment 5C2b there was no azoxybenzene while in the three following experiments with this catalyst azoxybenzene was produced besides the aniline and azobenzene. The yields of azoxybenzene were not determined. With catalyst C2b (from the sublimed litharge) when the azobenzene yield decreased the aniline yield decreased also; while with catalyst C10, which was the catalyst from the yellow litharge, when the azobenzene yield decreased the aniline yield increased, even up to 85.2% in the last experiment. Also the total material yield was higher with the catalyst from the yellow litharge than with the one from the sublimed litharge. This would indicate that the catalyst from the yellow litharge was a little more active than the one from the sublimed litharge while the one from red litharge is far below either one of these two in activity.

A catalyst was prepared by reducing 26 grams white lead for one hour in hydrogen at 290°. The white lead was prepared by electrolysis from a bath consisting of 12 grams sodium acetate, 3 grams sodium carbonate and 2 grams peptone per liter. Lead electrodes were used. The current density was 2 amperes per square decimeter. A stream of CO<sub>2</sub> was passed through the solution during electrolysis. The resulting white lead was a fine amorphous product. This catalyst, in an iron tube, gave good material yields in the first few experiments but its activity decreased very rapidly with use and later at 310° with 4 grams introbenzene and 17 liters hydrogen per hour gave only 59% yields of aniline with practically no azobenzene. This would place this catalyst near the bottom in the scale of activity, its aniline yields being a little better than those with the catalyst from red litharge at this same temperature.

Another catalyst was prepared from an amorphous red lead. This red lead contained 32.46% PbO<sub>2</sub> and had an apparent density of 16.5. It was a commercial product and had been prepared by roasting white lead residues. Fifty-seven grams of this material were put in the furnace and reduced at 270°. The catalyst tube was again an iron pipe. This catalyst was used in a few experiments at 270° and was then used at

290°. The second experiment at 290° with 17 liters hydrogen and 3.9 grams nitrobenzene per hour gave a total material yield of 94.6%. It was then used with different rates of hydrogen and nitrobenzene but its activity increased and in the eleventh experiment at 290°, which was carried out under the same conditions as the second experiment, the yield of azobenzene was only 4.7% while the yield of aniline had increased to 87.3%, making a total material yield of 92.0%. Thus at 290° the yields of azobenzene decreased while the yields of aniline increased.

When this catalyst was used at 308° the yield of aniline was 96.5% with practically no azobenzene. Thus this catalyst at 308° gave 4.5% higher yields of aniline than the first catalyst. This first catalyst had been prepared by roasting sublimed litharge. This litharge had been made by subliming lead and allowing the lead fumes to burn to the oxide, which gives an extremely finely divided material. The catalyst from the red lead that was made from white lead, which had never been heated to as high a temperature in its preparation as had the sublimed litharge, showed the higher activity. In fact its activity was so high that it led to the production of aniline instead of azobenzene. Also the azobenzene yields at 290° decreased more rapidly with this catalyst than with the one from orange mineral, made by roasting sublimed litharge. This would indicate that of these two catalysts from red lead, the one from the red lead made from sublimed litharge is the better for producing azobenzene while the one from red lead made from white lead is the better for producing aniline.

The catalyst from red lead made by roasting white lead was much more active than the one made from white lead directly, the latter giving only 59% yields of aniline while the former under the same conditions gave 96.5% aniline. The catalyst from orange mineral (see Table I) gave higher aniline yields but lower azobenzene yields than the catalyst from the sublimed litharge directly (see Table II, catalyst C2b). Also the former gave higher total material yields than the latter. This would indicate that the catalyst from the red lead made

by roasting sublimed litharge had a higher activity than the catalyst from sublimed litharge directly. Hence in both these instances the catalyst from the red lead had a higher activity than the catalyst from the litharge and white lead, from which the red leads were made.

On comparing the yields of azobenzene with the different catalysts it will be seen that the catalyst from the sublimed litharge gave the highest yield, with the one from yellow litharge a close second. However the much higher aniline yields with the one from the yellow litharge would place this catalyst before the one from sublimed litharge for making azobenzene. For producing aniline the catalyst from the red lead from white lead is best with the one from the red lead made from sublimed litharge a close second.

Lead was the first catalyst that was found to produce azobenzene. The yield of azobenzene was high at first but decreased with use. Azobenzene, when made by electrolysis from nitrobenzene, is produced only in an alkaline solution. Lead oxide is alkaline in reaction. This suggested that the formation of azobenzene by the lead catalyst might be due to the alkalinity of the lead oxide. On this theory the decrease in yield of azobenzene could be easily explained. If the red lead was not completely reduced to the metal, the unreduced oxide might make the catalyst alkaline which should result in the formation of azobenzene. At 290° in the presence of hydrogen these last traces of oxide are slowly reduced to metallic lead. As the oxide is reduced the alkalinity is reduced and the yield of azobenzene should diminish while the yield of aniline should increase.

With this idea in mind the effect of adding sodium hydroxide and magnesium oxide to the red lead was tried. The red lead used was that obtained from white lead by roasting. Catalyst C5 consisted of 57 grams of the original red lead. Catalyst C6 of Table III contained 0.27% NaOH. It was prepared by adding 18.9 cc of a sodium hydroxide solution (containing .3 gram of NaOH) and 150 cc water to 110 grams of red lead and then digesting the mixture in the cold



for about one hour with stirring. It was then evaporated on a hot plate and 70 grams of the dried material put in the furnace. Catalyst C7 contained 5% NaOH, 57 grams of the dried material being used. Catalyst C8 consisted of  $\frac{1}{3}$  red lead and  $\frac{1}{3}$  magnesium oxide. The magnesium oxide used was a light fluffy material. The two were thoroughly mixed by grinding them together in a mortar. Twenty-three grams of the mixture were used. An iron tube was used each time and each catalyst was reduced by heating in hydrogen at 290° for about an hour before use.

TABLE III

Temperature of catalyst—290°.  
Rate of flow of hydrogen—17 liters per hour.  
Rate of flow of nitrobenzene—4 grams per hour.  
Excess of hydrogen—680%.

Catalyst	Material yield of azobenzene in % of theory	Material yield of aniline in % of theory	Total material yield in % of theory
C5 <sup>1</sup>	37.5	57.1	94.6
C5 <sup>1</sup>	4.7	87.3	92.0
C6 (.27% NaOH)	30.4	45.4	75.8
C6 (.27% NaOH)	34.7	40.7	75.4
C6 (.27% NaOH)	....*	77.6	....
C6 (.27% NaOH)	19.3	74.7	94.0
C6 (.27% NaOH)	19.2	72.8	92.0
C7 (5% NaOH)	19.0	18.0	37.0
C7 (5% NaOH)	....	15.1	15.1
C8 ( $\frac{1}{3}$ MgO)	32.5	19.5	52.0
C8 ( $\frac{1}{3}$ MgO)	26.3	21.4	47.7
C8 ( $\frac{1}{3}$ MgO)	19.7	69.4	89.1
C8 ( $\frac{1}{3}$ MgO)	....*	59.9	....
C8 ( $\frac{1}{3}$ MgO)	11.5	81.0	92.5

From the results of Table III it will be seen that the addition of 5% NaOH was decidedly injurious while 0.27% had no appreciable effect. The magnesium oxide likewise failed to produce the desired result. With catalysts C6 and C8 the total material yield increased with use and aniline yield in-

<sup>1</sup> Between these two experiments eight others were carried out with different rates of flow of hydrogen and nitrobenzene.

\* The azobenzene yield was not determined in these two cases.



creased even to a greater extent, while the azobenzene yield decreased.

All of the above experiments were carried out with the catalyst in an iron tube. Several of these catalysts were also used in a glass combustion tube. When a glass tube was substituted for the iron tube the hydrogen and the capillary tube were led into the catalyst tube by means of a glass T tube. The connection between the glass combustion tube and the T tube was made by a short piece of rubber tubing, the combustion tube extending out of the furnace about 4 inches. The one end of the glass T tube did not extend into the furnace but the capillary tube extended into the furnace as before.

The results with different catalysts in a glass tube are given in Table IV. Catalyst C45 was prepared from 46 grams of red lead made from white lead by reducing in hydrogen for one hour at 290° before use, and catalyst C46, which was prepared from the same material as C45, was heated in hydrogen at 308° for one hour before use. Catalyst C24 consisted of 34 grams of orange mineral made from sublimed litharge. Results with this catalyst in an iron tube were given in Table I. A very heavy litharge with an apparent density of 37.5 was also used in both iron and glass tubes. Catalyst C27 consisted of 52 grams of this heavy litharge in an iron catalyst tube while C43 consisted of 52 grams of the same material in a glass tube. Catalyst C26 was a mixture consisting of 50% heavy litharge and 50% of iron filings. The iron filings had previously been heated at about 310° in a current of hydrogen and nitrobenzene vapors for about 3 hours. Forty-nine grams of this mixture were used in the furnace. Catalyst C19 consisted of 48 grams of the heavy litharge but in front of this column of catalyst was placed a column of iron filings of about equal length and consisting of 39 grams of the filings. So the vapors in the case of C19 first pass over the column of iron filings and then over the column of catalyst.

The results with the catalysts in a glass tube are altogether different from those with the catalysts in an iron tube. In an iron tube the catalyst from red lead made from white

lead at 308° and with the same rates of hydrogen and nitrobenzene gave a 96.5% yield of aniline with practically no azobenzene. The iron seems to have had a tremendous influence increasing the activity of the lead. The effect of the iron is not merely additive. At 302° in a glass tube the yield of aniline was only 4.1% with practically no azobenzene while

TABLE IV

Rate of flow of hydrogen—17 liters per hour.  
Rate of flow of nitrobenzene—4 grams per hour.  
Excess of hydrogen—680%.

Catalyst	Temperature of catalyst ° C	Material yield of azobenzene in % of theory	Material yield of aniline in % of theory	Total material yield in % of theory
C45	302	....	4.1	4.1
C45	302	....	4.7	4.7
C45	320	37.3	57.0	94.3
C45	320	32.2	63.3	95.5
C45	320	30.2	65.8	96.0
C46	320	36.9	52.0	88.9
C46	320	33.9	41.4	75.3
C46	320	37.0	56.4	93.4
C46	320	29.2	37.3	66.5
C24	283	....	0.6	0.6
C24	283	....	6.0	6.0
C24	302	38.2	24.1	62.3
C24	302	....	11.9	11.9
C24	302	....	17.9	17.9
C24	302	....	17.5	17.5
C27 (Iron tube)	283	....	25.7	25.7
C27 (Iron tube)	302	....	39.8	39.8
C27 (Iron tube)	320	....	45.7	45.7
C43	320	42.5	46.7	89.2
C43	320	....	19.7	19.7
C26	283	....	30.1	30.1
C26	302	....	26.0	26.0
C19	283	8.7	83.7	92.4
C19	302	17.7	68.6	86.3

in an iron tube at 290° the second experiment gave a 37.5% yield of azobenzene and a 57.1% yield of aniline making a total material yield of 94.6%. The activity of the catalyst at 302°, instead of being less, should have been greater than at 290°. In our first paper it was shown that an empty iron tube

at 300° gave about 15% material yields of aniline, so that this tremendous increase in activity of the lead catalyst when used in an iron tube instead of glass is surely not merely the added activity of the iron.

In each case in this table the catalyst when used in a glass tube gave higher yields of azobenzene and lower yields of aniline than when used in an iron tube. However in a glass tube the yield of azobenzene decreased very rapidly with use while the aniline yield decreased also. Thus the catalyst from heavy litharge in glass (C43) gave a high yield of azobenzene, 42.5%, in the first experiment but practically nothing in the second experiment. At the same time the aniline yield decreased from 46.7% to 19.7%. In an iron tube this same heavy litharge catalyst (C27) gave practically as high a yield of aniline in the third experiment as it did in the first experiment when used in glass. The azobenzene yield cannot be compared in this case for the first experiment in the iron tube was carried out at a lower temperature than the first experiment in the glass tube. The azobenzene yield in iron and glass can however be compared with the catalyst from orange mineral that was made from sublimed litharge. The results with this catalyst in an iron tube were given in Table I. The results with this same catalyst in a glass tube are given in Table IV under catalyst C24. The results are similar to those where the heavy litharge was used. The catalyst from orange mineral gave 38.2% yield of azobenzene and a 24.1% yield of aniline in the third experiment when used in glass while the highest azobenzene yield when used in iron was 33.8% with a 35% yield of aniline. The azobenzene yield is increased and the aniline yield decreased when used in a glass tube. However both decrease very rapidly with use and in the second experiment in glass at 302° the azobenzene yield is practically nothing, while when used in iron the yield of azobenzene was maintained for several experiments and the yield of aniline increased to 88.0%.

Catalysts C26 and C19 were both used in glass tubes. Catalyst C26 consisted of a mixture of the heavy litharge

with iron filings while in C19 the iron filings were placed in front of the litharge. Mixing the iron filings with the litharge was decidedly detrimental while the placing of the filings in front of the litharge in C19 was beneficial, the second experiment at 302° giving 17.7% azobenzene and 68.6% aniline, while the second experiment at 320° with the catalyst C43, which was exactly like C19 but without the column of iron filings, gave only 19.7% aniline and practically no azobenzene.

TABLE V

Rate of flow of hydrogen—17 liters per hour.  
Rate of flow of nitrobenzene—4 grams per hour.  
Excess of hydrogen—680%.

Catalyst from	Temperature of catalyst °C	Material yield of azobenzene in % of theory	Material yield of aniline in % of theory	Total material yield in % of theory
PbO	320	42.5	46.7	89.2
PbO	320	....	19.7	19.7
PbO 1/2% Fe <sub>2</sub> O <sub>3</sub>	300	24.9	27.9	52.8
PbO 1/2% Fe <sub>2</sub> O <sub>3</sub>	300	....	9.7	9.7
PbO 1/2% Fe <sub>2</sub> O <sub>3</sub>	320	25.0	45.7	70.7
PbO 1/2% Fe <sub>2</sub> O <sub>3</sub>	320	28.0	44.8	72.8
PbO 1/2% Fe <sub>2</sub> O <sub>3</sub>	340	22.2	73.9	96.1
PbO 5% Fe <sub>2</sub> O <sub>3</sub>	300	....	37.6	37.6
PbO 5% Fe <sub>2</sub> O <sub>3</sub>	300	5.2	23.2	28.4
PbO 5% Fe <sub>2</sub> O <sub>3</sub>	320	....	83.7	83.7
PbO 5% Fe <sub>2</sub> O <sub>3</sub>	340	....	88.4	88.4
PbO 2% CuO	300	14.7	22.6	37.3
PbO 2% CuO	300	....	8.5	8.5
PbO 2% CuO	320	14.8	35.4	50.2
PbO 2% CuO	320	....	29.1	29.1
PbO 2% CuO	340	23.2	72.7	95.9
PbO 2% CuO	340	20.3	74.5	94.8
PbO 2% CuO	360	....	90.5	90.5
PbO 5% CuO	300	....	15.7	15.7
PbO 5% CuO	300	....	6.3	6.3
PbO 5% CuO	320	....	28.8	28.8
PbO 5% CuO	340	....	42.6	42.6

In order to avoid the effect of the iron tube a glass tube was used to study the effect of mixing iron and copper oxides with the heavy litharge. The ferric oxide was prepared from ferric nitrate by precipitation with ammonium hydroxide,

the oxide being dried in an oven at 110°. The copper oxide was prepared by ignition of the nitrate at 470°. The results are given in Table V.

The activity of the catalyst with the 1/2% of Fe<sub>2</sub>O<sub>3</sub> as measured by both the azobenzene and aniline yields did not decrease as rapidly as it did without the addition of the 1/2% Fe<sub>2</sub>O<sub>3</sub>. Thus in the second experiment at 320° with 1/2% Fe<sub>2</sub>O<sub>3</sub> the azobenzene yield was 28% and the aniline yield 44.8% while without the addition of the 1/2% Fe<sub>2</sub>O<sub>3</sub> the second experiment at 320° gave practically no azobenzene and only 19.7% aniline. The half per cent of ferric oxide increased both the azobenzene and aniline yields. However a larger amount of the ferric oxide, 5%, caused a large decrease in azobenzene yield and a correspondingly large increase in aniline yield. With 5% ferric oxide the effect of the iron catalyst seems to be secured instead of the effect of the lead, as the azobenzene yield is decreased to practically nothing. When copper oxide was used the addition of 2% seemed to decrease the activity of the catalyst for producing both azobenzene and aniline. Likewise 5% of CuO caused a decrease in both azobenzene and aniline yields, while 5% ferric oxide caused a decrease in yield of azobenzene but an increase in yield of aniline.

It will be noted that these catalysts have been used above the melting point of lead, the one with 2% CuO being used 33° above its melting point. Also the lead catalyst containing 2% CuO was quite active, giving a yield of 90.5% aniline, when used at 360°, 33° above its melting point. One would have expected that the particles of lead would have coalesced and run together when heated in hydrogen above their melting point and that this would have resulted in the catalyst losing its activity. However this did not happen and one could not tell by inspection that the catalyst had been used above its melting point as it was simply a loose mass of black powder. The fine particles of lead were 33° above the melting point of massive lead, yet something kept the particles from coalescing and running together. An oxide film is known to keep metals from coalescing but one would hardly expect to find an oxide

film on lead at a temperature of  $360^{\circ}$  in an atmosphere of hydrogen.

This was the behavior of the catalyst from the heavy litharge. The catalyst prepared from red lead that had been made from white lead acted differently. This catalyst after it had been heated to its melting point contained many little spheres of bright metallic lead and in a few places 2 to 5 grams had run together and formed a solid mass of bright metallic lead. This indicated that the particles of lead started to coalesce when heated to their melting point. This catalyst was not used above the melting point and had been heated to that temperature by accident. However it does show that the physical condition of the material from which the catalyst was made determines to a large extent whether or not the catalyst can be used above its melting point.

A study was made of the effect of the fineness of grain of the lead catalyst upon its activity. For this study a red lead with an apparent density of 16.63 was chosen. Eight hundred grams of this red lead were floated in water and separated into three portions. Fifty-three grams of the coarsest or heaviest constituted one portion, 32.5 grams of the finest or lightest constituted another portion and the balance of the 800 grams made up the middle portion. Catalysts were then prepared from the original red lead, from the coarsest portion and from the finest portion. The results with these different catalysts are given in Table VII. Catalyst C35 consisted of 36 grams of the original red lead, catalyst C15 consisted of 32 grams of the fine portion and catalyst C25 consisted of 41 grams of the coarse portion. Each catalyst was heated in hydrogen at  $285^{\circ}$  to  $290^{\circ}$  for one hour before use. The experiments are listed in the order in which they were carried out.

The results of Table VI show that the more finely divided the red lead (within the limits studied) the more active it is after reduction. The catalyst from the lightest red lead produced by far the highest total material yield and the highest aniline yield. Its yield of azobenzene was slightly lower than that of the catalyst from the original when used at a temper-

ature 6 degrees lower than the temperature at which the original was used. In fact the activity of the catalyst from the most finely divided red lead at 322° is so great that it carries on the reduction farther than the azobenzene stage and pro-

TABLE VI

Rate of flow of hydrogen—17 liters per hour.

Rate of flow of nitrobenzene—4 grams per hour.

Excess of hydrogen—680%.

Catalyst from	Temperature of catalyst °C	Material yield of azobenzene in % of theory	Material yield of aniline in % of theory	Total material yield in % of theory
C15 (Fine)	285	.....	3.1	3.1
C15 (Fine)	285	.....	3.1	3.1
C15 (Fine)	303	.....	11.3	11.3
C15 (Fine)	303	.....	20.1	20.1
C15 (Fine)	322	23.6	70.5	94.1
C35 (Orig.)	290	.....	3.1	3.1
C35 (Orig.)	290	.....	3.1	3.1
C35 (Orig.)	310	.....	11.9	11.9
C35 (Orig.)	310	.....	6.6	6.6
C35 (Orig.)	328	26.7	45.7	72.4
C25 (Coarse)	285	.....	5.9	5.9
C25 (Coarse)	285	.....	5.6	5.6
C25 (Coarse)	303	.....	8.5	8.5
C25 (Coarse)	303	.....	6.9	6.9
C25 (Coarse)	340	.....	17.5	17.5

duces over 70% aniline. The decrease in yield with the catalyst from the heavy red lead is very marked, the total material yield at 340° being only 17.5% while that with the lightest red lead at 322° is 94.1%.

When a lead catalyst that had been used at about 310° was taken out of the furnace, the end of the column of catalyst with which the nitrobenzene vapors first came in contact had been converted to litharge. The amount of litharge was not the same each time but frequently about the first inch of the column was litharge and the rest of the column black metallic lead. The litharge extended through the material and not just a little on the outside, which indicated that the gaseous mixture had penetrated into the mass of the catalyst and had not just passed over the top of it. When catalyst C25 was taken



out of the furnace after it had been used at 340° the end of the column of catalyst had not been converted to litharge but to red lead. This formation of litharge and red lead indicates that the nitrobenzene is partially reduced by the direct action of the lead.

A lead catalyst which had lost its activity could be activated to some extent by merely heating in hydrogen. The iron and antimony catalysts of the previous paper acted in a somewhat similar manner.

The effect of the method of preparation of the catalyst on its activity when used in glass is shown by the results of Table VII. Catalyst C44 was prepared from 39 grams of red litharge of an apparent density of 26.0. Catalyst C33 was prepared from 45 grams of yellow litharge of an apparent density of 31.9. Catalyst C34 was prepared from 26 grams of sublimed litharge of an apparent density of 11.7. Catalyst C14 was prepared from 46 grams of red lead made from red litharge. It had an apparent density of 22.0. Catalyst C24 was prepared from 34 grams of orange mineral. It had an apparent density of 11.4. Catalyst C16 was prepared from 26 grams of an amorphous white lead made by electrolysis as previously described.

From the results of Table VII it will be seen that the catalyst from the sublimed litharge, C34, gives better material yields of azobenzene and aniline than the catalysts from either the red or yellow litharges. It is the only one of the three that gave an appreciable amount of azobenzene after the first experiment. In the first experiment the catalyst from the yellow litharge gave a slightly higher yield of azobenzene than the catalyst from the sublimed litharge. The latter in all instances except in the second experiment with the catalyst from yellow litharge gave the highest yields of aniline.

The catalyst from the yellow litharge gave a 55.4% yield of azobenzene in the first experiment, while the catalyst from the red litharge did not give an appreciable amount of azobenzene in any experiment. Also the latter did not give as high aniline yields in any experiment as the former. This would place the



catalyst from the sublimed litharge as the best of the litharge catalysts and the one from the red litharge as the poorest for the production of both azobenzene and aniline.

TABLE VII

Rate of flow of hydrogen—17 liters per hour.  
Rate of flow of nitrobenzene—4 grams per hour.  
Excess of hydrogen—680%.

Catalyst	Temperature of catalyst ° C	Material yield of azobenzene in % of theory	Material yield of aniline in % of theory	Total material yield in % of theory
C44 (Red L.)	300	—	15.7	15.7
C44 (Red L.)	300	—	4.1	4.1
C44 (Red L.)	320	—	21.9	21.9
C44 (Red L.)	320	—	9.7	9.7
C44 (Red L.)	320	—	9.1	9.1
C44 (Red L.)	320	—	9.1	9.1
C33 (Yel. L.)	290	55.4	26.0	81.4
C33 (Yel. L.)	290	—	9.7	9.7
C33 (Yel. L.)	310	—	27.3	27.3
C33 (Yel. L.)	310	—	13.8	13.8
C33 (Yel. L.)	310	—	16.0	16.0
C33 (Yel. L.)	310	—	16.0	16.0
C34 (Sub. L.)	290	54.9	26.3	81.2
C34 (Sub. L.)	290	—	5.0	5.0
C34 (Sub. L.)	310	34.4	61.1	95.5
C34 (Sub. L.)	310	29.6	37.0	66.6
C34 (Sub. L.)	310	10.4	30.1	40.5
C34 (Sub. L.)	310	—	30.4	30.4
C14 (Red lead from red litharge)	285	—	2.8	2.8
C14 (Red lead from red litharge)	285	—	1.3	1.3
C14 (Red lead from red litharge)	303	45.6	27.3	72.9
C14 (Red lead from red litharge)	303	—	12.5	12.5
C14 (Red lead from red litharge)	303	—	12.5	12.5

TABLE VII (Concluded)

C14 (Red lead from red litharge)	303	—	16.3	16.3
C24 (Orange Min.)	285	—	0.6	0.6
C24 (Orange Min.)	285	—	6.0	6.0
C24 (Orange Min.)	303	38.2	24.1	62.3
C24 (Orange Min.)	303	—	11.9	11.9
C24 (Orange Min.)	303	—	17.5	17.5
C16 (White L.)	285	29.9	60.8	90.7
C16 (White L.)	285	22.2	44.5	66.7
C16 (White L.)	303	21.0	74.9	94.9
C16 (White L.)	303	22.4	71.8	94.2
C16 (White L.)	303	19.1	72.4	91.5

The catalyst from the white lead is very much more active than the one from sublimed litharge. The catalyst from white lead in the second experiment at 285° gave a 22.2% yield of azobenzene while the one from sublimed litharge gave no appreciable amount of azobenzene in the second experiment at 290°. In the first experiment the catalyst from the sublimed litharge gave a 54.9% yield of azobenzene while that from white lead gave only a 29.9% yield of azobenzene. However the latter catalyst in the same experiment gave 60.8% aniline while the one from the sublimed litharge gave only 26.3% aniline. The same is true in the third experiment. In every experiment the catalyst from white lead gave a much higher yield of aniline than the one from sublimed litharge. In fact the catalyst from the white lead was so active that it carried the reduction farther than the azobenzene stage and in three consecutive experiments gave yields of over 70% aniline.

The catalyst from the red lead made from red litharge is more active than the catalyst made from the red litharge directly. The latter did not give an appreciable yield of azobenzene in the third experiment while the former gave a 45.6% yield of azobenzene in the third experiment. The catalyst

from the sublimed litharge seems to be more active than the one from the red lead made from sublimed litharge but it is difficult to compare them because of temperature differences. The catalyst from the red lead made from white lead is not as active as the one from white lead directly. The results for the one from red lead made from white lead are given in Table IV. The former did not give any appreciable yields of azobenzene at 300° while the latter gave 20% yields of azobenzene and over 70% yields of aniline in three consecutive experiments at 303°.

In every instance an increase in temperature resulted in an increase in yield of aniline. Also, in every instance after reaching a temperature where an appreciable yield of azobenzene was secured (20% or more) any further increase in temperature caused a decrease in yield along with an increase in yield of aniline. Then increasing the temperature of C24 would probably have reduced the azobenzene yield below that of C45 at this temperature. Catalyst C16 would probably have acted similarly. Also an increase in temperature of C16 (catalyst from amorphous white lead) would probably have decreased the azobenzene yield to practically nothing with a corresponding increase in yield of aniline. As a result the catalyst from white lead would be the most active catalyst and would be the best of the lead catalysts for producing aniline, while the catalyst from the red lead made from white lead would be the best of the lead catalysts for making azobenzene in glass tubes. However when these catalysts were used in iron tubes it was found that the one from red lead made from white lead was the best for producing aniline while the one from yellow litharge was the best for making azobenzene.

Lead phosphate and lead chromate were also used as catalysts but no good results were secured.

#### **Experimental Results with Bismuth**

The bismuth catalysts were prepared by precipitating the hydroxide from a solution of the nitrate by ammonium hydrox-

ide. The hydroxide was filtered out, dried, put in the furnace and reduced in hydrogen at 230° to 240° C.

When the hydroxide was allowed to filter slowly without suction and dried in an oven, it remained light and fluffy. Catalyst G22 consisted of 7 grams of this light fluffy material and G32 consisted of 10 grams of the same material. Catalyst G22 was used in a glass tube while G32 was used in an iron tube. When the hydroxide was filtered rapidly with suction it became packed in the funnel. This was then put in a small evaporating dish and heated in an electrically heated muffle at 415° for about 15 minutes. The product was much heavier and apparently more granular than that made by the previous method. Catalyst G41 and G13 each consisted of 22 grams of this heavy material. Catalyst G13 was used in a glass tube while G41 was used in an iron tube.

Catalyst G22, the light oxide in a glass tube, did not give any appreciable yields of azobenzene while catalyst G32, which was the same oxide in an iron tube, gave a 70.2% yield of azobenzene in the third experiment. However the azobenzene yields decreased with use. The aniline yields likewise decreased, indicating a decrease in the activity of the catalyst.

Catalyst G13, the one from the heavy oxide in a glass tube, gave a 92% yield of azobenzene in the first experiment. However its activity dropped very rapidly and in the second experiment the yield of azobenzene was only 51.2% and in the other experiments no appreciable amounts of azobenzene were produced. Catalyst G41, which was the same as G13 except that G41 was in iron while G13 was in glass, gave a yield but slightly lower than that of the first experiment with catalyst G13. But its activity decreased very rapidly at the temperature of 240° and in the second experiment the yield of azobenzene was only 58.3%. At 280° the activity of catalyst G41 did not seem to decrease appreciably with use. At this temperature the first experiment yielded 30.3% azobenzene and 15.7% aniline while the third yielded 65.0% azobenzene and 28.2% aniline. Similarly at 300° three con-

secutive experiments did not show any tendency towards a decrease in activity with use.

TABLE VIII

Rate of flow of hydrogen—17 liters per hour.  
Rate of flow of nitrobenzene—4.2 grams per hour.  
Excess of hydrogen—640%.

Catalyst	Temperature of catalyst ° C	Material yield of azobenzene in % of theory	Material yield of aniline in % of theory	Total material yield in % of theory
G22 (Light in glass)	230	—	7.2	7.2
G22 (Light in glass)	248	—	4.7	4.7
G22 (Light in glass)	248	—	5.3	5.3
G22 (Light in glass)	267	—	8.8	8.8
G22 (Light in glass)	267	—	9.4	9.4
G32 (Light in iron)	235	—	4.7	4.7
G32 (Light in iron)	235	—	4.1	4.1
G32 (Light in iron)	271	70.2	20.4	90.6
G32 (Light in iron)	271	57.5	28.2	85.7
G32 (Light in iron)	290	49.7	30.1	79.8
G32 (Light in iron)	290	—	19.4	19.4
G32 (Light in iron)	290	—	10.7	10.7
G32 (Light in iron)	271	—	6.6	6.6
G13 (Heavy in glass)	230	92.0	4.4	96.4
G13 (Heavy in glass)	230	51.2	4.4	55.6
G13 (Heavy in glass)	248	—	2.8	2.8
G13 (Heavy in glass)	248	—	1.2	1.2
G13 (Heavy in glass)	267	—	6.3	6.3

TABLE VIII (Concluded)

G13 (Heavy in glass)	267	—	2.2	2.2
G41 (Heavy in iron)	240	89.2	9.1	98.3
G41 (Heavy in iron)	240	58.3	6.3	64.6
G41 (Heavy in iron)	260	—	9.4	9.4
G41 (Heavy in iron)	260	—	9.4	9.4
G41 (Heavy in iron)	280	30.3	15.7	46.0
G41 (Heavy in iron)	280	68.4	27.9	96.3
G41 (Heavy in iron)	280	65.0	28.2	93.2
G41 (Heavy in iron)	300	25.0	67.0	92.0
G41 (Heavy in iron)	300	19.3	73.9	93.2
G41 (Heavy in iron)	300	29.5	65.2	94.7
G41 (Heavy in iron)	240	53.2 <sup>1</sup>	34.8	88.0
G41 (Heavy in iron)	240	30.6	25.7	56.3

At the temperature of 300°, however, the yield of aniline has been very greatly increased over that at 280° at the expense of the azobenzene yields. The second experiment at 280° gave 68.4% azobenzene and 27.9% aniline while the same experiment at 300° gave only 19.3% azobenzene and 73.9% aniline while the following experiment gave 29.5% azobenzene and 65.2% aniline. This indicates that a high temperature leads to the formation of aniline while a lower temperature gives higher azobenzene yields.

On comparing the results of catalysts G32 and G41, both of which were used in iron pipes, it is seen that G41 is far the better catalyst both for the production of aniline and of azo-

<sup>1</sup> Just previous to this experiment the catalyst was heated in hydrogen to 340°.

benzene. The highest azobenzene yield with G41 was 89.2 while the highest with G32 was only 70.2%. Also the highest aniline yield with G41 was 67% while the highest with G32 was only 30.1%. Likewise G41 gave the highest total material yield of 98.3% while the highest given by G32 was 90.6%. Also G32 gave appreciable yields of azobenzene in only 3 experiments out of 8 while G41 gave good yields of azobenzene in 10 out of 12 experiments.

When a bismuth catalyst was taken out of the furnace it was found that the end of the column of catalyst with which the nitrobenzene first came in contact had been converted to the oxide. Also from the last two experiments of Table VIII it will be seen that the activity of a bismuth catalyst may be restored to some extent by merely heating in hydrogen somewhat similar to the iron, antimony and lead catalysts.

Although G41, which was the catalyst from the heavy oxide, gave the highest yields of aniline and azobenzene, it does not follow that it is the more active catalyst. The catalyst from the heavy oxide is undoubtedly the more active volume per volume. This does not mean that the catalyst from 1 gram of the heavy oxide is more active than that from 1 gram of the light oxide. Twenty-two grams of the heavy oxide were used for catalyst G41 while only ten grams of the light oxide were used for catalyst G32. Possibly if the same number of grams of oxide had been used in each case instead of the same volume the results might have been different.

In one experiment at 240° with a heavy oxide of bismuth as catalyst white crystals of hydrazobenzene were observed in the condenser. Sabatier<sup>1</sup> states that with platinum as catalyst and with an insufficient amount of hydrogen "there is a marked tendency to the formation of white crystals of hydrazobenzene." An experiment carried out with silver at 300° and with 6.1 grams nitrobenzene per hour and an insufficient amount of hydrogen (2.1 liters per hour) gave 45.4% aniline and no azobenzene or hydrazobenzene.

<sup>1</sup> Sabatier and Senderens: *Comptes rendus*, 133, 321 (1901).

### Discussion of Results

The action of different catalysts on this reduction of nitrobenzene seems to be more or less specific. Thus nickel reduces it to aniline or farther, even to methane and ammonia, but gives no azoxybenzene or azobenzene other than enough to slightly color the product under certain unfavorable conditions. Copper and silver reduce the nitrobenzene to aniline and give no azoxybenzene or azobenzene. Neither do they carry the reduction farther than the aniline stage. Lead gives azoxybenzene, azobenzene and aniline. This specific action of the different catalysts suggests chemical action. Sabatier looked upon nickel as forming a hydride with hydrogen and that this hydride reacted with the organic compound present and not the hydrogen directly. With lead and bismuth catalysts the oxide at the one end of the catalyst column was observed. The peculiar behavior of the iron and antimony was mentioned in our second paper. For the production of azobenzene the reaction may be looked upon thus  $2\text{C}_6\text{H}_5\text{NO}_2 + 4\text{Pb} = \text{C}_6\text{H}_5\text{N} : \text{NC}_6\text{H}_5 + 4\text{PbO}$ . Then  $\text{PbO} + \text{H}_2 = \text{Pb} + \text{H}_2\text{O}$ . It will be noted that only the removal of oxygen is necessary to produce azobenzene from nitrobenzene. To produce aniline however the introduction of hydrogen is necessary. However it would seem altogether possible to have both metallic lead and a hydride of lead acting as reducing agents at the same time which would give both azobenzene and aniline.

### Summary of Results

A. *Lead as catalyst.*—1. Nitrobenzene is reduced to azoxybenzene, azobenzene and aniline by hydrogen with lead as catalyst.

2. The best catalyst for the production of azobenzene in an iron catalyst tube is prepared by reducing yellow litharge.

3. The best temperature for the production of azobenzene in an iron catalyst tube is near  $290^\circ$ .

4. The best catalyst for the production of aniline in an iron catalyst tube is prepared by reducing red lead made from white lead.



5. The best temperature for the production of aniline in an iron catalyst tube is not below 308°.

6. A catalyst used in a glass tube gives higher azobenzene yields and lower aniline yields than when used in an iron tube. However its activity decreases much more rapidly in glass than in iron so that iron is preferable to glass.

7. In a glass catalyst tube the catalyst from white lead is best for producing aniline, and the one from red lead made from white lead is best for producing azobenzene.

8. The addition of NaOH and MgO to the lead catalyst in an iron tube did not increase its activity, and a larger amount of NaOH decreased it.

9. The addition of 1/2% Fe<sub>2</sub>O<sub>3</sub> to a heavy litharge increased the yield of both azobenzene and aniline, while 5% Fe<sub>2</sub>O<sub>3</sub> increased the yield of aniline at the expense of azobenzene.

10. The addition of 5% CuO to the heavy litharge in an iron tube was detrimental to its activity.

11. Within the limits studied the more finely divided the red lead the greater the activity of the catalyst prepared from it.

*B. Bismuth as catalyst.*—1. Nitrobenzene is reduced to azoxybenzene, azobenzene, hydrazobenzene and aniline by hydrogen with bismuth as catalyst.

2. With equal volumes of catalyst a catalyst prepared from a heavy bismuth oxide is more active than one prepared from a light oxide.

3. The activity of the bismuth does not decrease so rapidly when used in an iron as when used in a glass tube.

4. A good temperature at which to use the bismuth catalyst is between 280° and 300°.

*Laboratory of Physical Chemistry  
Indiana University, Bloomington*

## THE NATURE OF SECONDARY VALENCE

BY HOMER W. SMITH

- Part I Preliminary Communication, Jour. Phys. Chem., 25, 160 (1921).  
Part II Systems water: xylene and water:  
chloroform, Ibid., 25, 204 (1921).  
Part III System water: ether, Ibid., 25, 605 (1921).  
Supplementary note on extrapolation  
method of correction, Ibid., 25, 616 (1921).  
Part IV System glycerine: acetone, Ibid., 25, 721 (1921).  
Part V Systems containing water and paraffin  
oil; petroleum; tri-chlorobenzene;  
*iso*-amyl phenyl ether; toluene;  
benzene; bromo-benzene; carbon  
tetrachloride; dichlorobenzene; *n*-  
butyl bromide; *n*-butyl ether; ethyl-  
ene chloride; *sec*-octyl alcohol; *n*-  
butyl alcohol; *iso*-butyl alcohol;  
amyl alcohol and bromoform, Ibid., 26, 256 (1922).

### VI. Summary and Discussion

#### I. Summary

This investigation was prompted by the desire to ascertain something of the nature of the forces involved in liquid solutions. To this end the distribution of various organic solutes between immiscible solvents was chosen as the most promising and direct experimental procedure. In all, about twelve hundred final determinations have been presented, involving twenty-one systems each consisting of two immiscible liquids.

These results as they stand are not comparable with one another because of the complications introduced by dissociation, association and the mutual solubility of solvents. It has been shown, however, that these complications can be eliminated in part by an empirical method of correction, and the partition coefficients so obtained put on a mathematically comparable basis, even though their physical-chemical significance is still obscure. This method of correction consists

in determining by interpolation the partition coefficient when the concentration in one solvent has a fixed arbitrary value. The interpretation of the results obtained by means of this method of correction is independent of the arbitrary value chosen for interpolation.

The principal points established by a consideration of the experimental data are as follows:

When the partition coefficients of various substances for any one system are compared on a basis of molecular volume, it is found that they may be covered by the equation

$$\text{Log } 100 \mathfrak{P} = \frac{V_m}{60.00} \pm a$$

where  $V_m$  is the molecular volume at the boiling point.

A limited number of values of  $a$  are required to cover the behavior of all substances in any one system. (All substances covered by the same value of  $a$  in any one system have been called a "series," and the corresponding values of  $a$  the "series constants.")

The various values of  $a$  (or series constants) in any one system have been found to be related to each other by simple proportion.

It has also been found that the series constants for any one series in twenty systems containing a common solvent (water) are related to each other by simple proportion.

The above facts are interpreted as indicating that solubility is a function of the molecular volume of the solute. It is believed that the stepwise phenomena of series, as shown by the integrally related values of  $a$  in the above equation, are attributable to discrete or abrupt variations in the intensity of the intermolecular forces associated with various molecular species.

## 2. Homogeneity and Three-Dimensional Symmetry

Before discussing the fundamental significance of these results, it will be necessary to consider again certain points,

already discussed in Part I, disclosed by molecular volume relations. It has been said that the experimental facts relating to the molecular volumes of liquid chemical compounds indicate that every atom contributes a definite volume to the molecular volume. Some atoms vary in their atomic volumes as a result of constitutive influences (that is, interactions attributable to the chemical arrangement of the atoms in the molecule) but these constitutive variations in atomic volume are well defined and are related in no way to what we may conceive as spatial configuration. A consideration of molecular volume relations shows that the configurations suggested in structural formulae indicate only the chemical properties of the constituent atoms in the molecule, and in no way define the actual spatial relationships of the various parts or of the whole. The molecular volume is the simple sum of the volumes of the constituent atoms, and there is no additional space which can be attributed to interatomic or intermolecular crevices resulting from fixed spatial configurations as suggested by these formulae. To repeat the example previously used, there is no hole inside the benzene molecule or cracks or crevices between the atoms, as there would surely be if the molecule consisted of rigid spheres of carbon with smaller rigid spheres of hydrogen tacked on at various places. The principle of the perfect sum implies that the six carbons and their attendant hydrogens make up a domain which has the same shape, in the electro-dynamic sense, as has each of the components, much as though we had put several little spheres together to make one big sphere.

We have seen in the data presented in these papers that molecular volume appears to be one of the factors which determine the behavior of various molecular species in homogeneous liquid systems. This determinative rôle of molecular volume is independent of the chemical nature of the molecular species involved and constitutes new evidence of a most conclusive kind in regard to the shapes of molecules. We may summarize this evidence as follows: substances in the homogeneous liquid phase behave toward their environment as

though every molecule homogeneously filled a space which is symmetrical in three dimensions.<sup>1</sup>

An assumption somewhat of this nature has been made from time to time by mathematicians when considering the attraction of one molecule for another, but the chemist, in the absence of direct evidence to the contrary, has persistently clung to notions of chemical configuration and spatial relationships.<sup>2</sup> The mathematician speaks of point-to-point action, and avoids the difficulties arising from chemical considerations by arguing that this alleged point-to-point action is only a statistical result. As to how far this is so, it is hard to say because of course we cannot avoid statistical observation and we do not know the exact extent to which the real molecular domain is increased by the translational motion of heat. But the specific nature of the optical properties, the compressibilities and more especially the radiation of heat from liquids and solids indicate that only a small fraction of the apparent molecular domain is to be attributed to translational motion. It seems instead that when there is an expansion of the molecular domain on the absorption of energy, it is to be attributed to an actual expansion of the size of the molecule.<sup>3</sup>

But even if we agree to subtract a certain amount from the observed molecular volume to allow for space taken up by translational motion, we must still apply the principle of homogeneity and three-dimensional symmetry to the remaining real volume, for otherwise molecular volume could not

<sup>1</sup> Attention is called to the phrase "in the homogeneous liquid phase." The work of Langmuir (*Jour. Am. Chem. Soc.*, 39, 1848 (1917)) and Harkins and his collaborators (*Ibid.*, 39, 541 (1917)) shows that molecules at the surfaces of liquids are oriented and possess more or less definite shapes, but neither Langmuir's nor Harkins' work applies to molecules situated within a homogeneous liquid where the surrounding field of force is symmetrical.

<sup>2</sup> Among others who have argued from this premise are S. C. Bradford: *Phil. Mag.*, 38, 696 (1919); J. J. Thomson: 27, 757 (1914); W. C. McC. Lewis: 28, 104 (1914); W. D. Harkins and H. H. King: *Jour. Am. Chem. Soc.*, 41, 970 (1919).

<sup>3</sup> See Gervaise LeBas: "The Molecular Volumes of Liquid Chemical Compounds," p. 254 (1915).

function as a determinative factor in solubility in the precise manner in which it does. So taking into account the additive nature of molecular volume and the rôle of molecular volume in homogeneous liquid solutions, we must look upon this homogeneity and three-dimensional symmetry of liquid molecular domains as an actual fact and not an apparent one. We must picture the electrons of the atoms and molecules which make up a mass of liquid as filling, by their electrodynamic activity, the entire liquid domain, being at equilibrium at all points, and leaving no crevices or dead-spaces wherein other electrons or atoms or molecules can be inserted without disturbing this equilibrium.

### **8. The Nature of the Intermolecular Forces**

Besides the size of the molecule, there is yet another factor which influences its physical relations with other molecules; this is the intensity factor in the intermolecular forces. It has already been pointed out that slight variations in the arrangement of atoms result in the most profound variations in molecular behavior as regards nearly all physical properties and we see this fact illustrated especially well in relative solubility. The striking thing about these variations in this case is that they consist of abrupt or stepwise variations from one condition to another—the various conditions being related to each other by simple proportion.

As the evidence from partition coefficients now stands it is apparent we are dealing not only with the properties of undissociated molecules, but with associated complexes and ions and hence with the chemical forces underlying association and dissociation, as well. But despite the fact that this complication precludes more direct physical-chemical consideration, it gives the results greater physical significance because it brings all these phenomena under one category without in any way invalidating the physical interpretations based upon the results.

This simple stepwise variation in behavior mentioned above is shown by a large variety of substances: compounds

containing carbon, hydrogen, oxygen, nitrogen, chlorine, bromine, iodine and sulphur in a variety of chemical combinations. Hence this phenomenon cannot be attributed to peculiarities in molecular or atomic structure because it appears to be wholly independent of the kind of atoms or molecules involved. It must instead be attributed to something common to all atomic species and inherent in atomic structure itself. Undoubtedly, it is to be associated with the now generally accepted idea that atoms absorb and emit energy discontinuously, in whole multiples of a unit of energy  $h\nu$ , or Planck's quantum. This unit has a different value for every frequency of radiation,  $\nu$ , but it involves a universal constant,  $h$ . It is to be noted that this quantum is a unit of action, since it has the dimensions of energy multiplied by time, whereas the element of time does not enter into our present consideration. We are comparing various physical systems in their characteristic and essentially fixed equilibrium states.

Bohr has assumed that the electron in a hydrogen atom could revolve about the nucleus only in certain orbits which represent conditions of stable equilibrium. On the absorption or emission of a quantum of energy the electron would jump from one orbit to another and thus enter another stable state.<sup>1</sup>

No one has, as yet, satisfactorily explained the existence of stable states, though this conception underlies Bohr's explanation of the quantum and the theories of atomic structure as well. Thus Langmuir<sup>2</sup> has suggested that each electron occupied a more or less permanent position in the atom which he called a cell, the various cells being arranged in symmetrical positions around the nucleus of the atom. In discussing the properties of the electron he has said, "It seems that the electron must be regarded as a complex structure

<sup>1</sup> For a general discussion of the quantum theory see "The Quantum Theory," Edwin Plimpton Adams: Bull. of the National Research Council, Vol. I, Part 5, No. 5; Wm. C. McC. Lewis: "A System of Physical Chemistry," Vol. III, "Quantum Theory" (1919). Also Max Planck: Phil. Mag., 28, 60 (1914). On the application of the quantum theory to radiation from liquids and solids see H. Stanley Allen: *Ibid.*, 35, 338, 404, 445 (1918).

<sup>2</sup> Jour. Am. Chem. Soc., 41, 868 (1919).

which undergoes a series of discontinuous changes while it is being bound by the nucleus or kernel of the atom."<sup>1</sup>

Thomson<sup>2</sup> has considered the behavior of the electron on the hypothesis that the field of force in the immediate vicinity of the positive charge changes alternately from attraction to repulsion. At great distances these forces would reduce to the inverse square law but for atomic distances the change in sign would result in a series of positions of zero force which would be positions of stable equilibrium. Other assumptions of a more or less arbitrary nature have been made by Nicolson,<sup>3</sup> Brillouin,<sup>4</sup> Allen,<sup>5</sup> Lamar<sup>6</sup> and others to account for the discontinuous absorption and emission of energy as postulated under the quantum theory.

#### 4. The Conservation of Energy and Inter-electronic Equilibration

The intermolecular forces are commonly supposed to have their origin in the so-called "chemical" or valence electrons. No one has advanced any very definite suggestion as to how these electrons function while holding molecules together in the liquid state. It is usually assumed that the cohesive forces are due to stray fields of force, residual affinity, etc.<sup>7</sup>

It does not seem possible that an electron may be so situated that its electrostatic or electro-magnetic affinities are satisfied, and that it may still be able to permanently influence, without dynamic expense, other electrons by virtue of "stray fields of force." It seems much more consistent

<sup>1</sup> Phys. Rev., 8, 300 (1919).

<sup>2</sup> J. J. Thomson: Phil. Mag., 37, 419 (1919).

<sup>3</sup> J. W. Nicolson: Ibid., 28, 90 (1914).

<sup>4</sup> Marce Brillouin: Comptes rendus, 168, 1318 (1920).

<sup>5</sup> H. Stanley Allen: Phil. Mag., 41, 113 (1921).

<sup>6</sup> Joseph Lamar., Ibid., 42, 592 (1921).

<sup>7</sup> Albert P. Mathews: Jour. Phys. Chem., 20, 554 (1916); Herbert Chatley: Proc. London Phys. Soc., 29, 206 (1916); Irving Langmuir: Jour. Am. Chem. Soc., 39, 1848 (1917); S. C. Bradford: Phil. Mag., 38, 696 (1919); W. C. McC. Lewis: 28, 104 (1914); Wm. D. Harkins and H. H. King: Jour. Am. Chem. Soc., 41, 970 (1919).



to believe that a principle of conservation applies to all inter-electronic relations, including the intermolecular forces; that the intermolecular forces are expendable by the molecule to a definite and limited extent dependent on the electronic fabrication of the molecule, just as it has always been assumed in the case of the interatomic forces. Since the intermolecular forces have their genesis in the electrons of the constituent atoms, we can arrive at such a position simply by assuming that a state of conservative equilibration exists between all the electrons which are involved in the interatomic and intermolecular forces. That is, in the atom or molecule, or in any homogeneous system of atoms or molecules, all the electrons exert forces on all the other electrons, holding each other in certain positions of stable equilibrium. If any of the physical conditions of the system are altered by the absorption or emission of energy, or by admixture with another system, certain electrons are displaced and take up new positions of equilibrium. On the assumption that energy is added to or taken from a system only by a discontinuous process, it would necessarily follow that the alteration of any system from one physical state to another would likewise be discontinuous. Various systems (or various molecular species) could be treated as a single system in various equilibrium states, and the various systems would bear definite relations to each other which would result in simple mathematical relationships between the partition coefficients, the frequencies of spectral lines and all other physical properties.

It should be reiterated that the experimental data from partition coefficients deal with various systems in their characteristic equilibrium states, and that the element of time, a necessary consideration in the process of change from one equilibrium state to another, is not involved. In this respect, these data are unique, for they demonstrate that the existence of these discrete differences in the equilibrium states of a given system, or of various systems, is independent of the time element. The evidence warrants the assumption that these discrete differences are attributable to some property in-

herent in the fundamental charges themselves. Some such assumption as that made by Thomson, namely that the field of force around the fundamental charges changes alternately from attraction to repulsion, appears to offer the only explanation of the facts.

*Johns Hopkins University  
School of Hygiene and Public Health  
Department of Physiology  
Baltimore  
and  
The Lilly Research Laboratories  
Eli Lilly and Company  
Indianapolis*

1-1719

# THE VAPOR PRESSURE OF SULFUR DIOXIDE AND AMMONIA

358

BY F. W. BERGSTROM

## Introduction

In connection with a series of investigations on the physical properties of the constituents of natural gas, Burrell and Robertson<sup>1</sup> have measured the vapor pressures of ammonia and sulfur dioxide at temperatures ranging from the normal boiling points down to below  $-100^{\circ}$ . The wide discrepancies between the values of the vapor pressures around the normal boiling point of these two liquids as determined by Burrell and Robertson, and the values obtained previously by other investigators, and especially the disagreement, to the extent of a whole degree between the normal boiling points as interpolated from their results and the carefully determined values for these constants made some years ago in this laboratory by H. D. Gibbs<sup>2</sup> led to a redetermination of the vapor pressures of these two substances.<sup>3</sup>

## Description of Apparatus

The apparatus used for vapor pressure measurements is shown diagrammatically in Figs. 1, 2 and 3. The manometer and thermoregulator are separately represented in Figs. 2 and 3. The liquid whose vapor pressure was to be measured was confined in the bulb I. A capillary connected this with the left arm, J, of the manometer. By means of the two-way stopcock K, I could be connected either with the purification train, C, C', C'', or with a Töpler pump (not shown). E was

<sup>1</sup> Burrell and Robertson: Technical Paper 142, U. S. Bureau of Mines.

<sup>2</sup> Gibbs: Jour. Am. Chem. Soc., 27, 851 (1906).

<sup>3</sup> The measurements described in this paper were completed during the summer of 1918. Publication was delayed because of the appearance of the Bureau of Standards article on the vapor pressure of ammonia. Although the work done on sulfur dioxide is now of greater importance, it was thought worth while also to include the data obtained from ammonia, as confirmatory of the results of the Bureau of Standards.

a large Dewar tube vessel, 45 × 20 cm internal dimensions, containing petroleum ether for the constant temperature bath. G was a motor-driven stirrer. The resistance thermometer H was connected to three long heavy leads attached to a Wheatstone bridge. Liquid air contained in a five-liter Dewar flask, A, was forced over into the wide test tube M by air pressure exerted on the liquid thru C'. The magnitude of this pressure, and hence the rate of transfer of liquid to M was regulated by changing the depth of immersion of the tube under the water in D. This arrangement is a modification of Hen-

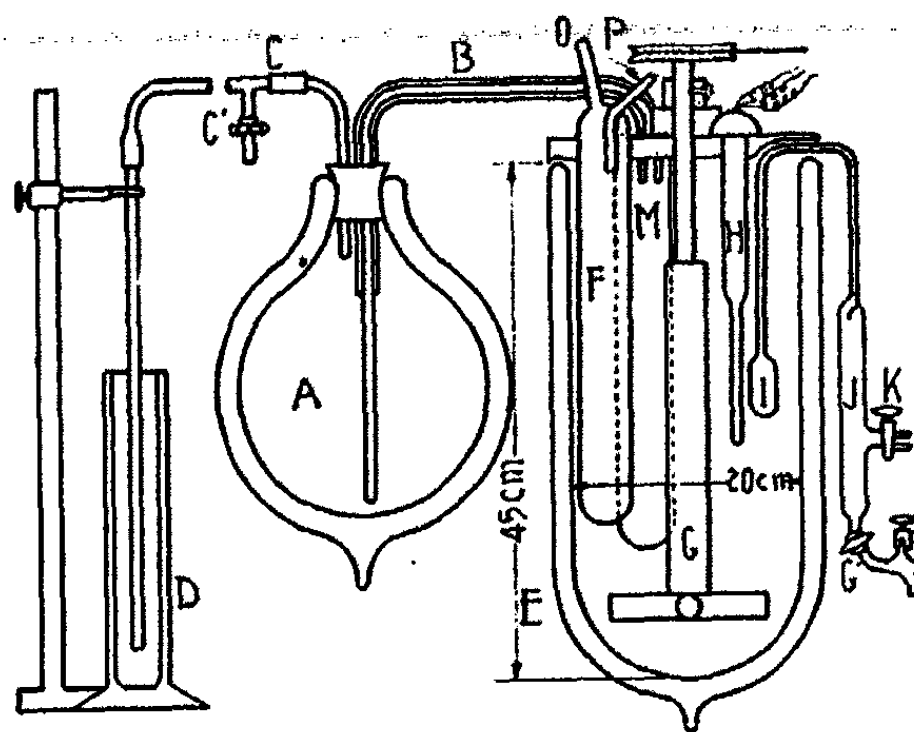


Fig. 1

Apparatus for Vapor Pressure Measurements  
(Thermoregulator shown separately in Fig. 3)

ning's low temperature thermostat.<sup>1</sup> The petroleum ether bath was cooled with liquid ammonia down to  $-30^{\circ}$  and with liquid air below this temperature. Ammonia from a compressor, after passing thru a pipe and needle valve, entered a wide closed tube, F, thru P, where it evaporated and was pumped back thru a second pipe attached to O.

The manometer, shown in detail in Fig. 2, is a modification of that described by Germann.<sup>2</sup> The dimensions are

<sup>1</sup> Henning: Zeit. Instrumentenkunde, 33, 33 (1913).

<sup>2</sup> Germann: Jour. Am. Chem. Soc., 36, 2456 (1914).

given in the figure. A stopcock, G, separating the two arms of the manometer, was opened only during adjustment of mercury level, and preceding vapor pressure measurements. With G closed, a pressure corresponding to a previously regulated temperature could be read while the bath was being cooled in readiness for the next observation. As the mercury level in J was kept near the glass index P during most of the time that liquid was in I, any entrance of air at low pressures could readily

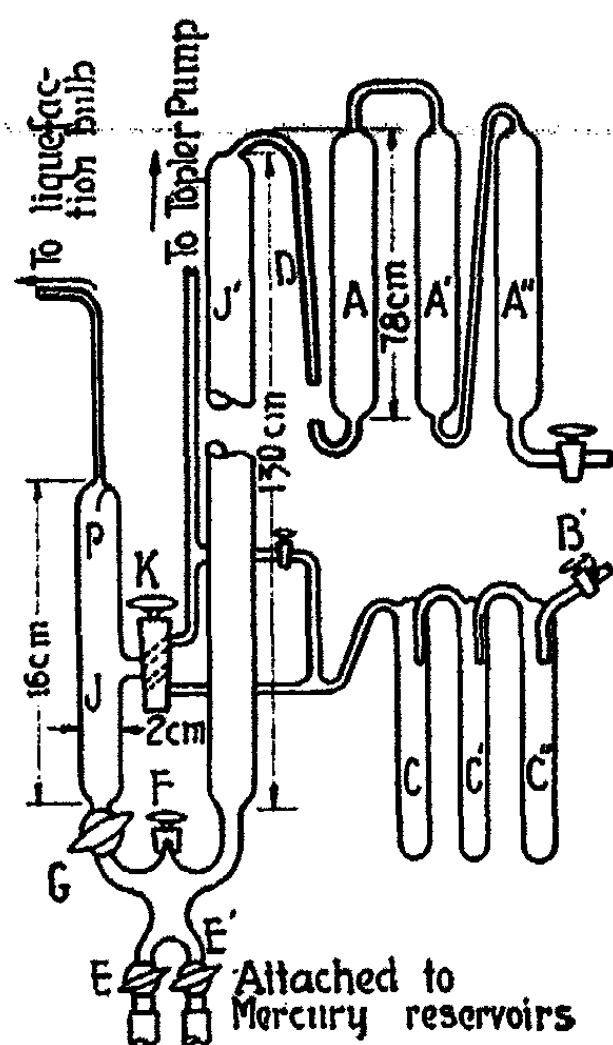


Fig. 2  
Manometer

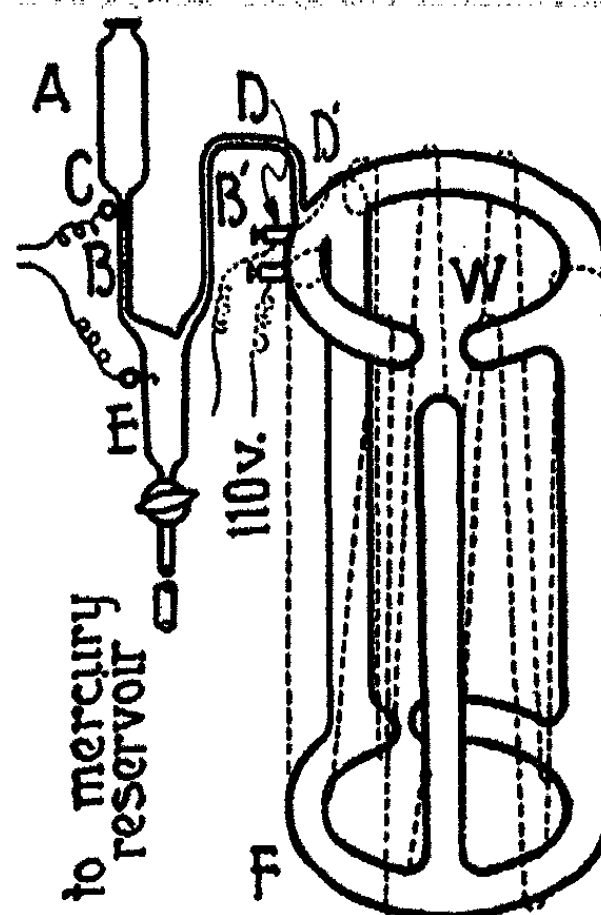


Fig. 3  
Thermoregulator

be detected. The mercury column prevented direct contact of the enclosed gas with the stopcock. The method of producing a high vacuum above the mercury in J', and the precautions necessary completely to free J' of traces of air are given in the original article by Germann. The apparatus was pumped out at intervals thruout the work to insure the maintenance of a perfect vacuum.

A large mercury reservoir for rough adjustments of level was attached below  $E'$ , and a small one for the more delicate adjustments necessary to bring the mercury level to the tip of the index  $P$  was connected to  $E$ . As the height of the index was determined at the beginning of a series of measurements, but one cathetometer reading was necessary for each pressure. The former was checked at frequent intervals. The total height of a mercury column could accurately be measured to within 0.2–0.4 mm.

The height of mercury in the manometer was read with a cathetometer at a distance of eight feet. The instrument used possessed a brass scale 1.2 meters in length, graduated in millimeters, with a vernier reading to twentieths. As it was slightly bent during the earthquake of 1906, it was necessary to level the telescope before each reading.<sup>1</sup>

The mercury used in the manometer was purified according to the method of Hulett.<sup>2</sup> A sample of this mercury melted at  $-38.9^\circ$  (resistance thermometer).

The observed manometer height was corrected to  $0^\circ$  for expansion of the mercury and of the brass cathetometer scale. Other corrections were within the limit of experimental error.

#### Temperature Regulation

Liquid air or ammonia was introduced in the manners described, into  $F$  and  $M$ , Fig. 1, at rates just sufficient slowly to cool the bath. The thermoregulator with its heating element then accomplished the close regulation desired.

The thermoregulator, Fig. 3, consisted of a framework of one cm glass tube,  $F$ , filled with toluene, and connected by a capillary with two tube reservoirs,  $A$  and  $E$ , the former for toluene, the latter for toluene and mercury. The heating wires  $W$ , strung on the frame, were connected to a 110 volt circuit thru a variable five-lamp resistance and a relay, operated

<sup>1</sup> This instrument was recently compared with a new Gaertner cathetometer, and found to be accurate.

<sup>2</sup> Phys. Rev., 33, 307 (1911).

by contacts at C and E. To set for temperatures, a small reservoir attached to E was raised until mercury had risen to the upper contact. While keeping the reservoir in this position, the bath was cooled to suck mercury up into the capillary B'. Upon closing the stopcock, and turning on sufficient current slowly to warm the bath in spite of the cooling due to liquid air or ammonia, the desired temperature could be held constant as long as necessary. Mercury should stand at least a centimeter high in B' for the best operation. This type of thermoregulator eliminates the use of a stopcock in contact with the toluene.

Temperatures have been regulated by this method to within  $0.02^\circ$ , as shown by the change in resistance of the platinum thermometer element. With liquid ammonia, temperatures could be held constant to within  $0.05^\circ$  without difficulty.

#### Thermometry

Temperatures were measured with a three-lead, compensated, platinum resistance thermometer. The resistances were determined with a dial Wheatstone bridge reading directly to 0.0001 ohm, the points of balance being found with a high sensitivity galvanometer. The instruments were manufactured by Leeds and Northrup.

The resistance thermometer was calibrated by the Bureau of Standards, with the following results:

Resistance at  $0^\circ = R_0 = 9.360$  ohms.

Fundamental Interval =  $R_{100} - R_0 = 3.210$  ohms.

$\delta$  in Callendar's difference formula = 1.47.

The calibration was checked in this laboratory at the freezing points of water and of mercury. Resistances of 9.3590, 9.3593, and 9.3597 ohms were observed at  $0^\circ$  in three experiments at different times. The resistance at the freezing point of mercury ( $-38.89^\circ$ , Henning;<sup>1</sup>  $-38.87^\circ$ , Wilhelm<sup>2</sup>) was found to be 8.089 ohms. The corresponding temperature was calculated to be  $-38.9^\circ$ .

<sup>1</sup> Henning: *Ann. Phys.*, (4) 43, 294 (1913).

<sup>2</sup> U. S. Bureau of Standards., *Sci. Paper No. 204*, 655-61 (1916).

As the simple Callendar formula does not hold below  $-40^{\circ}$  the thermometer was calibrated against the vapor pressure of liquid oxygen according to the methods of von Siemens<sup>1</sup> and Henning.<sup>2</sup> The oxygen was prepared and purified as described by von Siemens, but the apparatus was in most respects identical with that of Henning. A resistance of 2.924 ohms was found at  $-190.7^{\circ}$  (average of three values). The temperature was calculated from the observed pressure (317 mm), using the vapor pressure data of von Siemens.<sup>3</sup> The temperatures below  $-40^{\circ}$  were determined from a formula of Henning's<sup>3</sup> involving this calibration.

The temperatures as determined by the resistance thermometer are probably accurate to within  $0.1^{\circ}$ .

#### Preparation and Purification of the Gases

The vapor pressure measurements were checked in each instance by determinations upon a second sample prepared by a different method.

*Sulfur Dioxide.*—The first sample of sulfur dioxide was obtained from a stock cylinder of the commercial liquid, and was purified in the following manner:

The gas was condensed in the first of the fractionation tubes C'' (Fig. 2), containing phosphorus pentoxide, and allowed to stand for an hour to insure complete removal of moisture. A vacuum of a few millimeters of mercury was produced in the tubes, and some sulfur dioxide distilled into C'', with this surrounded by an alcohol bath at about  $-90^{\circ}$ . Most of the gases of high vapor pressure at that temperature were thus removed. The liquid, after reaching room temperature, was caused to boil vigorously by opening stopcock B' until its volume had diminished one-third (to remove gaseous impurities). Following this, the sulfur dioxide was frozen, and the entire system, including the bulb I, Fig. 1, evacuated as completely as possible. The frozen mass was melted, a portion

<sup>1</sup> Von Siemens: *Ann Phys.*, (4) 42, 871 (1913).

<sup>2</sup> Henning: *Ibid.*, (4) 43, 294 (1913).

<sup>3</sup> *Loc. cit.*



boiled off under reduced pressure, and the process repeated. This treatment served to remove the last traces of dissolved gas and to free the liquefaction bulb and connecting tubes from air. Two-thirds of the purified sample were distilled into I, and half of this was pumped off to make sure that no air had been trapped in the transfer. With stopcock K closed, mercury was raised to the pointer, sealing the opening.

The second sample of sulfur dioxide, prepared by the action of concentrated sulfuric acid on copper, was washed successively with water and concentrated sulfuric acid, then passed over ignited pumice saturated with water (to remove  $H_2SO_4$ ), and thru drying tubes to remove the greater part of the moisture before condensation in C''. The subsequent treatment was the same as described above.

*Ammonia.*—Ammonia was obtained (1) from a small stock cylinder of the commercial liquid, (2) by distillation of C. P. ammonia water. The gas was condensed in a tube, C'' (not the one used for sulfur dioxide), containing sodium and allowed to stand for an hour to remove moisture. One-third of the sample was rapidly boiled off by opening stopcock B'. The ammonia was fractionated from C'' to C', and thence to C, traces of sodium which ordinarily would have been carried over having been removed by an ignited asbestos filter sealed between C'' and C'. The sample was frozen in C' with liquid air, the entire system evacuated, and dissolved gases removed by a process of alternate freezing, melting, and boiling, as described for sulfur dioxide. The introduction into the vapor pressure bulb I was carried out with the same precautions as before. The second sample was partially dried with soda-lime, condensed, and treated as described.

#### Results of Measurements

The results of the vapor pressure measurements made are presented in Table 1, while the values interpolated for every five degrees of the temperature scale, together with similar data of other investigators, are given in Table 2 (for sulfur dioxide).

TABLE I  
Sulfur Dioxide

Observed resistance ohms	Corresponding temperature °C	Observed pressure corr. to 0° mm	Observed resistance ohms	Corresponding temperature °C	Observed pressure corr. to 0° mm
9.179	-5.5	924.8	7.591	-54.0	60.2
9.133	-7.0	867.2	7.471	-57.6	52.0
9.068	-9.0	799.0	7.259	-64.0	32.4
9.039	-9.9	765.4	7.091	-69.1	21.4
9.001	-11.0	727.5	6.975	-72.6	16.5
8.949	-12.6	676.7	6.927	-74.1	14.1
8.845	-15.8	583.6	6.850	-76.3	11.7
8.716	-19.7	483.2	6.805	-77.7	11.0
8.640	-22.1	430.7	6.572	-84.7	4.4
8.498	-26.4	345.5	6.391	-90.1	2.5
8.374	-30.2	282.5			
8.365	-30.5	278.2	9.169	-5.9	911.6
8.221	-34.9	219.1	9.047	-9.6	774.4
8.054	-40.0	162.9	8.911	-13.8	641.2
7.846	-46.3	110.7	8.765	-18.2	519.2

Second Sample

Ammonia

Second Sample

Observed resistance ohms	Corresponding temperature °C	Observed pressure corr. to 0° mm	Observed Resistance ohms	Corresponding temperature °C	Observed pressure corr. to 0° mm
8.383	-30.0	903.3	8.374	-30.2	891.0
8.261	-33.7	751.3	7.716	-50.2	304.4
8.109	-38.3	593.6	7.152	-67.3	101.2
7.956	-43.0	460.0	6.951	-73.3	64.8
7.795	-47.8	350.8	6.843	-76.5	50.6
7.631	-52.8	261.4	6.732	-79.9	37.2
7.440	-58.6	182.2	6.579	-84.4	24.2
7.228	-65.0	117.4	—	-77.9 <sup>1</sup>	45.5 <sup>1</sup>

<sup>1</sup> Triple point.

TABLE 2  
Sulfur Dioxide

Vapor pressure measurements interpolated for every five degrees of the temperature scale compared with data of other investigators.

Temp. °C	Bergstrom <sup>1</sup> mm	Burrell <sup>2</sup> mm	Regnault mm	Pictet mm	Blümcke mm	Faraday mm
0	—	—	1165	1148	1149	—
-5	947	—	947	950	—	—
-7.2	860	—	—	—	—	851
-10	762	792	763	760	—	—
-11.5	712	—	—	—	722	—
-15	607	639	608	578	—	—
-17.8	530	—	—	—	—	551
-19.5	488	—	—	—	456	—
-20	478	507	479	463	—	—
-25	373	396	374	418	—	—
-30	286	306	287	253	—	—
-35	217	234	—	—	—	—
-40	162	174	—	—	—	—
-45	120	115	—	—	—	—
-50	87	89	—	—	—	—
-55	62	62	—	—	—	—
-60	43	43	—	—	—	—
-65	30	30	—	—	—	—
-70	19.9	20.4	—	—	—	—
Solid	— <sup>3</sup>	—	—	—	—	—
-75	12.8	12.8	—	—	—	—
-80	8.0	8.0	—	—	—	—
-85	4.1	4.1	—	—	—	—
-90	2.5	2.5	—	—	—	—

In all of the observations above  $-30^{\circ}$  (i. e., when the bath was cooled with liquid ammonia) the temperature was held constant for from twenty to thirty minutes before making readings; otherwise, from five to ten minutes (with liquid air cooling).

#### Other Measurements

Several years ago, Murray E. Tucker and George Ziser independently made measurements of the vapor pressure of ammonia and sulfur dioxide in this laboratory. Observations

<sup>1</sup> Calculated from formula.

<sup>2</sup> Interpolated from large-sized plot of Burrell's data.

<sup>3</sup> Observed.

were made with practically the same apparatus described in this paper, but the methods of use were not the same. Calibrated toluene thermometers were used thruout. The measurements, while insufficient to determine the entire vapor pressure curve with accuracy, are especially numerous near the normal boiling and triple points. These observations are plotted in Figs. 4 and 5.

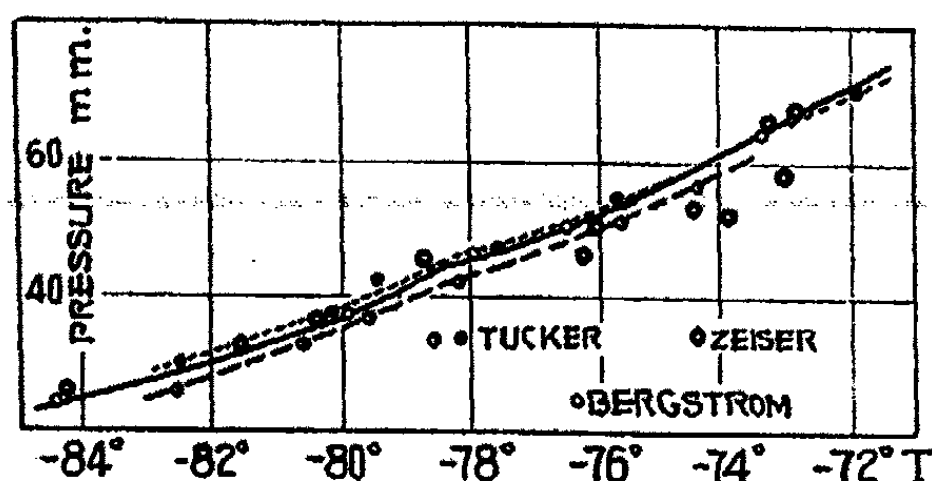


Fig. 4  
Vapor Pressure Determinations near the Triple Point of Ammonia

#### The Triple Point of Ammonia

No definite information regarding the triple point of sulfur dioxide was obtained. A well-defined triple point was found for ammonia (see Fig. 4). The constant temperature bath was allowed to warm up slowly, after being cooled to  $-85^{\circ}$ , and the pressure observed just as the solid began to melt. This pressure at the triple point was found to be 45.5 mm. The corresponding temperature calculated from the formula for the vapor pressure curve is  $-77.9^{\circ}$ .

The measurements made by Ziser and Tucker in the region of the triple point are plotted in Fig. 4. Tucker's observations were made on different occasions, and the curves, while not in agreement, are both markedly discontinuous from liquid to solid. He was able to obtain at one time two points upon the supercooled ammonia curve. The observations of Ziser and Tucker, with the exception of some scattered results, show the triple point to be slightly below  $-78^{\circ}$ .

Brill<sup>1</sup> found a discontinuity between the vapor pressure curves for liquid and solid phases, altho no mention is made of the fact. Burrell found no such break.

The Bureau of Standards<sup>2</sup> has recently accurately determined the pressure and temperature at the triple point of ammonia. The observed pressure was 44.9 mm. The observed temperature was  $-77.70^{\circ}$ , while that calculated from their vapor pressure formula was  $-77.84^{\circ}$ .

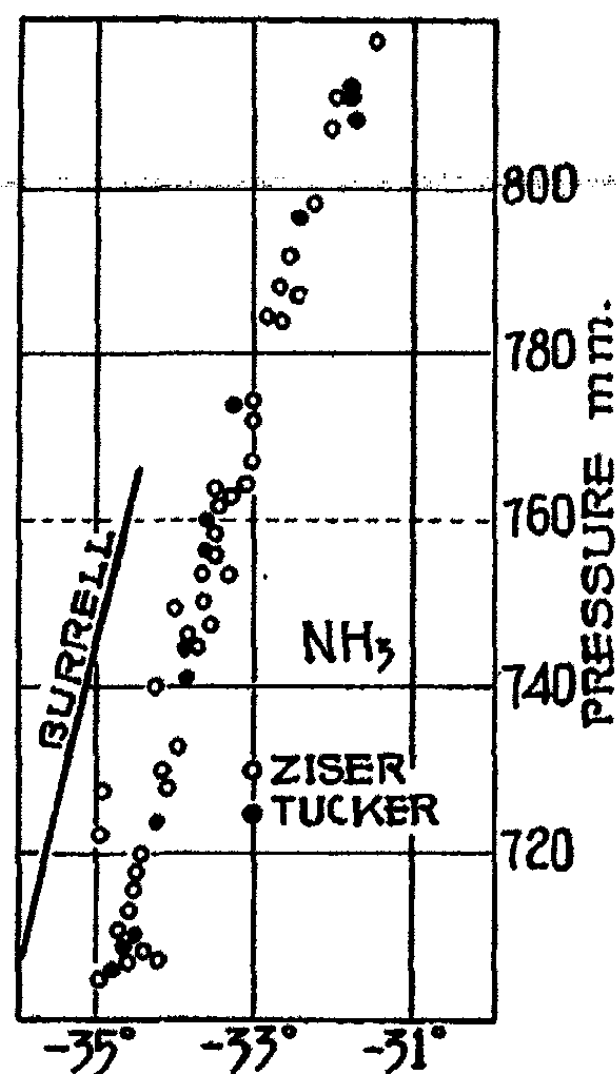


Fig. 5  
Measurements near the Normal Boiling Point

#### Formula for Vapor Pressure Curve

The experimental results were expressed by the partially theoretical Nernst formula:

$$\text{Log}_{10} P = -\frac{\lambda^{\circ}}{4.571T} + 1.75 \log T - \frac{\epsilon T}{4.571} + C.$$

<sup>1</sup> Ann. Phys., (4) 21, 170 (1906).

<sup>2</sup> Jour. Am. Chem. Soc., 42, 222 (1920).

Sulfur Dioxide ( $P$  in mm of mercury):

$$\text{Log}_{10} P = -\frac{1577.3}{T} + 1.75 \log T - 0.006411T + 6.3286$$

The average deviation from the experimentally determined values (disregarding sign) is about one mm.

**Discussion of Results and Comparison with Previous Work. Sulfur Dioxide**

The only vapor pressure determination covering the range from the normal boiling point to solid was made by Burrell.<sup>1</sup> Regnault's<sup>2</sup> and Pictet's<sup>3</sup> results extend only to  $-30^{\circ}$ . Faraday<sup>4</sup> and Blümcke<sup>5</sup> have made a few observations below  $0^{\circ}$ .

Burrell's results vary considerably from previously determined values. The normal boiling point,  $-11.0^{\circ}$ , interpolated from his data, is nearly a whole degree lower than determinations made by Regnault<sup>2</sup> ( $-10.08^{\circ}$ ), Pictet<sup>3</sup> ( $-10.0^{\circ}$ ), Gibbs<sup>6</sup> ( $-10.09^{\circ}$ ) and the author ( $-10.05^{\circ}$ , manometric and direct). His sample was prepared by the action of concentrated sulfuric acid on copper, and purified by fractionation at low temperatures. The sulfur dioxide finally used for measurements distilled within  $0.2^{\circ}$ , altho the method of determining this range is not indicated.

Burrell's work appears accurate from his descriptions, but the vapor pressures of ammonia and sulfur dioxide have been carefully determined in this laboratory, and results have been obtained agreeing in each case much more closely with previous observations than do his. The close agreement with the first determinations of the check measurements made upon the second samples affords a good indication of the purity of our material.

Regnault's results agree very closely with those of the author (see Table 2 and Fig. 9). The maximum variation is

<sup>1</sup> Loc. cit.

<sup>2</sup> Regnault: *Mém. de l'Acad.*, 1863, 535.

<sup>3</sup> Pictet: *Arch. de Genève*, 13, 212.

<sup>4</sup> Faraday: *Phil. Trans.*, 135, 1, 155 (1845).

<sup>5</sup> Blümcke: *Wied. Ann.*, 34, 10 (1888).

<sup>6</sup> Gibbs: *Jour. Am. Chem. Soc.*, 27, 851 (1905).

about 3 millimeters. He made two series of observations which were not in good agreement. In one of the series he admits that he did not completely remove air from the apparatus. This may also have been true of the second series.

Pictet's results do not fall on a smooth curve.

Blümcke determined the vapor pressure of sulfur dioxide at two temperatures below  $-10^{\circ}$ . His measurements were not intended for an accurate and complete determination, but merely as a check upon an apparatus used for finding the vapor pressure of solutions. His normal boiling point,  $-10^{\circ}$ , agrees with that of the author.

Faraday likewise made two determinations below  $0^{\circ}$ . They do not agree well with the other measurements mentioned.

#### Ammonia

Regnault,<sup>1</sup> Pictet,<sup>2</sup> Brill,<sup>3</sup> Perman and Davies,<sup>4</sup> Burrell,<sup>5</sup> Keyes and Brownlee,<sup>6</sup> and the Bureau of Standards<sup>7</sup> have previously made measurements covering the whole, or a part of the range from  $-30^{\circ}$  to  $-85^{\circ}$ . The determinations of Brill, Burrell and the Bureau of Standards are the only ones extending below the freezing point. With the exception of Perman and Davies, the others made observations only as low as the normal boiling point,  $-33.4^{\circ}$ .

Brill made one series of measurements around  $-79^{\circ}$  by passing hydrogen thru several layers of solid ammonia, and determining the partial pressure of the latter in the mixture of the exit gases. The second series, made by the static vapor pressure method, covered the range from  $-33^{\circ}$  to  $-80^{\circ}$ . Brill's vapor pressure-temperature curve is lower than the author's in the region of the normal boiling point, and below  $-61^{\circ}$ , but higher at intermediate points. The differences may be due to thermometry.

<sup>1</sup> Regnault: *Mém. de l' Acad.*, 26, 535 (1862).

<sup>2</sup> Pictet: *Arch. Genève*, 13, 212.

<sup>3</sup> Brill: *Ann. Phys.*, (4) 21, 170 (1906).

<sup>4</sup> Perman and Davies: *Proc. Roy. Soc.*, 78, 28, 42.

<sup>5</sup> Burrell: *loc. cit.*

<sup>6</sup> Keyes and Brownlee: *Jour. Am. Chem. Soc.*, 40, 39 (1918).

<sup>7</sup> Cragoe, Meyers, and Taylor: *Ibid.*, 42, 206 (1920).

Burrell's observations were made by the static method upon a sample prepared by boiling C. P. ammonia water. It was purified by repeated distillations until the entire final sample distilled over within  $0.2^\circ$  (or less?). As the molecular boiling point elevation constant of ammonia is only  $3.4^\circ$ , the boiling point of a normal solution would be  $-33.06^\circ$ . It can readily be seen that the constancy of the boiling point of ammonia, unless very accurately measured, is no indication of its purity. Burrell's curve agrees with that of the author below  $-54^\circ$ , but diverges at higher temperatures, the difference at the normal boiling point amounting to  $1.2^\circ$ . The value found for this constant,  $-34.6^\circ$ , is over a degree lower than any determination previously made by manometric means.

Perman and Davies made three measurements below  $-30^\circ$  in order to determine the normal boiling point, which they found to be  $33.5^\circ$ . The results are in agreement with the writers' only near  $-34^\circ$  and at  $-46^\circ$ . As only three measurements below  $-30^\circ$  were made, an error in one or more of the values would seriously affect the entire vapor pressure curve.

The data of Brill, Burrell, Perman and Davies, and the author are compared graphically in Fig. 9.

Regnault and Pictet, respectively, found the normal boiling point to be  $-32.8^\circ$  and  $-33.0^\circ$  by manometric means. Regnault removed water by passage thru a U tube surrounded with liquid ammonia and thru a calcium oxide drying tube. Air was washed from the apparatus by pumping ammonia from the condensed liquid. The latter method, especially, is inadequate.

Keyes and Brownlee by manometric methods found the normal boiling point to be  $-33.25^\circ$ , and by direct determinations  $-33.21^\circ$ . Twenty-eight vapor pressure measurements were made in the region of the normal boiling point. The pressures, reduced to  $33^\circ$  for comparison, vary from 747.6 mm to 786.9 mm and are too erratic for conclusions drawn from the mean.

The Bureau of Standards has carefully determined the vapor pressure between the limits of  $+70^\circ$  and  $-80^\circ$ . Their



normal boiling point,  $-33.35^\circ$ , is  $0.1^\circ$  higher than was found by the author. The average deviation of all the experimental results for ammonia cited in this paper from their curve is three-quarters of a percent. The average deviation of the values above  $-50^\circ$  is only half a percent. The scale of Fig. 9 is too small to show these differences clearly.

M. Tucker and G. Ziser, whose measurements upon ammonia with the apparatus described in this paper have previously been mentioned, made a number of observations around the normal boiling point. These are shown in Fig. 5, in comparison with a portion of Burrell's curve. The normal boiling point from Tucker's results is  $-33.5^\circ$ , and from Ziser's data  $-33.4^\circ$ . Both of these support our values, and constitute further evidence that Burrell's results are in error. The maximum variation of Ziser's measurements for any temperature is 33 mm at  $-34.3^\circ$ . The variation at the normal boiling point is 10 mm.

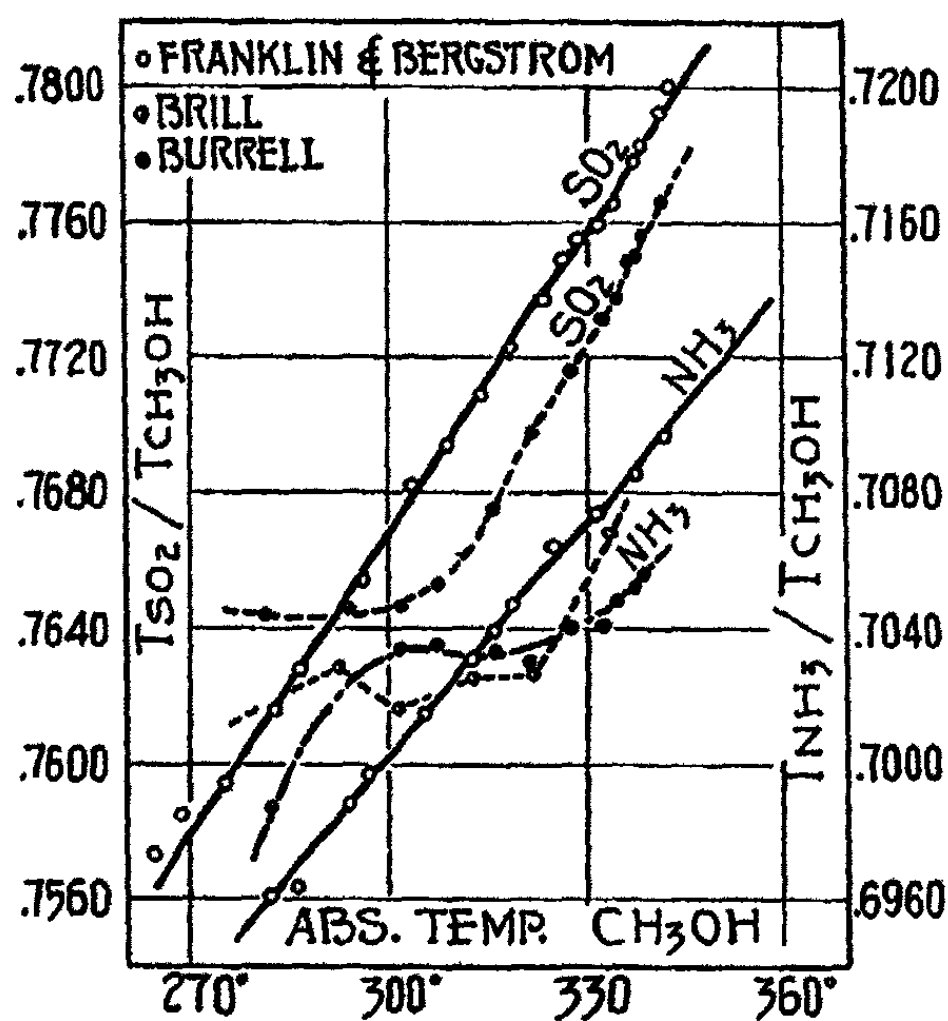


Fig. 6

**Data Plotted by Method of Ramsay and Young**

The vapor pressure measurements described in this paper, together with data of other investigators, have been tested by the Ramsay-Young relation:

$$R' = R + c(T' - T)$$

$c$  is a constant for every pair of substances.<sup>1</sup>

$R'$  is the ratio between the absolute temperatures of any liquid and of a standard substance (such as water or methyl alcohol) at a given vapor pressure.

$R$  is the ratio at another vapor pressure.

$T' - T =$  the difference between the absolute temperatures of one of the liquids at the two vapor pressures.

The graph of the equation is a straight line, as  $c$  is a constant.

The measurements of Brill, Burrell and the author on ammonia, and of Burrell and the author on sulfur dioxide, are plotted in Fig. 6, with methyl alcohol as standard. The results of the author are separately plotted in Fig. 7, with water as standard. As the vapor pressures of methyl alcohol were taken from a fairly large-sized plot of Ramsay and Young's data,<sup>2</sup> absolute accuracy could not

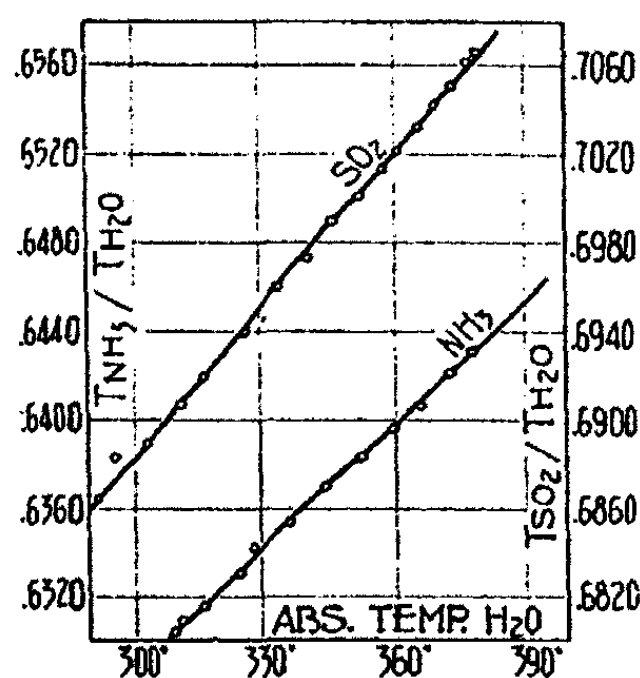


Fig. 7

be expected in the interpolation of the temperatures, especially at low pressures. The general trend of the curves would not be affected. The vapor pressures of water were taken from Marx and Davis' steam tables, and represent the most accurate work yet published. The remainder of Burrell's measurements are plotted in Fig. 8 to a smaller scale, with methyl alcohol as standard.

The author's measurements give straight lines whether

<sup>1</sup> Zeit. phys. Chem., 38, 666 (1901).

<sup>2</sup> Phil. Trans., 188, 320.



the exception of two points on each, the graphs for ethylene and ethane are nearly straight lines.

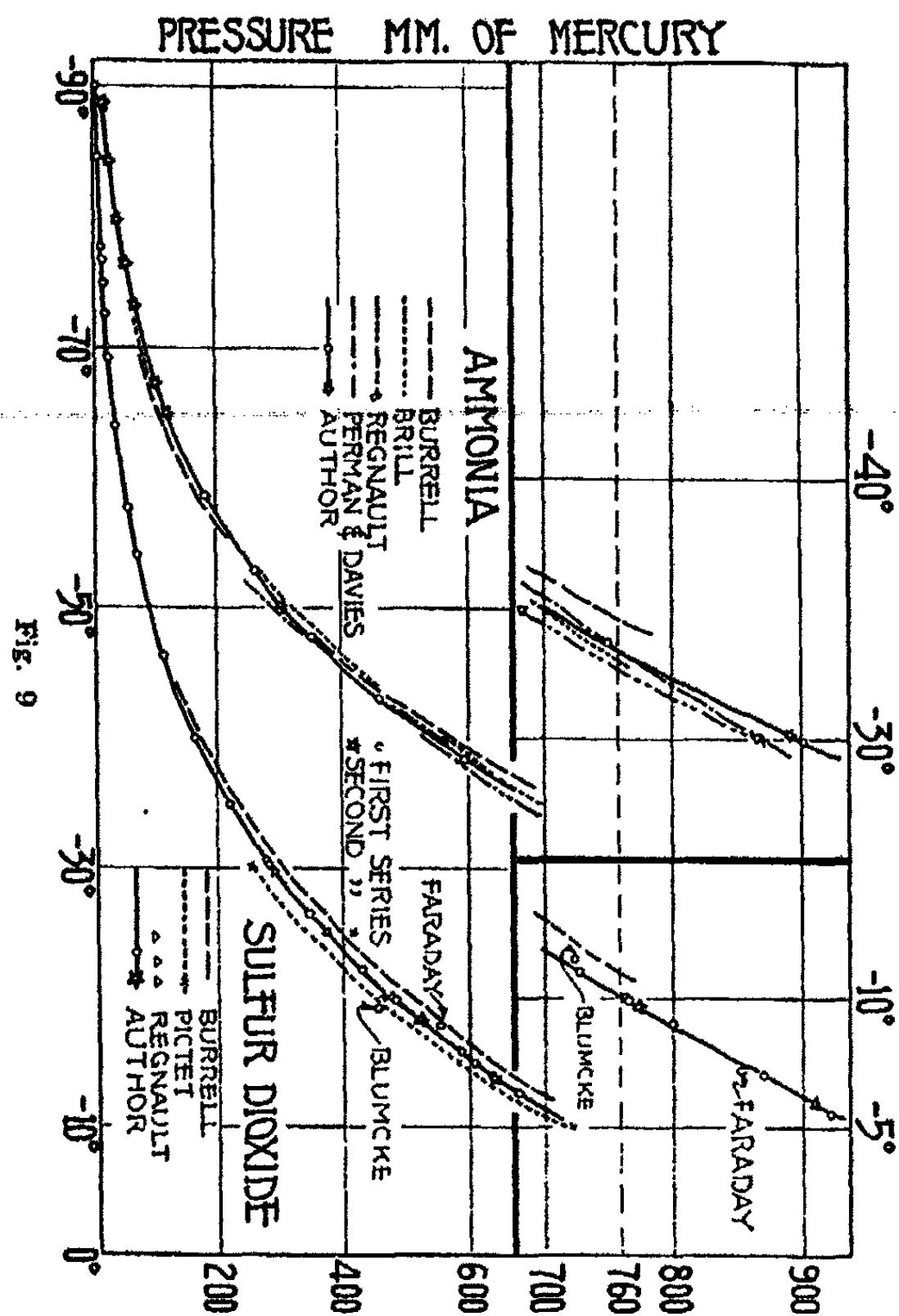


Fig. 9

Summary

1. Vapor pressures of ammonia and sulfur dioxide were determined from temperatures slightly above the normal boiling points to solid. Two samples were used in each case, and the results of the measurements are in excellent agreement.

2. An improved form of apparatus for measurements of vapor pressures below 900 mm and at low temperatures has been described.

3. The measurements of Brill and Burrell do not satisfy the Ramsay-Young relation, while those of the author do. It has been experimentally shown in this laboratory that Burrell's vapor pressure measurements on ammonia and sulfur dioxide are in all probability erroneous.

4. The triple point of ammonia has been determined.

In conclusion, the writer wishes to acknowledge his great indebtedness to Professor E. C. Franklin, at whose suggestion and under whose direction this work was undertaken, and to Prof. H. P. Cady for many valuable suggestions.

A-1716

## A STUDY OF THE ABSORPTION OF LIGHT BY SOLUTIONS OF CUPRIC LITHIUM CHLORIDE

BY FREDERICK H. GETMAN

A garnet-red double chloride of copper and lithium corresponding to the formula  $\text{CuCl}_2 \cdot \text{LiCl} \cdot \text{H}_2\text{O}$  was obtained by Chassevant<sup>1</sup> in 1891. In a subsequent investigation of the solubility of this salt by Meyerhoffer<sup>2</sup> it was shown that Chassevant's analysis was erroneous and that the correct formula of the salt is  $\text{CuCl}_2 \cdot \text{LiCl} \cdot 2\text{H}_2\text{O}$ . In his "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," Werner assigns to the salt the formula  $\text{CuCl}_2 \cdot \text{LiCl} \cdot 3\text{H}_2\text{O}$ , and points out that its reddish brown color may be regarded as an indication of the fact that all of the water is linked to the lithium, otherwise the salt would possess the characteristic blue color of copper salts where, in all probability, the water is bound directly to the copper.

In view of the results recently obtained in a study of the color of solutions of cupric chloride alone and in the presence of several other chlorides,<sup>3</sup> it seemed of interest to carry out a similar investigation of solutions of cupric lithium chloride.

The double salt was prepared by mixing moderately concentrated solutions of the two chlorides and allowing them to crystallize out together at room temperature. The amount of lithium chloride taken was considerably in excess of that required by the formula of the double salt, owing to the fact that a solution containing the two chlorides in molecular proportions yields on evaporation a mixture of crystals of the double salt with crystals of cupric chloride, the latter being the first to separate from the solution. The salt was drained free from mother liquor on a Büchner funnel and dried, as rapidly as possible, by means of heavy filter paper. Owing to the ex-

<sup>1</sup> Comptes rendus, 113, 646 (1891).

<sup>2</sup> Wien. Monatsheft, 13, 716 (1892); Sitz. Wien Akad., 101, II, 599 (1892)

<sup>3</sup> Jour. Phys. Chem., 26, 1922.

tremely hygroscopic character of the salt, it was essential that the entire process of filtering and drying be carried out in as dry an atmosphere as possible. The results of a typical analysis of the salt are given in the following table:

	Found	Calculated
Copper	29.05%	29.86%
Lithium	3.44%	3.26%
Chlorine	49.99%	49.97%
Water	17.52%	16.91%
	100.00%	100.00%

The percentage composition of the salt will be seen to be in agreement with Meyerhoger's formula, viz.,  $\text{CuCl}_2 \cdot \text{LiCl} \cdot 2\text{H}_2\text{O}$ .

The apparatus used in measuring the absorption of light by the solutions was a Hilger wave-length spectroscopie in conjunction with a Nutting photometer, and the method of procedure was similar to that followed in the study of cupric

TABLE I  
Mean temp. 23.1°

$\lambda$	1.493 $\epsilon$	1.344 $\epsilon$	1.194 $\epsilon$	1.045 $\epsilon$	0.896 $\epsilon$	0.747 $\epsilon$	0.597 $\epsilon$	0.299 $\epsilon$	0.149 $\epsilon$
600	—	—	—	—	—	—	—	—	0.305
590	—	—	—	—	—	—	—	—	0.214
580	—	—	—	—	—	—	—	0.152	0.083
570	—	—	—	—	—	—	0.255	0.106	0.062
560	—	—	—	—	0.270	0.227	0.172	0.072	0.045
550	—	0.300	0.267	0.212	0.182	0.152	0.120	0.048	0.031
540	0.231	0.188	0.180	0.140	0.124	0.101	0.081	0.031	0.021
530	0.163	0.126	0.115	0.092	0.080	0.061	0.052	0.019	0.013
520	0.129	0.091	0.078	0.060	0.048	0.035	0.031	0.012	0.008
510	0.129	0.082	0.066	0.043	0.029	0.020	0.016	0.007	0.004
500	0.167	0.097	0.077	0.036	0.020	0.011	0.006	0.003	0.002
490	—	0.160	0.117	0.044	0.020	0.008	0.002	0.001	0.001
480	—	—	0.260	0.080	0.033	0.012	0.004	—	—
470	—	—	—	0.165	0.067	0.025	0.010	—	—
460	—	—	—	—	0.157	0.052	0.023	—	—
450	—	—	—	—	—	0.180	0.046	—	—

chloride.<sup>1</sup> The experimental data are given in Table I where  $\epsilon$  denotes the extinction coefficients for that portion of the visible

<sup>1</sup> Loc. cit.

spectrum which is included between  $\lambda = 660 \mu\mu$  and  $\lambda = 450 \mu\mu$ ; the concentrations of the solutions, expressed in gram-molecules per liter, are given at the heads of the columns.

The curves shown in Fig. 1 are plotted from the data of the foregoing table. On comparing these absorption curves with the corresponding curves for cupric chloride, it is found that the minima in the latter lie nearer the violet end of the spectrum than the minima in the former. This was to be expected, since it has already been shown that lithium chloride displaces the absorption of solutions of cupric chloride toward the red end of the spectrum. In dilute solutions, the absorption spectra of cupric lithium chloride and cupric chloride are identical: this may

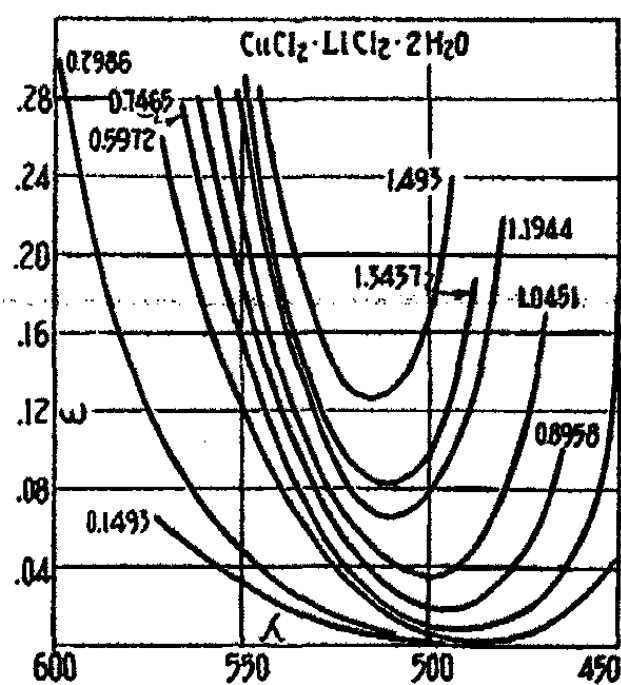


Fig. 1

be shown by plotting the wave-lengths corresponding to the absorption minima for each of the two salts against the concentration, as in Fig. 2, when it will be seen that the two curves converge with decreasing concentration and ultimately become coincident.

It is noteworthy that the color of cupric lithium chloride changes instantaneously from reddish brown to olive-green, on the addition of a single drop of water, and then, on further addition of water, the color of the solution passes through various shades of green and greenish blue, until it finally acquires the familiar blue color which is characteristic of the copper ion. These facts suggest that the double salt probably undergoes dissociation into the two-component salts on the addition of water. In order to secure further evidence on this point, the conductivity of the salt was measured at several different dilutions, and the results were then compared with the sum of the conductivities of the two-component salts. It has been shown



by Bender,<sup>1</sup> and also by Klein,<sup>2</sup> that the conductivity] of a [mix-  
ture of the two salts having an ion in common is somewhat less  
than the sum of the conductivities of the two salts taken sepa-  
rately, but when the two salts are capable of forming a double  
salt, then the conductivity is very much less than the sum of the

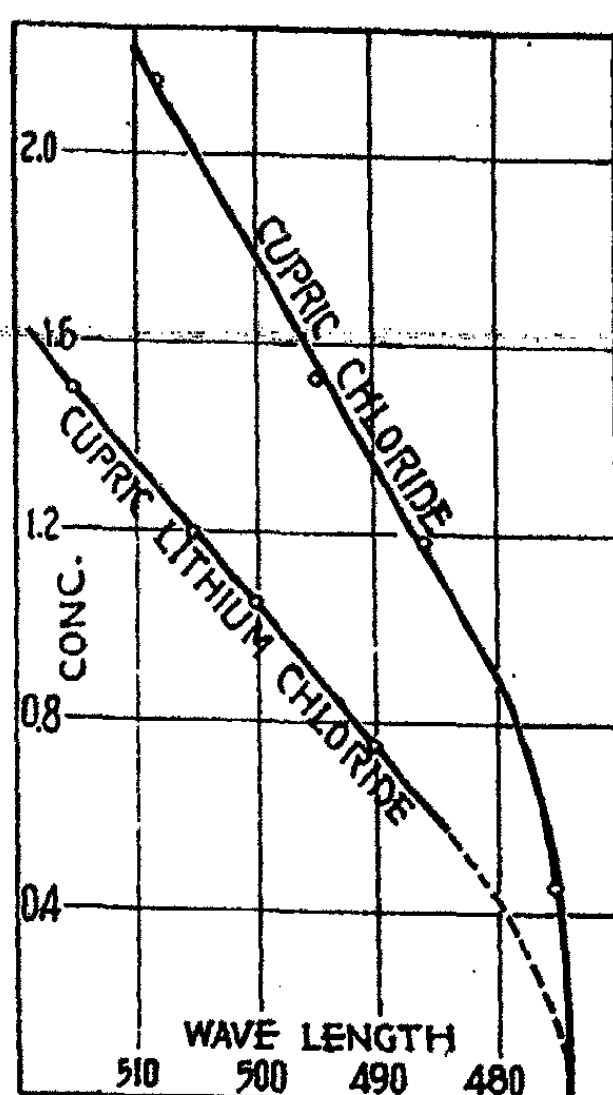


Fig. 2

conductivities of the component salts. These conclusions have received abundant confirmation through the work of Jones and several of his students.<sup>3</sup> The conductivity of a series of dilutions of 0.4634 molar  $\text{CuCl}_2 \cdot \text{LiCl} \cdot 2\text{H}_2\text{O}$  at  $25^\circ$  is given in the following table.

<sup>1</sup> Wied. Ann., 22, 179 (1884).

<sup>2</sup> Ibid., 27, 151 (1886).

<sup>3</sup> See papers by Jones and Mackay, Am. Chem. Jour., 19, 83 (1897); Jones and Ota, Ibid., 22, 5 (1899); Jones and Knight, Ibid., 22, 110 (1899); Jones and Caldwell, Ibid., 25, 349 (1901); Lindsay, Ibid., 25, 62 (1901).

TABLE II  
Temp. 25°

$\nu$	$\mu$
2.158	186.10
6.474	242.54
12.947	270.02
25.895	293.54
51.790	312.13
103.58	330.00
207.16	345.90
414.37	358.9
828.63	364.0

From the data of the foregoing table, the conductivities of the double salt at even volumes were obtained by graphic interpolation and these values, together with the sum of the conductivities of the two-component salts at the same dilutions, are given in Table III.

TABLE III

$\nu$	$\mu$	$\mu_{\text{LiCl}} + \mu_{\text{CuCl}_2}^*$	Difference
8	252.5	263.0	10.5
16	278.5	286.0	7.5
32	295.0	300.0	5.0
64	317.8	319.5	1.7
128	340.0	340.0	0.0

It will be observed that not only does the difference between the measured and computed values of the conductivity decrease with dilution, but also that it is so small in the most concentrated solutions as to justify the conclusion that only a very small proportion of the molecules of the double salt remains undissociated. We are thus led to conclude that the chromophores which are present in solutions of cupric lithium chloride are identical with those present in solutions of cupric chloride containing an equivalent amount of lithium chloride.

\* The conductivity data used in calculating the values recorded in this column were derived from the following sources: LiCl, Green: Jour. Chem. Soc., 94, 2042 (1908); CuCl<sub>2</sub>, Jones and West: Am. Chem. Jour., 34, 409 (1905).

In other words, the chromophores are complex ions such as  $(\text{Cu.4Cl})$ ,  $(\text{Cu.3Cl.H}_2\text{O})$ ,  $(\text{Cu.2Cl.2H}_2\text{O})$ ,  $(\text{Cu.Cl.3H}_2\text{O})$  and  $(\text{Cu.4H}_2\text{O})$ , the composition of the ions being conditioned largely by concentration and temperature.

If the color of the solid double salt is due to the removal of the water which is directly linked to the copper by the lithium, as has been suggested by Werner,<sup>1</sup> we may reasonably assume dissociation to have taken place within the salt itself, as indicated by the following equation:



The possibility of such a dissociation has already been pointed out by Donnan.<sup>2</sup>

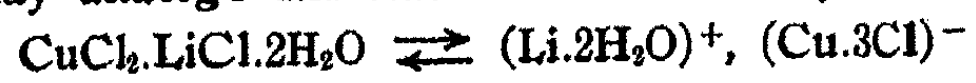
The results of this investigation may be briefly summarized as follows:

1. A sample of cupric lithium chloride was prepared from pure cupric and lithium chlorides by crystallization from a solution of the last-named salts, and the product was found on analysis to have the composition represented by the formula  $\text{CuCl}_2 \cdot \text{LiCl} \cdot 2\text{H}_2\text{O}$ , this being the formula assigned to the salt by Meyerhoffer.
2. The absorption of light by solutions of the salt was studied by means of the spectrophotometer, and the resulting absorption curves were compared with corresponding curves previously obtained with solutions of cupric chloride. The minima in the absorption curves were found to lie nearer the red end of the spectrum than the corresponding minima in the curves obtained with solutions of cupric chloride.
3. In dilute solutions the absorption curves of cupric lithium chloride and cupric chloride were found to be identical.
4. From a comparison of the conductivities of solutions of cupric lithium chloride with the sum of the conductivities of cupric chloride and lithium chloride at the same dilutions, it was found that the double salt, when dissolved in water, undergoes almost complete dissociation into the two-component salts.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Zeit. phys. Chem.*, 53, 317 (1905).

5. The possibility suggested by Donnan that the solid salt may undergo dissociation as indicated by the equation



is emphasized as offering a satisfactory explanation of the fact that the color of the compound departs widely from that which is characteristic of copper salts.

In conclusion, it is with pleasure that I acknowledge the assistance rendered by Mr. Kenneth Tate in making the spectrophotometric measurements.

*Hillside Laboratory  
Stamford, Conn.*

*Oct. 22, 1921*

Sp. 9774

## DYEING OF DEAMINATED WOOL

BY W. W. PADDON

The experiments of Richards,<sup>1</sup> followed by those of Richardson, Dreaper, and Watson Smith, have shown that amino groups are a part of the chemical constitution of wool. It has been believed that the presence of this amino nitrogen in wool might explain the ease with which that fibre is dyed, insofar as the acid dyes are concerned, the free dye acid being attached to the wool through chemical union with these amino groups. On the contrary Bentz and Farrell<sup>2</sup> found that wool which had been deaminated by treatment with nitrous acid followed by washing and boiling with either alcohol or water or acidified cuprous chloride solution, "dyes with acidic coloring matters apparently as well as wool in the ordinary state. The dye baths are exhausted in both cases to the same extent and so far as our experiments range are as fast to soaping and light." The experiments described below verify this work of Bentz and Farrell by obtaining quantitative data regarding the dyeing of deaminated and ordinary wool by typical acid dyes.

Pure white sweater yarn was used in the experiments being first washed in dilute soap solution and then rinsed repeatedly in hot distilled water. It was then dried in air and kept in a constant humidity atmosphere.

About forty grams of this wool were deaminated by being immersed in 1200 cc of a solution containing 10% by volume of conc. HCl and 20 grams of sodium nitrite at a temperature of 4° C. The temperature of the bath rose from 4° C to 10° C and brown fumes were evolved. The wool was kept in this bath with frequent stirring and addition of sodium nitrite for 16 hours. The wool, now yellow in color, was removed and

<sup>1</sup> Richards: Jour. Soc. Chem. Ind., 7, 841 (1888); Richardson: 12, 426 (1893); Dreaper: 13, 95 (1894); Watson Smith: 15, 245 (1896).

<sup>2</sup> Bentz and Farrell: Jour. Soc. Chem. Ind., 16, 405 (1897).

washed in lukewarm distilled water until the wash waters gave no test for chlorides of nitrous acid. It was next placed in boiling distilled water and boiled for five hours, the water being repeatedly replenished. The fibre became changed to a very dark brown during this boiling, becoming thicker, and short-

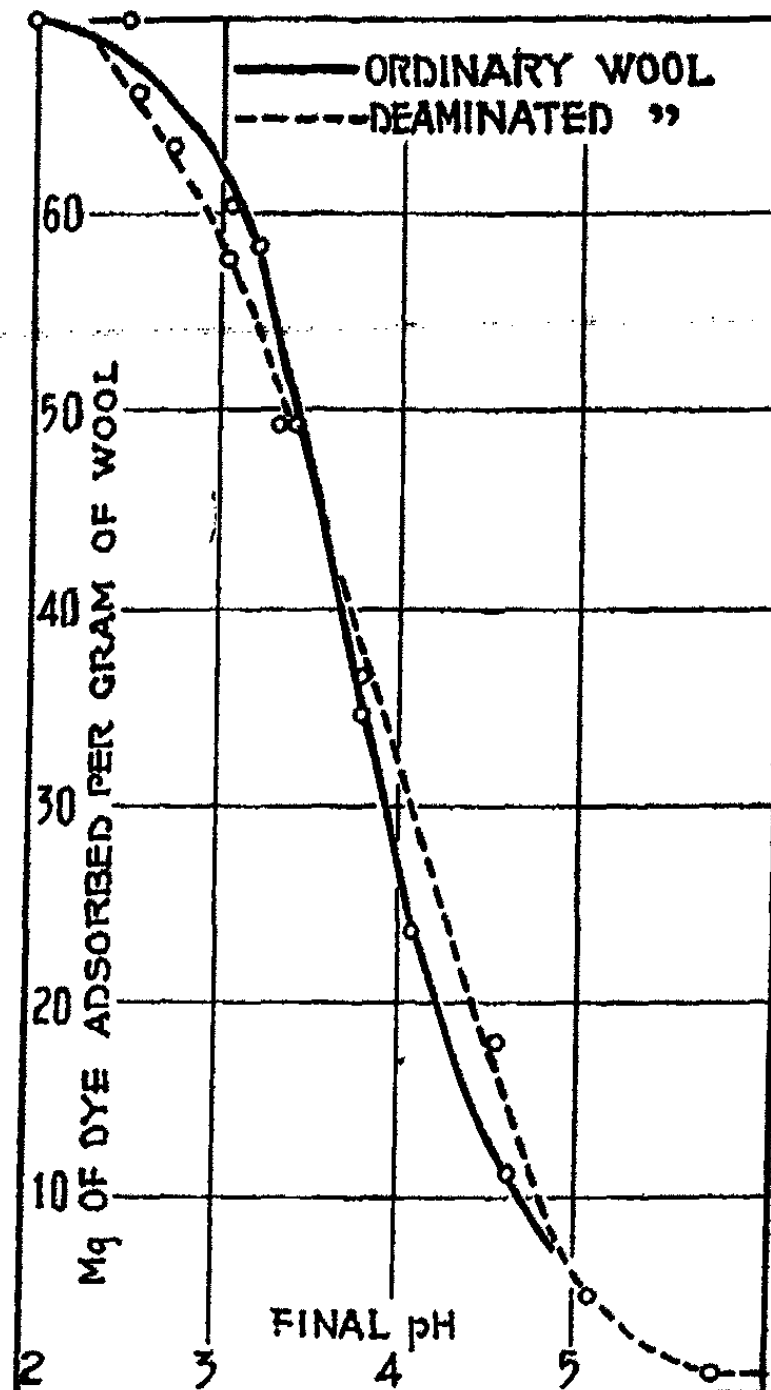


Fig. 1  
Dyeing with Orange II

ening to about two-thirds of its original length. The final wash waters gave no test for either nitrous acid or chlorides. The wool was dried in the open room and placed in a constant humidity atmosphere under the same conditions as the ordinary

wool used in these experiments. A sample of the wool thus deaminated when treated further with nitrous acid and then immersed in alkaline phenol solution underwent no change in color whatsoever. It was therefore concluded that all the amino nitrogen had been removed.

In dyeing, two typical acid dyes were used, Orange II (duPont) and Lake Scarlet R (National Aniline and Chemical Co.). The following conditions were constant throughout the experiment.

Total volume of bath, 250 cc.

Milligrams of dye used, 75 mg.

Grams wool used in each bath, 1000 gr.

Time of boiling, 45 min.

Wool entered and removed at the boil.

The amount of dye remaining in the bath was determined by titrating with a standard  $TiCl_3$  solution according to the method of Knecht.<sup>1</sup>

The pH values were obtained by means of a hydrogen electrode of the Lewis, Brighton, and Sebastian type,<sup>2</sup> slightly modified.

The data concerning the dyeing of the deaminated wool have been compared with the data for the dyeing of ordinary wool previously obtained in this laboratory in the same way by Mr. A. W. Bull.

Dyeing with duPont Orange II  
Dyeing of deaminated wool

Cc N/10 HCl	Final pH	Mg dye left in bath	Mg of dye adsorbed
0.0	5.75	74.0	1.0
0.5	5.10	69.2	5.8
1.0	4.60	57.0	18.0
2.0	3.80	40.5	34.5
3.0	3.40	25.5	49.5
5.0	3.03	17.3	57.7
10.0	2.57	9.0	66.0

<sup>1</sup> Ber. deutsch. chem. Ges., 36, 1552 (1903); 40, 3819 (1907).

<sup>2</sup> Jour. Am. Chem. Soc., 39, 2250 (1917).

## Dyeing of ordinary wool

0.0	4.09	63.7	11.3
0.5	4.10	51.2	23.8
1.0	3.80	38.5	36.5
2.0	3.32	25.2	49.2
3.0	3.20	16.9	58.1
4.0	3.04	14.5	60.5
6.0	2.76	12.0	63.0
10.0	2.49	5.3	69.7
25.0	2.00	6.2	68.8

Dyeing of deaminated wool; stripping effect of Na<sub>2</sub>SO<sub>4</sub>

Cc N/10 H <sub>2</sub> SO <sub>4</sub>	Cc M/10 Na <sub>2</sub> SO <sub>4</sub>	Final pH	Mg dye left	Mg dye adsorbed
0.5	24.75	4.72	63.7	11.3
5.0	22.50	3.14	42.7	32.3

Dyeing of ordinary wool; stripping effect of Na<sub>2</sub>SO<sub>4</sub>

0.3	24.7	4.08	61.5	13.5
3.0	23.5	3.24	46.2	28.8

## Dyeing with Lake Scarlet R

## Dyeing of deaminated wool

Cc N/10 HCl	Final pH	Mg dye left in bath	Mg dye adsorbed
0.0	6.02	66.4	8.6
0.5	5.17	60.9	14.1
1.0	4.99	52.3	22.7
2.0	4.04	33.2	41.8
3.0	3.55	18.5	56.5
5.0	3.08	7.7	67.3
10.0	2.61	1.8	73.2

## Dyeing of ordinary wool

0.0	6.43	74.4	0.6
0.5	5.58	64.8	10.2
1.0	4.90	49.4	25.6
1.5	4.31	35.1	39.9
2.0	3.88	23.7	51.3
3.0	3.37	7.0	68.0
5.0	2.85	1.1	73.9
8.0	2.57	0.6	74.4
15.0	2.13	0.2	74.8



Dyeing of deaminated wool; stripping effect of  $\text{Na}_2\text{SO}_4$ 

Cc N/10 $\text{H}_2\text{SO}_4$	Cc M/10 $\text{Na}_2\text{SO}_4$	Final pH	Mg dye left in bath	Mg dye adsorbed
0.5	24.75	4.99	59.6	15.4
5.0	22.50	3.15	33.8	41.2

Dyeing of ordinary wool; stripping effect of  $\text{Na}_2\text{SO}_4$ 

0.5	25.0	4.55	66.4	8.6
3.0	25.0	3.36	31.0	44.0
5.0	25.0	2.88	20.5	54.5

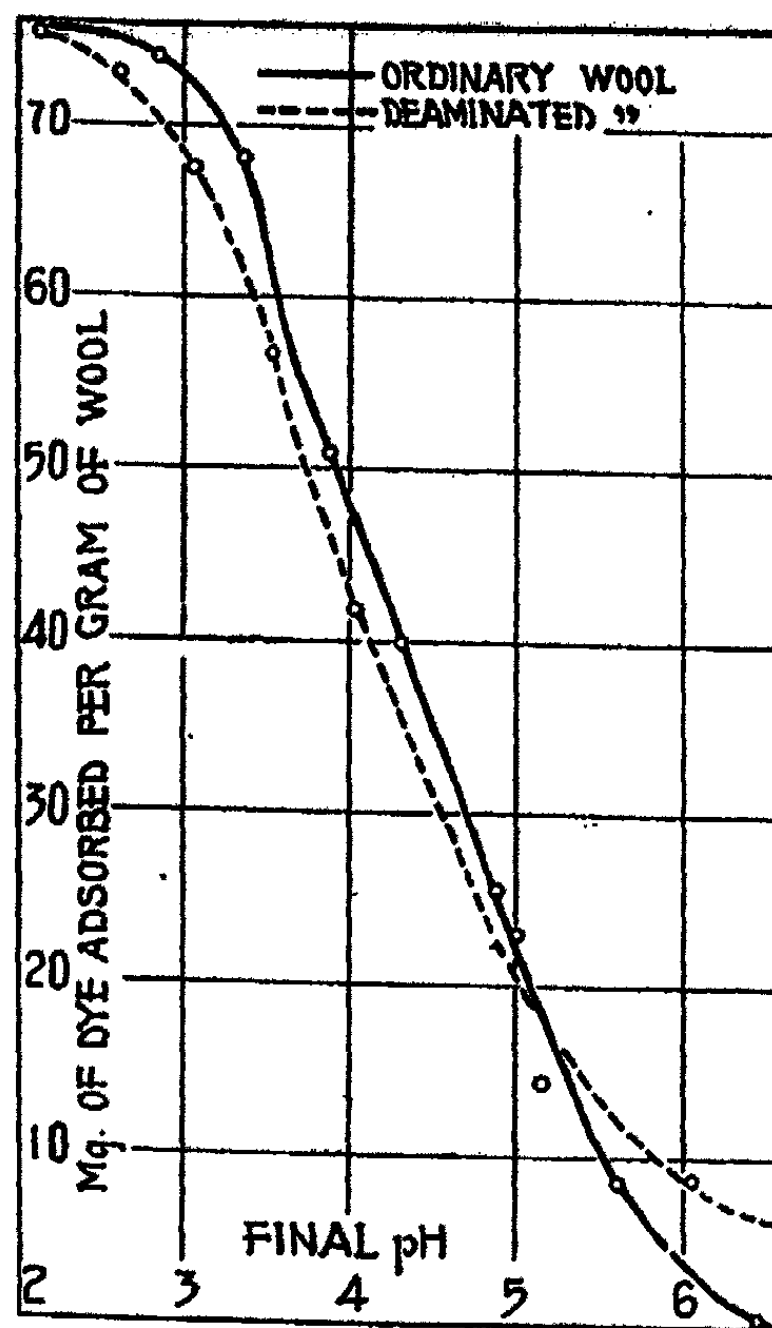


Fig. 2  
Dyeing with Lake Scarlet R

These data have been placed in the form of curves, Figs. 1-2, by plotting milligrams of dye adsorbed against pH values. The curves for deaminated and ordinary wool for the same dye are of the same shape and lie very close together, any difference being well within the limit of experimental error. This is rather surprising in view of the very marked change in the appearance of the wool.

The above quantitative experiments show that the amino groups in wool play no part whatever in the dyeing of that fibre by acid dyes.

The work has been carried on under the supervision of Professor Bancroft, and was made possible by a grant from the Chemical Foundation.

*Cornell University*

## NEW BOOKS

**The Silver Bromide Grain of Photographic Emulsions.** By A. P. H. Trivelli and S. E. Sheppard. 22 × 15 cm; pp. 143. New York: D. Van Nostrand Co., 1921. Price: \$2.50.—This is the first of a series of monographs on the theory of photography which the Research Laboratory of the Eastman Kodak Company is going to write. The next two volumes are to be on gelatine and the fourth on the theory of development. This is an admirable thing to do and should mark the beginning of a new period in the science of photography.

In the monograph the chapters are entitled: the influence of ammonia on photographic emulsions and a theory of ripening; von Weimarn's theory and the determination of the dispersion of silver bromide precipitates; accessory factors influencing the dispersity of silver bromide emulsions; crystallization catalysis; capillarity and crystalline growth; experimental study of the crystallization of silver bromide; the classification of silver halide crystals; the silver bromide crystals of photographic emulsions; the directions of most rapid growth in silver bromide crystals, and the occurrence of anomalous forms; the behavior of silver bromide and silver iodo-bromide crystals in polarized light.

When silver bromide plates are treated with ammonia vapor, they become more transparent, apparently owing to the formation of a silver bromide ammonia compound having approximately the same index of refraction as the gelatine. No independent proof of this is given, though a reference is made, p. 25, to Ephraim's work. Ammonia also causes an increase in the size of the grains but does not cause development except for long exposures. The authors believe that under the combined action of ammonia and gelatine silver bromide may be reduced somewhat with production of colloidal silver.

The authors apparently consider that optical sensitizers act by resonance, p. 50. "The operation of a sensitizer may be regarded in respect of either wave length or phase. It would be very possible for a crystalline substance to absorb only a limited amount of light of suitable wave-length, but of such irregular phase ordering that the equilibrium radiation field of the crystal would get only partially in resonance. We can conceive then that a non-crystalline body in solid solution or absorbed would increase the photochemical sensitiveness, acting as a resonance complement. Thus colloidal silver acts as a panchromatic sensitizer for silver halides. The behavior of traces of calcium, bismuth, etc., in developing phosphorescence in the alkaline earth sulphides is a similar case. If the above conception is true, it is possible that silver iodide acts both as a wave-length sensitizer and as a phase-sensitizer for silver bromide, as well as acting as an independent source of nuclei by its direct photolysis."

On p. 100 the authors say that "the forms of the silver bromide crystals in photographic emulsions are very varied, though all belong to the same crystallographic system [regular] and the same class [dyakisdodecahedral]. In 122 different emulsions which were examined at a magnification of 2500 diameters, only octahedra could be positively identified. . . . The presence of cubes and of combinations of cubes with octahedra or other forms could never be determined.

From ammoniacal solutions silver iodide is precipitated in the metastable, regular form, which is isomorphous with silver bromide."

The book is an interesting one and contains some remarkable photographs of silver bromide crystals; but it is a little puzzling to know just what the scope of the book was meant to be. What one would have liked would have been a theory of ripening and one is left with an uneasy feeling that the authors think that they have given one. It is possible that they have; but the reviewer has read the book three times already without learning what it is. Some of the difficulties to the reader may be illustrated by the following paragraph which is said to sum up the fundamental relation existing between photochemical catalysts, positive and negative, and crystallization catalysts, p. 51. "Crystallization is a process of approach to a complete (static) equilibrium of the radiation fields (chemical affinities) of the component atoms and constituent molecules. The attainment of static equilibrium may be accelerated or retarded by alien substances, or crystallization catalysts, which, from the actino-chemical nature of crystallization, are consequently likely to be also photochemical catalysts, affecting the transformation and redistribution of catalytic light energy."

*Wilder D. Bancroft*

**Qualitative Chemical Analysis.** By *M. Cannon Sneed*. 21 × 14 cm; pp. xiii + 198. New York: Ginn and Company, 1921. Price: \$1.50.—The author believes that a course in qualitative analysis "should serve as a means of reviewing, fixing in the mind of the student, and extending his knowledge of the principles of general chemistry. On the experimental side its aim should be to train the beginner to acquire methods of careful manipulation and to do exact, dependable, and intelligent work. To this end an attempt has been made to present the experimental exercises in a concise form and to give laws and theories in such a way that the student may understand and correctly interpret his observations."

The chapters are entitled: introduction; gases, solution, and the theory of electrolytic dissociation; physical and chemical equilibrium and Group V; ionic equilibrium treated quantitatively and Group IV; hydrolysis, amphoterism, oxidation and reduction, and Group III; precipitation of hydrogen sulphide, complex ions, colloidal condition, and Group II; Group I; the anions; the systematic analysis of an unknown.

There is a great deal of physical chemistry in this book and the question is whether this is a good thing or a bad thing. The reviewer does not quite see what the gas laws, quantitative ionic equilibrium, and amphoterism have to do with qualitative analysis. Even supposing they are essential, should they be taught here or somewhere else? It seems to the reviewer that either the book presupposes a lack of co-ordination at the University of Minnesota or else that the author wishes to present the subject of qualitative analysis as complete in itself—which comes to the same thing and is apparently hard on the student.

On p. 10 the author introduces the term "diffusion pressure" in what seems to be a new and undesirable sense.

*Wilder D. Bancroft*

**Elementary Qualitative Analysis of the Metals and Acid Radicals.** By *F. C. Reeve*. 19 × 13 cm; pp. vii + 143. New York: D. Van Nostrand Co.,

1921. Price: \$1.50.—This book claims to present the subject of elementary qualitative analysis in such a way as to interest the high school student. The aim of the author has been: to present the main scheme of analysis without the complication of special conditions; to give working directions for each test rather than its description; and to write the chemical equations for all reactions. The reviewer is not qualified to tell what will interest a high school student. There are one or two points which interested him as a chemist. On p. 2 the author says that addition of small amounts of an acid, a base, or a salt makes water a conductor. The electrolyte does not increase the conductance of water. It would apparently have been just as simple and certainly more accurate to say that the solution conducts instead of saying that the water conducts. On p. 16 the author says that ammonia reacts with lead chloride to form basic lead chloride,  $PbCl(OH)$ . Is there any reason beyond a desire for simplification why basic lead chloride should not be  $PbO_2 \cdot H_2 \cdot PbCl_2$ ? On p. 20 there is the very interesting statement that the filtration of silver chloride can usually be made easy by "the addition of a number of crystals of ammonium nitrate and the application of gentle heat to the mixture before filtration." Very few chemists could tell why this addition is effective and it is rather a pity that no explanation is given. It is not desirable that a student should follow directions blindly.

On p. 37 the student is told to "acidulate 5 cc of a solution of copper nitrate or other copper salt with a few drops of dilute hydrochloric acid. Add two or three small iron nails to this solution and gently warm it. In a few moments the iron nails will be covered with a coating of metallic copper." This would seem to be the worst possible way of doing the experiment because there will certainly be a formation of cuprous chloride which must complicate matters, and to which no reference is made in the equation.

These few comments are not intended in disparagement of the book, which is doubtless an admirable one. They do show how difficult it is to write anything clearly, simply, and accurately.

Wilder D. Bancroft

**Red-Lead and how to use it in Paint.** By A. H. Sabin. Third edition. 19 × 13 cm; pp. xi + 139. New York: John Wiley and Sons, 1920. Price: \$2.00.—In the preface the author says that in the last few years there has been a great increase of interest in the subject of red-lead paint; "due, no doubt, to the rise in the cost of bridges and other metal structures, which makes their preservation more important; this incidentally leads to more discussion of it in the meetings of engineers; and partly to the comparatively recent introduction of red lead in paste form, which, as is explained in the text, is made possible by improvements in the pigment, and increases its availability for more extensive use. The writer is willing to predict that the next step will be its sale as a liquid paint, ready for use; and that this will so much promote its use as a finishing coat and for general repainting, that the demand for it will be several times as much as now; perhaps will equal that for white lead. Holding this belief, which is based on thirty years' experience and study of protective coatings, the writer has tried to give information as to the character of these liquid paints; for all paint must be reduced to this form before it can be applied."

The author discusses briefly the manufacture of litharge, red lead, and orange mineral; gives a very cursory statement of the objections to red lead;

and points out that a certain brand of red lead contains less than two percent of litharge and is a very superior product. In certain cases the presence of litharge is an advantage, it being added when the paint is to be applied to the interior of stand-pipes and conduits, because it makes a harder film which is not softened so much by the water with which it is continually in contact. Lampblack in paste form can be mixed easily with red lead; but there is apt to be difficulty if one uses dry lampblack.

When considering how much pigment is needed, p. 25, the author says "that there must be some proportion of oil and pigment which gives most durability. If too much oil is added, we finally get a film which is essentially an oil film, much less durable than a paint, and less impervious to air and moisture. If we add too much pigment, we make a paste which, though fluid, is too viscid [?] for a paint; still more pigment makes putty which is not a fluid at all, but a plastic solid; it has uses but it is not paint." The author answers the question himself by saying that 33 pounds of red lead to a gallon of oil, plus what turpentine seems desirable, is satisfactory.

Speaking of mixed pigments, p. 37, the author says that "while no one should pretend that the particular paint he fancies is the only one which has any merit, it is not likely that for durability, or the protection of metal from corrosion, a mixture of pigments is ever better than a single one, except in cases where an inferior paint is improved by the addition of a better one; that is, a good paint is not made better by being mixed with a worse. And yet there are people who admit that silica, for example, made by itself with oil into a paint, is worthless, either as to durability or anything else, but who maintain that 30 to 40 percent [by volume] of such paint may profitably be added to a red-lead paint."

The latter part of the book is devoted to specifications for painting and to methods of analysis.

As the quotations indicate, the book is interesting reading. The only drawback to it is that it is obviously an advertising pamphlet put out in book form; but with no attempt at a non-partisan, scientific presentation of the subject. It is a pity that the author should have done this; but he probably had reasons for his course which satisfied him.

*Wilder D. Bancroft*

**The Electric Furnace.** By J. N. Pring. 22 X 14 cm; pp. xii + 485. London and New York: Longmans, Green and Co., 1921. Price: \$10.50.—This is a book that should have been written by an American. Excellent as the book is, it omits two important developments of electric furnace service that have been brought to their present state by American engineers—namely, brass melting and heat treating. But even in a much larger sense the real success of the electric furnace has been the work of Americans. Its history follows fairly close to that of the many processes that were laboratory experiments or commercial installations on a small scale abroad, and really came into their true worth on being brought to this country. A notable instance of that was the Bessemer steel method, where the first American improvement, by Holley, added 50% in output and others following in rapid order made a total gain of several hundred percent. The discovery and partial development abroad of the electric furnace

was merely the opening chapter of its history. The American engineer, with his fine disregard for classical traditions and his eager desire to do things in a better way for a bigger output, in which he is amply justified by his skill and ingenuity, takes hold of the admittedly imperfect foreign design and turns it into a tool to be used with confidence. A striking proof of this is found in this book. Taking at random 100 consecutive pages (*e. g.*, pages 259 to 358) there are 59 technical references of which 32 are to American sources.

There can be little adverse criticism of a book like this; prepared with great care, written in very good style, well printed on better paper than some we have recently seen, plenty of excellent illustrations, and with a very good bibliography. It will be found equally at home with the practical engineer or in the classroom of technical schools. It might be better for its American edition had some of its cost-data been reduced to United States figures, but as these figures, in the present state of exchange are exceedingly relative, the criticism is rather captious.

R. R. Reed

**The Emission of Electricity from Hot Bodies.** By *O. W. Richardson*. Second edition. 22 X 15 cm; pp. vii + 320. New York and London: Longmans, Green and Co., 1921. Price: \$5.25.—The subject is presented under the following headings: mainly considerations of a general character; theory of the emission of electrons from hot bodies; temperature variation of electron emission; the effect of gases on the emission of electrons; energetics of electron emission; the emission of positive ions by hot metals; the effect of gases on the liberation of positive ions by hot metals; the emission of ions by heated salts; ionization and chemical action.

While the whole subject is a fascinating one, there are certain portions of the book which are of exceptional interest to the chemist and it will therefore be well to concentrate on them. The most important of these is the section dealing with the question of contact potential, p. 41. "There is an intimate connection between the rate of emission of electrons from different substances and their contact differences of potential. This can be shown very simply by considering the case of an insulating evacuated enclosure containing two bodies, A and B, of different materials maintained at the uniform temperature  $T$ . The electrons emitted by A will ultimately either return to A or reach B, and vice versa. Now suppose that both A and B are uncharged initially, and that A emits electrons at a faster rate than B. The greater rate of loss of negative electrons by A will cause A to acquire a positive potential relative to that of B. This difference of potential will not increase indefinitely because the electric field thus set up will tend to stop the transference of electrons from A to B. A steady condition will finally be established in which each of the bodies A and B receives in a given time as many electrons as it emits in that time. This condition is also characterized by the occurrence of a constant difference of potential  $V$  between any two points close to the surfaces of A and B, respectively. The number of electrons in unit volume of the space will then vary from point to point, but will not change with time. A consideration of the nature and number of the variables entering into the equations governing the equilibrium of the electrons shows that  $V$  is independent of the size, shape and relative position of the bodies A and B, and depends only on their nature and the temperature  $T$ . This result holds true both on the basis of the classical dynamics and on that of the quantum theory. The difference of



potential  $V$  is, therefore, the intrinsic contact potential difference of the bodies A and B at the temperature  $T$ ."

"It follows from equation (35) that the relative powers of electronic emission of different bodies at a given temperature will be determined by their contact differences of potential; so that whether bodies show much or little difference one from another in the former respect will depend on the magnitude of the latter quality. There is still a great difference of opinion as to the magnitude of the contact difference of potential between metals whose surfaces are free from gas and in a good vacuum. The school which attributes these differences of potential to chemical action between metals and the surrounding atmosphere holds that under the conditions referred to the contact potentials would completely disappear. If this view is correct we should expect all hot metals to give nearly equal thermionic currents per unit area at any given temperature, provided they were in a perfect vacuum and their surfaces were uncontaminated. The opposite school regards these potential differences as an intrinsic property of the metals affected and considers the changes caused by gases and other contaminating agents to be of a secondary character. From this standpoint we should expect to find potential differences between metals in a good vacuum of the same order of magnitude as those observed in a gaseous atmosphere. The advocates of these opposing views have waged an intermittent warfare for a century without coming to a definite settlement.

"Until recently most investigators who have attempted to decide this question experimentally have concluded that their results favoured the chemical theory. In 1912 the writer pointed out that none of these experiments were conclusive, all the observed phenomena being explicable on the intrinsic theory when due account was taken of various secondary actions which were bound to occur under the conditions of the experiments. Quite recently a considerable amount of evidence favouring the intrinsic theory has accumulated. Thus Richardson and Compton examined the photoelectric currents obtained when monochromatic light fell on small discs of various metals placed at the centre of a large spherical electrode. With this arrangement the saturation value of the current should be reached when there is no difference of potential between the two electrodes. This was found to be the case if the contact potentials were included among the potential differences operative. Somewhat similar experiments have been made by Page. In all these experiments good vacuum conditions were attained. In addition, in Richardson and Compton's experiments with sodium, and in all Page's experiments, the metal surfaces tested were cut mechanically *in vacuo*. Still more recently the contact difference of potential has been measured directly under the best vacuum conditions with surfaces machined *in vacuo* by A. E. Hennings, who finds that the potential differences are still of the order usually observed, the metals being more electropositive when freshly cut. All these experiments support the intrinsic potential theory, although there is abundant evidence that gases produce definite and complicated changes in the observed values. On the other hand, Hughes, working with surfaces of metals freshly distilled *in vacuo*, found the metals to be initially most electronegative and to become more electropositive under the action of small quantities of air. Millikan and Souder, also, have found that surfaces of sodium are most electronegative when freshly cut and become more electropositive on oxidation. It is clear that



the experimental evidence as to the origin of contact potential differences is still conflicting, but the balance would seem to favour the view that it is due to an intrinsic property of the materials and not to surface films of foreign matter."

Fredenhagen believes that the emission electrons from Wehnelt cathodes—hot metal cathodes coated with lime or baryta—is a secondary effect, arising from the recombination of the earth metal with the oxygen liberated by electrolysis during the passage of the current through the oxide. This view is not shared by the author, p. 101.

"Taking all the evidence together it seems to the writer that the view which attributes the emission from metallic oxides to the escape, owing to increased kinetic energy, of those electrons which give rise to the electrical conductivity of such materials has much more to be said for it than any other so far put forward. This position is strengthened by the recent experiments of Germershausen, who has shown that the removal of the last traces of gas from a Wehnelt cathode and its surroundings increases the emission from it. Under these conditions the discharge from the lime becomes very steady and shows temperature and voltage characteristics similar to those exhibited by tungsten filaments under the best vacuum conditions.

"In recent years oxide-coated cathodes have been very thoroughly studied in the Research Laboratory of the American Telephone and Western Electric Companies. One result of these researches has been to establish thoroughly the view that the emission from such cathodes is an intrinsic property of the oxide similar to the emission from pure metals and is not a secondary phenomenon due to chemical action, bombardment of the cathode by positive ions, or the like. Tests have shown that the oxycathodes maintain their emitting power unimpaired *in vacuo* in which the measured pressures were as low as  $10^{-9}$  to  $10^{-10}$  mm. Filaments have been maintained in operation for such long periods that the mass of the electrons emitted by them exceeded fifteen times the mass of the oxide coating. It appears that the value of  $b$  for filaments coated with a mixture of the oxides of barium, strontium, and calcium is much less than that for a pure lime filament and their emitting power at a given temperature is correspondingly greater. The value of  $b$  deduced from the temperature variation of the emission is very close to the value deduced from the cooling effect. Direct tests by Davison and Germer show that any electron emission which may be due to positive ion bombardment must in general under the conditions in which the tubes are operated be under one ten-thousandth of the total emission and such effects can therefore play no important part in the phenomena. Very interesting experiments have been made with filaments coated with oxide evaporated from a second oxide-coated filament. It appears that exceedingly small amounts of the oxide (enough to cover the underlying metal to about 30 percent of its area with a layer of oxide one molecule deep) are sufficient to increase the emission from the value appropriate to the pure metal to that characteristic of the oxide. This corresponds to an increase in the current by a factor of about  $10^9$  under the conditions of the experiments. The variation of the emission with the amount of oxide deposited has been investigated. It is found that for very minute deposits the emission practically remains at the value for the pure metal, as the deposit increases the emission begins to rise rapidly in two steps to a maximum value after which it falls with similar rapidity to the value characteristic of a thick oxide layer. Up

to beyond the maximum the emission can be represented as the sum of two terms of the form  $Cx^ne^{x/a}$  when  $C$ ,  $n$  and  $a$  are constants and  $x$  is the amount deposited. The drop in the emission over the falling part beyond the maximum appears to be due to a drop in the value of  $A$  from that for the pure metal to the smaller value appropriate to the oxide, the other constant  $b$  in the emission formula remaining unaltered. Apparently the thinnest deposit has already established the value of  $b$  appropriate to the oxide."

Working with platinum wires which had not been heated in hydrogen for a long period, Wilson found that the emission varied with the pressure of the hydrogen, whereas Richardson found that the emission from a platinum wire in hydrogen is practically constant when the pressure varies from one millimeter to 0.001 mm, p. 119. "It is clear from the facts which have been described that the emission from platinum in an atmosphere of hydrogen shows two quite distinct types of behaviour, under conditions which at first sight appear to be identical. The cause of this difference was investigated by Wilson who found that the condition in which the emission was sensitive to changes in the pressure of the hydrogen occurred only with 'fresh' wires, that is to say, with wires which had not been heated in hydrogen for any considerable length of time. The condition of insensitiveness to change of pressure, on the other hand, was found to be characteristic of wires which had been subjected to continued heating in hydrogen. Such wires may, for brevity, be described by the term 'old.' Wilson has pointed out that the observed facts are consistent with the view that in a fresh wire the hydrogen exists in a state of solution, whereas in an old wire most of it is present in the form of a compound which is formed with extreme slowness. The essential difference between solution and chemical combination lies in the fact that the amount of gas dissolved is a continuous function of the external pressure, whereas the amount chemically combined, once the reaction has been completed, is constant, if the external pressure exceeds the dissociation pressure, or zero if the pressure is below that value. Since the amount of hydrogen present in the wire is held to determine the value of the emission at a given temperature, on this view the emission will only be a continuous function of the pressure of the external hydrogen with fresh wires, in which the gas is present in the dissolved state. The dissociation pressure of the hydrogen compound must be very small (under 0.001 mm.) at the temperature of the experiments referred to (up to 1400° C), since the large emission from an old wire could not be removed by pumping. However, dissociation pressures vary rapidly with temperature, and Wilson has found that the large emission from an old wire can be 'pumped out' if the temperature is raised to about 1700° C. This view is also substantiated by the fact that the large emission from an old wire can be 'burnt out' almost instantaneously in an atmosphere of oxygen at much lower temperatures; since the pressure of hydrogen in equilibrium with water vapour and its dissociation products under the conditions of such an experiment is very low. It is, however, possible that the burning out process contaminates the platinum surface and reduces the emission to a value less than that which would characterize a clean platinum surface."

There are some curious things about the emission of ions by heated salts, p. 261. "The phenomena exhibited by cadmium iodide have been examined in some detail by Sheard, who tested both the conductivity and the emission of ions from the salt. At temperatures below the melting-point of the salt (400° C) the

saturation currents in the vapour decayed continuously from a maximum initial value, in agreement with Schmidt's results. At higher temperatures there was a rise to a maximum in about 15 minutes followed by a slower decay. The currents due to the emission of ions from the heated salt showed a different behaviour from those in the vapour. At 470° C, for example, there was an enormous negative emission which decayed very rapidly with time. The positive emission was at first too small to measure, but it gradually increased to a maximum value in 90 minutes and then fell away. At this stage the positive emission was greater than the negative, but the greatest positive emission was less than one two-hundredth part of the large negative emission observed on first heating. A similar but less marked contrast between the positive and negative emissions was observed when iodine was similarly tested. Sheard also examined the behaviour of the salt which distilled out of the experimental tube in successive experiments. He found that the first distillate gave a small negative and a large positive emission whereas the second showed the contrary behaviour. In all the distillates there was a great disparity in the magnitudes of the positive and negative emissions; and in almost every case the distillate from a preparation which gave a large negative and a small positive emission, or vice versa, showed the contrary behaviour. The currents from all the distillates were much smaller than the large initial emission from the fresh salt. The distilled salt showed no appreciable change in appearance, but chemical analysis showed that successive distillation reduced the percentage of iodine.

"There can be little doubt that these interesting time changes in the emission of ions from salts and in the conductivity of salt vapours are symptomatic of the occurrence of chemical changes; but it is very difficult to form a definite opinion as to what the precise nature of the change is, in any particular case. When the currents are increasing with time it seems fairly clear that a substance possessing greater thermionic activity is being formed and when the currents are diminishing the resulting products are less active in this respect. One difficulty in forming a judgment as to the nature of the chemical changes arises from the delicacy of the electrical test. This is so sensitive that the amount of matter concerned might often be incapable of detection by chemical methods. It is also possible that many of the effects are due to the occurrence of unstable forms which are not persistent enough to be recognized by chemical methods. This is especially likely since the time changes show that the bodies concerned have only a transitory existence. In many cases these time changes are attributable to the presence of contaminants. Thus ordinary laboratory specimens of 'pure' aluminum phosphate give an initial emission which is large compared with that from the pure salt and which after a time falls to a small value. Horton has shown by spectroscopic examination that this decay in the emission is accompanied by the disappearance of sodium salts.

"The complicated phenomena in the case of cadmium iodide have been studied more fully, perhaps, than those shown by any other salt, and here it does seem possible to form, at any rate, a limited judgment as to the nature of the phenomenon from the chemical side. Schmidt has ventured the opinion that the time changes in the vapour arise from the decomposition of the molecules of  $\text{CdI}_2$  into  $\text{Cd}^{++}$  and  $\text{I}_2^{--}$  with a subsequent interchange resulting in  $\text{Cd}^{+-}$  and  $\text{I}_2^{+-}$ , that is to say, two neutral molecules. It does not seem to the writer, however,

that any theory of this type will account for the observed time changes in the vapour in presence of an excess of salt. So long as there is any excess of salt the vapour will be supplied at a steady rate and the phenomena observed in it should be independent of time until the salt disappears. It is necessary to suppose that the actions in the vapour are not conditioned solely by the amount of  $\text{CdI}_2$  vapour present but rather by some other substance coming from the salt. The time changes must in fact be conditioned by something the amount of which is determined by actions occurring at the salt and not simply by a decomposition of cadmium iodide vapour. In one respect this question has been definitely settled by Kalandyk who has shown that the currents in cadmium iodide vapour under the conditions of these experiments are independent of the time, provided every trace of water is removed from the salt and from the apparatus. The way in which water brings about the time changes usually observed is unknown. Kalandyk's experiments only tell us that there are no time changes when water is absent, they do not offer an explanation of the changes which occur in the presence of water or water vapour. Sheard's results point to the conclusion that the large negative initial emission, when it is present, is connected with the liberation of iodine. On this view the smaller negative emission from the distillates would be related to the reduced iodine content of the salt, which after distillation probably consists of a solution of an unrecognized subiodide of cadmium in  $\text{CdI}_2$ . The presence of the subiodide would reduce the equilibrium pressure of iodine in presence of cadmium iodide vapour. The probable existence of a subiodide of cadmium is distinctly indicated by the work of Morse and Jones who succeeded in isolating a body having the composition  $\text{Cd}_{12}\text{I}_{22}$ , probably a solution of the subiodide in  $\text{CdI}_2$ .

The behavior of quinine sulphate is apparently not what LeBon thought it was, p. 304. "The ionization, discovered by LeBon, which accompanies the hydration and dehydration of certain crystals has frequently been attributed to chemical action. The case which has attracted most attention is that of quinine sulphate. This substance, when allowed to cool after heating to a certain high temperature, phosphoresces and causes the surrounding gas to become conducting. Miss Gates showed that the ionization was not caused by rays capable of penetrating the thinnest aluminum foil. She also found that the current from the salt was greater when it was positively than when it was negatively charged and that the hydration of a given amount of salt caused a greater conductivity than the dehydration. These results were confirmed by Kalaehne, who concluded, in addition, that the hydration of a given amount of the salt at a fixed temperature liberated a constant quantity of electricity independently of the rate of hydration, although the actual instantaneous currents depend very considerably on the rate of hydration. Recent experiments by deBroglie and Brizard suggest that in all these cases the ionization is only an indirect effect of the absorption or liberation of water vapour. Both the ionization and the luminosity observed with the sulphates of quinine and cinchonine seem to be due to minute sparks arising from the triboluminescence of the crystals of these substances which takes place during hydration and dehydration. Although it is almost impossible to saturate the currents from these substances the ions have a high coefficient of re-combination. Both the ionization and the scintillations increase as the pressure is reduced from atmospheric."

*Wilder D. Bancroft*

**Elementary Chemical Microscopy.** By *Émile Moulin Chamot*. Second edition. 23 × 15 cm; pp. xv + 470. New York: John Wiley and Sons, 1921. Price: \$4.25.—The first edition was reviewed six years ago (20, 175). At that time the reviewer was able to bear witness from first-hand knowledge of the importance of the microscope in the study of alloys. Quite recently Mr. Chamot's assistant has cleared up with only six month's work the whole question of the blue colors and the metallic colors in birds' feathers. When one remembers that men like Rayleigh and Michelson have worked at this problem without settling it, this must be considered a triumph for chemical microscopy. There will never be any doubt as to the value of the microscope to the chemist in the minds of those who are privileged to know the remarkable work on primers done by Mr. Chamot during the war. The same statement is made in a very modest way in the preface. "The Great War brought us face to face with a multitude of intricate industrial and economic problems, in the solution of which the chemist was not slow to appreciate the importance and the value of industrial chemical microscopy. It is probable that a greater number of new applications of microscopic methods were made in our industries than in the entire preceding quarter of a century."

According to the author the changes in the new edition "have been chiefly in the rearrangement of the chapters, in the elaboration of the data presented, and in the rewriting of obscure passages. Comparatively little new apparatus has been described or new methods introduced." In the appendix is a brief synopsis of the course in Introductory Chemical Microscopy as now given in the Department of Chemistry at Cornell University.

The subject is now presented under the following headings: objectives and oculars; illumination of objectives and illuminating devices; microscopes for use in chemical laboratories; vertical illuminators and metallurgical microscopes; ultramicroscopes and apparatus for the study of ultramicroscopic particles; useful microscope accessories, laboratory equipment, work tables, and radiants; micrometry and micrometric methods; quantitative analysis by means of the microscope; the determination of melting and subliming points; the determination of refractive index by means of the microscope; crystals under the microscope; methods for handling small amounts of material; the methods of microchemical qualitative analysis; characteristic microchemical reactions of the common elements and acids when in simple mixtures; preparing opaque objects for the microscopic study of internal structure; appendix.

The reviewer was interested in the statement, p. 310, that "in the microchemical examination of rock sections, aluminum hydroxide can be stained with Congo red and gelatinous silica with malachite green—tests which may be employed in testing for 'weathering,' etc." Off-hand one would have expected an acid dye to have worked better with alumina than a substantive dye.

*Wilder D. Bancroft*

#### ERRATUM

The price of Gildemeister and Hoffmann's "The Volatile Oils" is \$10 per volume and not \$7.50 as stated (25, 762).

## HYDROUS OXIDES. III

BY HARRY B. WEISER

### Hydrous Chromic Oxide

Earlier communications in this series<sup>1</sup> have dealt primarily with the colloid chemistry of the hydrous oxides of iron and aluminum. In this paper will be considered the properties of the various hydrous chromic oxides prepared under different conditions.

#### Composition and Properties of Precipitated Chromic Oxide

*The Question of Hydrates.*—The addition of ammonia or an alkali to a solution of a chromic salt precipitates a gelatinous oxide, the composition and properties of which vary widely depending on the conditions of precipitation and the subsequent treatment. The drying of the precipitated oxide may be carried out under such conditions that the resulting product approaches the composition of a hydrate. Accordingly, the older literature contains numerous references to such definite hydrates. Thus to the oxide precipitated with KOH and NH<sub>4</sub>OH Schaffner<sup>2</sup> assigned the formulas, Cr<sub>2</sub>O<sub>3</sub>.4H<sub>2</sub>O and Cr<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O respectively. The oxide dried over sulphuric acid was represented by Cr<sub>2</sub>O<sub>3</sub>.7H<sub>2</sub>O. Similarly, Siewert<sup>3</sup> found that the composition of the bluish oxide prepared by treating a dilute solution of a chromic salt with ammonium hydroxide could be represented by the formula Cr<sub>2</sub>O<sub>3</sub>.7H<sub>2</sub>O when dried with sulphuric acid; by Cr<sub>2</sub>O<sub>3</sub>.4H<sub>2</sub>O when dried in vacuo; and by Cr<sub>2</sub>O<sub>3</sub>.H<sub>2</sub>O when dried at 200° to 220°. The investigations of Siewert were repeated by van Bemmelen<sup>4</sup> who showed conclusively that no definite hydrates were formed at any

<sup>1</sup> Jour. Phys. Chem., 24, 177, 505 (1920).

<sup>2</sup> Liebig's Ann., 51, 169 (1844).

<sup>3</sup> Jahresber., 1861, 242. Cf. Loewel: Jour. Pharm., (3) 7, 323, 401, 424 (1845); Frémy: Comptes rendus, 27, 269; 30, 415 (1847); 47, 883 (1858); Leforte: Jour. Pharm., (3) 18, 27 (1850); Vincent: Phil. Mag., (4) 13, 191 (1850).

<sup>4</sup> Rec. Trav. chim. Pays Bas, 7, 37 (1888).



temperature between 15° and 280°. By heating the precipitated oxide at temperatures varying from 15° to 100° in (a) saturated atmosphere (b) ordinary air and (c) dry air, until the weight was constant, van Bemmelen found that at every temperature equilibrium was established between the vapor tension of the colloid and that of water at the same temperature. It was noted that at 65° in a saturated atmosphere, the oxide retained more water than at 15° in dry air. These observations have been recently confirmed and extended by von Baikow.<sup>1</sup> In the light of this work it is evident that a composition corresponding to the formula for a definite hydrate just happened to be obtained under the conditions of drying employed by earlier chemists.

Although chromic oxide as ordinarily prepared forms no definite hydrate, Ferée<sup>2</sup> claims to have prepared the compound  $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$  by electrolysis of a neutral solution of  $\text{CrCl}_3$  with a platinum cathode. The brownish black amorphous powder loses water on heating to 80°. Whether this is a definite inversion point and all the water is lost at this temperature is not stated. When heated to 400° the powder glows and the ordinary green oxide is formed. It is also claimed by some that a green hydrate known as Guignet's green<sup>3</sup> is formed by fusing one part of a bichromate of sodium or potassium with 3 parts of boric acid. Salvetät<sup>4</sup> represents the composition by the formula  $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . Scheurer-Kestner<sup>5</sup> prepared the oxide in a purer condition and assigned it the formula  $2\text{Cr}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . Wöhler and Becker<sup>6</sup> obtained a similar product using ammonium bichromate instead of the alkali salt and also by heating the ordinary oxide in an autoclave at 180° to 250°. It was noted that a green product containing 37 percent of water did not change in color when dried at 80°. Under these condi-

<sup>1</sup> Jour. russ. phys. Chem. Ges., 39, 660 (1907).

<sup>2</sup> Bull. Soc. chim. Paris, (3) 25, 620 (1901); Cf. Bunsen: Pogg. Ann., 91, 619 (1854); Geuther: Liebig's Ann., 118, 66 (1861).

<sup>3</sup> Guignet: Jahresberichte, 1859, 761.

<sup>4</sup> Comptes rendus, 48, 295 (1859).

<sup>5</sup> Dingl. Jour., 176, 386 (1865).

<sup>6</sup> Zeit. angew. Chem., 21, 1600 (1908); 24, 484 (1911).

tions the water content was 15.10 percent corresponding to the formula  $2\text{Cr}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . The color darkened gradually as more water was driven off by raising the temperature so that Wöhler and Becker concluded that the green oxide must be a definite hydrate. Ebner and Hue<sup>1</sup> also believed that Guignet's green is a definite hydrate to which they assigned the formula  $2\text{Cr}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ . The oxide prepared in any way is distinctly amorphous in character and behaves like the ordinary precipitated oxide in this respect that it loses water continuously as the temperature is raised. While it is entirely possible to dry the oxide under such conditions that the percentage composition approaches that of a definite hydrate it is extremely doubtful whether any hydrate is formed. This point will be considered further under the discussion of the color of the oxide.

*Aging.*—Hydrous chromic oxide freshly precipitated from a cold chromic salt solution with an alkali or ammonia is readily soluble in acids with the formation of the corresponding salts and is peptized by alkali hydroxides with the formation of a colloidal solution. On standing the oxide "ages" quite rapidly, the velocity of change increasing with the temperature. In this process the physical character and water content of the precipitated oxide undergoes a change that is accompanied by a marked decrease in solubility and reactivity. The oxide peptized by alkali ages particularly rapidly.

TABLE I  
Molar Heat of Solution of Hydrous Oxides precipitated from Solution in Alkali

Time	Molar heat of solution. Cal.	Time	Molar heat of solution. Cal.
0	20.70	7 hr.	2.40
10 min.	7.90	1 da.	1.75
1 hr.	5.80	7 da.	1.20
2 hr.	3.90	30 da.	0.75
4 hr.	2.85	60 da.	0.50

<sup>1</sup> *Farbenztg.*, 15, 2106, 2157, 2213, 2268, 2319 (1910).



Recoura<sup>1</sup> followed the change by determining the molar heat of solution in hydrochloric acid of the oxide precipitated with acid from the colloidal solution in alkali after definite intervals of time. His results are given in Table I.

It will be noted that the change in the heat of solution is very marked during the first few minutes. This change is accompanied by a similar decrease in solubility. Since the aging is more rapid at higher temperatures we should expect the oxide precipitated at 100° to be much less soluble than that thrown down at room temperature. This is in accord with the facts. The change from a very soluble to a less soluble form of hydrous chromic oxide has led to the conclusion that the compound exists in definite allotropic or isomeric modifications.<sup>2</sup> This is very unlikely, particularly in view of the fact that there is no inversion point for a soluble and an insoluble modification. Between these two extremes of solubility it is possible to prepare an indefinite number of hydrous oxides each differing slightly from the others in water content, in size of particles, in structure of the mass and consequently in reactivity with acids and alkalis. This behavior is entirely analogous to the behavior of the hydrous oxides of iron and aluminum that have been considered in the earlier papers in this series.

*The Glow Phenomenon.*—When hydrous chromic oxide is heated at a suitable rate to temperatures around 500°, it evolves enough heat to cause it to become incandescent. The temperature at which the glowing takes place varies with the sample and with the method of heating. Berzelius,<sup>1</sup> Wöhler<sup>3</sup> and Endell and Rieke<sup>4</sup> give approximately 500° for the glow temperature; LeChatelier<sup>5</sup> gives 900°; and Rothaug<sup>6</sup> showed that the "glow temperature varies between 420° and 680°

<sup>1</sup> Comptes rendus, 120, 1335 (1895).

<sup>2</sup> Berzelius: Lehrbuch, 5th Edition, 2, 315 (1848).

<sup>3</sup> Zeit. Kolloidchemie, 11, 241 (1913).

<sup>4</sup> Zentralblatt Min. Geol., 1914, 246.

<sup>5</sup> Bull. Soc. chim. Paris, 34, 70 (1880).

<sup>6</sup> Zeit. anorg. Chem., 84, 165 (1913).

depending on whether the precipitate was in a powdery or granular form." The glow phenomenon is regarded by some as strong evidence in support of the view that there are two allotropic modifications of the oxide. Thus Berzelius, who observed it first, believed that the glow attended the transformation from one modification to another. This view seems to be shared by Moissan,<sup>1</sup> LeChatelier<sup>2</sup> and Mixer.<sup>3</sup> Siewert<sup>4</sup> considers that the glowing is merely an accompaniment of the dehydration process since the dehydrated oxide does not glow when heated. The latter observation was confirmed by Mixer<sup>3</sup> who showed that if the hydrous oxide was heated gradually to 500° and above, the olive green oxide lost most of the water and became clear green without any glowing taking place. Since the glowing of the precipitated oxide depends on the rate of heating and since the glow temperature varies widely depending on the size of the particles, it seems altogether unlikely that the phenomenon accompanies the transformation from one definite modification to another. Moreover, Wöhler<sup>5</sup> and Endell and Rieke<sup>6</sup> have observed a similar phenomenon with a number of hydrous oxides as well as other substances; and it is improbable that all of them should exist in two forms. From the results of his investigations Wöhler concludes that the glow is due to a sudden decrease in the very large surface of the hydrous oxide prepared by precipitation. In support of this view he showed that the glowing is increased by all conditions which favor hydrosol formation in the preparation of the oxide, for example, the use of dilute solutions of reagents; the use of chloride rather than sulphate and of KOH rather than NH<sub>4</sub>OH. Moreover, the glow was found to be greater, the greater the adsorption capacity of the precipitate, indicating that the phenomenon

<sup>1</sup> Bull. Soc. chim. Paris, (2) 34, 70 (1880); Ann. Chim. Phys., (5) 21 199 (1880).

<sup>2</sup> Bull. Soc. chim. Paris, (2) 47, 303 (1887).

<sup>3</sup> Am. Jour. Sci., (4) 26, 125 (1908); 39, 295 (1915).

<sup>4</sup> Jahresberichte, 1861, 243.

<sup>5</sup> Zeit. Kolloidchemie, 11, 241 (1913).

<sup>6</sup> Loc. cit.

is connected closely with the extent of surface. He showed that the heat evolved by 1 gram of oxide was sufficient to raise its temperature from 50° to 100°, depending altogether on the extent of surface. In summing up his conclusions, Wöhler says: "The glowing of the surface appears to be the final stage in the spontaneous loss of surface energy by continuous condensation: from the hydrosol, whose coagulation is accompanied by an evolution of heat, through the hydrogel and the anhydrous pseudomorphous gel to the ignited oxide whose surface is almost nil, judging from its adsorption capacity."

In view of Wöhler's interesting observations, there is little doubt but that the glowing which frequently accompanies the ignition of hydrous oxides is a surface phenomenon. The oxides prepared in different ways vary in the size of the particles and the amount of enclosed water and hence in the extent of surface. The maximum glow and heat evolution is obtained when the sample made up of finest particles is heated rapidly to the glow temperature which is in the neighborhood of 500°. If a fine-grained precipitate is heated very slowly or kept for some time below the glow temperature, there is a gradual, instead of a sudden diminution of surface which is not accompanied by incandescence.

*Color.*—Hydrous chromic oxide can be obtained in various shades from a clear gray blue to a dark green. Certain of these colors such as chrome green and Guignet's green constitute the most permanent green pigments. The color of the oxide freshly precipitated in the cold is variously described by different people as bluish, violet blue, clear blue, clear gray blue and gray violet. The shade differs somewhat depending on whether it is precipitated from a green or violet chromic salt. On drying the precipitate the color changes to a distinct green and the dry amorphous oxide is described as a vivid green. Wöhler and Becker<sup>1</sup> converted the ordinary precipitated oxide which they described as gray violet into

<sup>1</sup> Loc. cit.

Guignet's green by aging in an autoclave at 180° to 250°. The rate of precipitation seems to have a marked effect on the color. Thus, Casthelaz and Leune<sup>1</sup> claim to have prepared an oxide with a richer and purer color than Guignet's green simply by slow precipitation at ordinary temperatures of a green solution of a chromic salt with  $\text{Al}(\text{OH})_3$ ,  $\text{ZnCO}_3$ ,  $\text{ZnS}$  or  $\text{Zn}$ .

As might be expected the variation in the color of the hydrous oxide is regarded by many as due to different allotropic modifications of the oxide. Thus Loewel<sup>2</sup> distinguishes four distinct modifications based on difference in color and solubility. Leforte<sup>3</sup> attributes the different colors to different hydrates. Frémy<sup>4</sup> concludes that the hydrous oxide formed from a cold violet solution is an instable meta-chromium hydroxide while that precipitated from a green solution is a stable isomer. He is led to this conclusion by the observation that a compound having different properties from the so-called meta-oxide is formed by precipitation from boiling solution or by allowing the oxide precipitated from the violet solution to stand under water or salt solution, or to dry in the air. As we know, Frémy observed the aging or transformation from the highly hydrous form of the oxide to the less hydrous insoluble form—a continuous process in which there is no indication of definite isomeric modifications. Berzelius<sup>5</sup> likewise recognizes two modifications the evidence for which is that the oxides precipitated from violet and green solutions, respectively, redissolve in acids giving solutions with the original color. This seems to depend altogether on the method of procedure. Thus Recoura<sup>6</sup> added alkali to a green solution until a precipitate was formed which was dissolved at once with  $\text{HCl}$  forming a violet solution. Olie<sup>7</sup> obtained similar

<sup>1</sup> Bull. Soc. chim. Paris, (2) 10, 170 (1868).

<sup>2</sup> Jour. Pharm., (3) 7, 323, 401, 424 (1845).

<sup>3</sup> Comptes rendus, 30, 416 (1850); Jour. Pharm., (3) 18, (1850).

<sup>4</sup> Ann. Chim. Phys., (3) 23, 388 (1848).

<sup>5</sup> Lehrbuch, 5th Ed., 2, 315 (1848).

<sup>6</sup> Comptes rendus, 104, 1227 (1887); Ann. Chim. Phys., (6) 10, 1 (1887).

<sup>7</sup> Zeit. anorg. Chem., 52, 48 (1907).

results by adding alkali just short of precipitation and then acidifying the solution. However, Recoura<sup>1</sup> did obtain a green solution by dissolving the hydrous oxide precipitated from what he claimed to be  $\text{Cr}_2\text{OCl}_4$ . From the results of his investigations Recoura distinguishes three isomers of hydrous chromic oxide but he recognizes no differences in color. Thus he states that one and the same modification is obtained from either green or blue  $\text{CrCl}_3$ ; a second modification from  $\text{Cr}_2\text{OCl}_4$ ; and a third from the solution of either of the other two in alkali. The reasons given for regarding these as isomeric modifications, is their different "solubilities in alkalis and their different heats of solution in acids." Since an unbroken series of hydrous oxides can be prepared each differing slightly from the others in their behavior with acids and alkalis, it seems to me that Recoura's so-called isomers are not definite allotropic modifications but merely represent certain ones of the many hydrous oxides that may be prepared by a suitable choice of conditions of formation.

Reference has been made to the observations of Wöhler and Becker which led them to the conclusion that Guignet's green is a definite hydrate. They conclude further that this pigment is a hydrate isomer bearing a relation to the ordinary blue oxide similar to the relationship between blue and green chromic chloride. I have pointed out that their evidence in support of a definite hydrate is altogether inconclusive. Their conclusion that the gray blue oxide and Guignet's green are hydrate isomers is equally questionable. In support of their view they show that the precipitated oxide and the clear green pigment having the same water content, have a distinctly different vapor pressure at the same temperature. This difference is to be expected when we consider that the conditions of formation of the two oxides are quite different. As has been demonstrated by van Bemmelen<sup>2</sup> the vapor pressure of a hydrous oxide is determined not only by the amount of water

<sup>1</sup> Comptes rendus, 101, 435 (1885).

<sup>2</sup> "Die Absorption," 239 et seq. (1910).

it contains but by its structure. Since the conditions of forming Guignet's green and the ordinary oxide are so different we are not surprised to find that there is a difference in the size of the particles and the structure of the masses of each, as is evidenced not only by difference in vapor pressure but by difference in color. In the second place, Wöhler and Becker point out that heating the ordinary precipitated oxide in an autoclave converts it to Guignet's green. However, they were unable to find a definite inversion temperature for two isomers and it is extremely doubtful whether any exists as the subsequent experiments will show.

#### Experimental

*Effect of Temperature of Precipitation on Color.*—Twenty cubic centimeter portions of a solution containing 0.2 gm of  $\text{CrCl}_3$  were treated with just enough  $\text{NaOH}$  solution to cause complete precipitation at the various temperatures shown in Table II; and the precipitates were kept at this temperature for a definite length of time. For temperatures above  $100^\circ$  the precipitations were carried out in an autoclave in the following way: The chromic salt solution was placed in a 50 cc pyrex beaker which was set on a wire gauze in the center of an autoclave vessel. The alkali solution contained in a small vial was set in the beaker. When the desired temperature was reached, the solutions were mixed by shaking the autoclave,

TABLE II  
Effect of Temperature of Precipitation on the Color of Hydrous Chromic Oxide

Temperature	Time of heating	Color of precipitate
$0^\circ$	30 min.	gray blue
$50^\circ$	30 min.	greenish blue
$100^\circ$	30 min.	bluish green
$150^\circ$	30 min.	green with faint tinge of blue
$200^\circ$	30 min.	clear green
$200^\circ$ - $225^\circ$	15 hr.	bright green

thus upsetting the vial. The temperature was determined from the reading on a calibrated pressure gauge.

From the results recorded in Table II it is evident that the color varies continuously from gray blue to clear green with increasing temperature of precipitation. There is no indication whatsoever that the different colors are due to different isomers but to a difference in the size of the particles, the structure of the mass and the amount of water enclosed under the different conditions of formation. As the color changes from blue to clear green with increasing temperature of precipitation, the oxide becomes less gelatinous, less soluble in acids and less readily peptized by alkalis. The variation in color is quite similar to that observed with hydrous ferric oxide prepared under different conditions.<sup>1</sup>

*Effect of Rate of Precipitation on Color.*—If hydrous chromic oxide is precipitated very slowly from a chromic salt solution, it should come down in a much more granular and less hydrous condition than when precipitated rapidly. Under these conditions one should expect to get a clear green hydrous oxide. It will be recalled that Casthelaz and Leune<sup>2</sup> prepared a green pigment which they called imperial green by the slow precipitation of a chromic salt with  $\text{Al}(\text{OH})_3$ ,  $\text{ZnCO}_3$ ,  $\text{ZnS}$  or  $\text{Zn}$  at  $10^\circ$ . Their observations were confirmed by adding  $\text{Zn}$  to a solution of  $\text{CrCl}_3$  and allowing to stand for several days at  $25^\circ$ . A clear dark green oxide was obtained which was very much more granular than the oxide prepared by rapid precipitation. The compound was quite insoluble in  $\text{N H}_2\text{SO}_4$ .

### Preparation and Properties of Colloidal Hydrous Chromic Oxide

#### A The Positively charged Colloid

*Peptization of Hydrous Chromic Oxide by Chromic Chloride.*  
—Graham<sup>3</sup> prepared colloidal hydrous chromic oxide by peptiz-

<sup>1</sup> Weiser: Jour. Phys. Chem., 24, 313 (1920).

<sup>2</sup> Bull. Soc. chim. Paris, (2) 10, 170 (1868).

<sup>3</sup> Phil. Trans., 151, I, 183 (1861).



ing the freshly precipitated oxide with chromic chloride and dialyzing to remove excess electrolyte. After thirty days' dialysis in the cold a colloidal solution was obtained containing 1 equivalent of acid to 10.6 of oxide; after thirty-eight days, it contained 1 equivalent of acid to 31.2 of oxide but a part of it had jelled on the dialyzer. The colloidal solution was dark green, could be diluted with water or heated but was very instable in the presence of salts.

Neidle and Barab<sup>1</sup> investigated the dialysis of a colloidal solution of chromic oxide peptized by excess chromic chloride. The colloid was placed in a parchment membrane which was surrounded with water. In one series of experiments the water was changed at intervals; while in a second series, a continuous flow of water through the dialyzer was maintained. The interesting observation was made that the colloidal particles passed through the membrane used, in both cases. In the intermittent dialysis, the colloid continued to diffuse until but little remained in the membrane; while in the continuous dialysis, the passage of the colloid ceased after a time and 75 percent remained within the membrane. Neidle and Barab conclude that two factors influenced the growth of the colloidal particles during dialysis: agglomeration following removal of peptizing agent and growth of nuclei by hydrolysis of adsorbed chloride by adsorbed water. In the intermittent dialysis the removal of peptizing agent was not rapid enough to cause sufficient agglomeration to prevent the passage of the colloid through the particular membrane; while in the continuous dialysis, a gradual growth of the particles resulted finally in their retention by the membrane. In a later communication Neidle and Barab<sup>2</sup> showed that a colloidal solution of hydrous chromic oxide in chromic chloride could be dialyzed continuously at a high temperature<sup>3</sup> thereby shortening by weeks the time to get a colloidal solution containing a minimum amount of peptizing agent.

<sup>1</sup> Jour. Am. Chem. Soc., 38, 1961 (1916).

<sup>2</sup> Ibid., 39, 70 (1917).

<sup>3</sup> Neidle: Ibid., 38, 1270 (1916).



Certain investigators<sup>1</sup> are of the opinion that colloids prepared according to the Graham method above described, are chlorides of condensed hydroxides or oxychlorides of variable composition. But little support is given to this view by the fact that a large number of basic chromic chlorides are described in the literature<sup>2</sup> since all of them are amorphous powders and it is extremely doubtful whether any of them are definite compounds. Certainly in most cases they are mixtures, the composition of which just happened to be expressible by a formula. Bjerrum<sup>3</sup> has shown that basic chlorides having the formulas  $\text{Cr}(\text{OH})\text{Cl}_2$  and  $\text{Cr}(\text{OH})_2\text{Cl}$  may be formed in small amounts on adding alkali to chromic chloride and Recoura<sup>4</sup> claims to get  $\text{Cr}_2\text{OCl}_4$  by the oxidation of  $\text{CrCl}_2$  in the air; but it is unlikely that any quantity of basic salt is present in the well dialyzed solution of hydrous chromic oxide in chromic chloride. Neidle and Barab dialyzed such a colloidal solution in the hot for 29 hours and found the ratio, equivalents Cr : equivalents Cl to be above 1500. It seems absurd to regard such a solution as a basic salt. Hydrous chromic oxide is peptized by chromic chloride owing to preferential adsorption of  $\text{Cr}^{+++}$  and  $\text{H}^+$  ions. The excess  $\text{Cl}^-$  ion after dialysis is not an indication of the presence of basic chloride but is a measure of the amount of adsorbed cations which give the colloid its stability.

*Hydrolysis of Chromic Acetate.*—If a solution of a ferric or aluminum salt is boiled with sodium acetate, the acetate of the trivalent metal is formed which hydrolyzes precipitating the respective hydrous oxides. By working at low concentrations, colloidal solutions of the hydrous oxides of iron and

<sup>1</sup> Wyruboff: *Bull. Soc. chim. Paris*, 21, 137 (1899); Jordis: *Zeit. anorg. Chem.*, 35, 16 (1903); Duclaux: *Comptes rendus*, 138, 144, 809 (1904); 140, 1468, 1544 (1905); 143, 296, 344 (1906); *Jour. Chim. Phys.*, 5, 29 (1905); Linder and Picton: *Jour. Chem. Soc.*, 81, 1920 (1905). Nicolardot: *Ann. Chim. Phys.*, (8) 6, 344 (1905); Malfitano: *Zeit. phys. Chem.*, 68, 232 (1909); Michel: *Comptes rendus*, 145, 185, 1275 (1907); 147, 1052, 1288 (1908).

<sup>2</sup> See Moberg: *Jour. prakt. Chem.*, 29, 175 (1843); Loewel: *Jour. Pharm.*, 4, 424 (1843); Péligot: *Comptes rendus*, 21, 24 (1845); Ordway: *Am. Jour. Sci.*, (2) 26, 202 (1858); Olie: *Zeit. anorg. Chem.*, 52, 62 (1906).

<sup>3</sup> *Zeit. phys. Chem.*, 73, 72 (1910).

<sup>4</sup> *Ann. Chim. Phys.*, (2) 10, 1 (1887).

aluminum may be prepared by hydrolysis of the acetates.<sup>1</sup> Chromic acetate behaves differently. Reinitzer<sup>2</sup> boiled solutions of chromic chloride and sulphate with sodium acetate for a short time and obtained a violet solution but no precipitate. This solution gave no precipitate in the cold with sodium or potassium hydroxide, ammonia, ammonium hydrosulphide, ammonium carbonate, sodium phosphate, barium hydroxide or barium carbonate. A precipitate was obtained in the hot with all of the above reagents except sodium phosphate. A similar solution which gave no test for Cr<sup>+++</sup> ion was obtained by allowing the solution of chromic salt and sodium acetate to stand in the cold for a sufficient length of time. That there is a slow action even in the cold in the presence of alkalis is evidenced by a change in color of the solution and the formation of a jelly on standing. Recoura<sup>3</sup> and Werner<sup>4</sup> point out that the hydrolysis of chromic acetate does not form hydrous chromic oxide but a basic acetate. Although some colloidal hydrous chromic oxide may be formed by boiling a chromic salt solution with sodium acetate, it is altogether probable that this process results chiefly in the formation of one or more of the complex chromic acetates, a number of which have been isolated in a definite crystalline form by Werner<sup>2</sup> and by Weinland and his pupils.<sup>5</sup> Solutions of these salts do not give the usual reactions for Cr<sup>+++</sup> ion since the chromium is a constituent of a complex ion. It is an interesting fact that in the presence of excess violet chromic acetate, iron and aluminum acetates cannot be detected either by heating to the boiling point or by adding caustic alkalis or ammonia. As will be pointed out later in this paper, we know that hydrous chromic oxide peptized by hydroxyl ion adsorbs and so carries into colloidal solution, a number of hydrous oxides not peptized by alkalis. This suggests that the

<sup>1</sup> Cf. Weiser: *Jour. Phys. Chem.*, 24, 277, 505 (1920).

<sup>2</sup> *Monatshefte für Chemie*, 3, 257 (1882).

<sup>3</sup> *Comptes rendus*, 129, 158, 208, 288 (1899).

<sup>4</sup> *Ber. deutsch. chem. Ges.*, 41, 3447 (1908).

<sup>5</sup> *Ber. deutsch. chem. Ges.*, 41, 3236 (1908); 42, 2997, 3881 (1909); *Zeit. anorg. Chem.*, 67, 167 (1910); 69, 158, 217 (1910); 75, 293 (1912); 82, 426 (1913).

hydrous ferric oxide formed by hydrolysis of ferric acetate is kept from precipitating owing to adsorption by colloidal hydrous chromic oxide. This explanation does not seem to be in accord with the facts. In the first place, the evidence seems to indicate that hydrous chromic oxide is not the primary product of the hydrolysis of chromic acetate; and in the second place, Reinitzer<sup>1</sup> showed that green chromic acetate formed by boiling and so hydrolyzing the violet salt does not prevent the precipitation of hydrous ferric oxide: "The influence of a chromic salt on the precipitation of ferric or aluminic salts varies to a certain extent according as to whether it is in the violet or the green modification. When a green solution of chromic acetate is mixed with a small quantity of ferric acetate, and the mixture is boiled, the iron is separated in the form of a flocculent precipitate; but if a solution of ferric acetate be added to an originally violet solution of chromic acetate and the mixture boiled, then, whatever may be the quantity of ferric solution added, no precipitation of iron will take place. Exactly the same is the case with a violet solution of chromic acetate obtained by boiling a green solution with sodium acetate; also with a green chromic acetate boiled without any addition. Green chromic acetate, therefore, acts like most metallic salts when heated, in precipitating a solution of ferric acetate; whereas violet chromic acetate, so far from producing a precipitate, even renders a large portion of the iron acetate as indifferent towards reagents as itself." In the light of these observations it seems quite probable that the behavior of mixtures of ferric and violet chromic acetates is due to the formation of one or more iron chromic acetate complexes. At least two series of such complex salts have been prepared by Weinland and Guszmann.<sup>2</sup>

Reinitzer<sup>3</sup> claims to have prepared a colloidal solution by dialysis of chromic acetate. A violet acetate solution was evaporated on a water bath giving a green amorphous mass

<sup>1</sup> Jour. Chem. Soc., 42, 825 (1882).

<sup>2</sup> Ber. deutsch. chem. Ges., 32, 3881 (1909).

<sup>3</sup> Monatshefte für Chemie, 3, 249 (1883).

soluble in water. The green solution was treated with an excess of sodium acetate and boiled. A violet solution was again formed which was dialyzed giving what was claimed to be a violet colloid that gave a violet deposit on evaporation. Woudstra<sup>1</sup> followed a similar procedure: A solution of hydrous chromic oxide in acetic acid was evaporated to dryness at 40° and a greenish black residue was obtained, which was subsequently dissolved. A part of this solution was dialyzed (the method and time of dialysis is not stated); and a part was distilled with steam until there appeared a green precipitate which was filtered off. These two preparations showed slightly different properties, but each had a lilac or violet color in transmitted light similar to Reinitzer's preparation. Neither solution was precipitated by the addition of 20 percent solutions of MgSO<sub>4</sub>, BaCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, KCN, KSCN, KMnO<sub>4</sub>, NaOH, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, or (NH<sub>4</sub>)<sub>2</sub>(COO)<sub>2</sub>, or by the addition of concentrated H<sub>2</sub>SO<sub>4</sub>, HCl or HNO<sub>3</sub>. The acids gave green solutions.

While the preparations of Reinitzer and of Woudstra may contain some colloidal hydrous chromic oxide, the amount must be small and the colloid very impure, particularly in view of the extraordinary stability in the presence of an excess of salts that ordinarily would precipitate colloidal chromic oxide in very low concentration. Since chromic acetate can form such a variety of complexes under varying conditions, it seems probable that the Reinitzer and Woudstra solutions were chiefly complex salts. The more recent observations of Neidle and Barab<sup>2</sup> support this view. These investigators passed steam into a chromic acetate solution and dialyzed. Although such a procedure would favor the growth of any particles of colloid it was found that all the chromium passed through the membrane.

*Hydrolysis of Chromic Nitrate.*—Since nitrate ion usually has a smaller precipitating action on positive colloids than

<sup>1</sup> Zeit. Kolloidchemie, 5, 33 (1909).

<sup>2</sup> Jour. Am. Chem. Soc., 38, 1961 (1916).

chloride ion, Biltz<sup>1</sup> undertook the preparation of a number of colloids from the nitrate solution. Chromic nitrate was placed in parchment paper thimbles and was dialyzed at room temperature for 8 days changing the wash water three times a day. The colloid so prepared was clear, dark green in color and comparatively stable toward electrolytes. Both the stability of the colloid and the presence of excess nitrate indicate that eight days' dialysis in the cold is insufficient to prepare a pure colloid. Woudstra<sup>2</sup> dialyzed chromic nitrate in the cold for 4 weeks and obtained a clear green colloid that contained relatively little nitrate. However, most of the chromium had diffused through the membrane so that the solution was very dilute.

*Hydrolysis of Chromic Chloride.*—Graham failed to get a colloid by dialysis of chromic chloride. Since he used an intermittent method of dialysis Neidle and Barab<sup>3</sup> attribute his failure to the experimental method. The latter investigators dialyzed a solution of commercial chromic chloride in the cold changing the diffusate continuously for 11 days; and found that 7.72 percent of the salt was transformed into colloid. A specially prepared green chromic chloride gave but a trace of colloid in the same time. The difference is accounted for by the fact that the presence of a little colloid in the commercial chloride accelerates the hydrolysis.<sup>4</sup> Since the temperature coefficient of hydrolysis of chromic chloride is considerable,<sup>5</sup> very much higher yields were obtained by dialysis at 75° to 80°. The colloids were clear deep green and perfectly mobile when first prepared; but they jelled on standing if the dialysis was carried too far.

*Reduction of Ammonium Chromate with Colloidal Platinum.*—Paal<sup>6</sup> prepared a colloidal solution of hydrous chromic

<sup>1</sup> Ber. deutsch. chem. Ges., 35, 4431 (1902).

<sup>2</sup> Zeit. Kolloidchemie, 5, 33 (1909).

<sup>3</sup> Jour. Am. Chem. Soc., 39, 71 (1917).

<sup>4</sup> Goodwin and Grover: Phys. Rev., 11, 193 (1900).

<sup>5</sup> Bjerrum: Zeit. phys. Chem., 59, 343 (1907).

<sup>6</sup> Ber. deutsch. chem. Ges., 47, 2211 (1914).

oxide by reduction of a solution of ammonium chromate with colloidal platinum in the presence of the sodium salt of protalbinic acid which acts as a protecting colloid. The preparation contained colloidal hydrous oxide, colloidal platinum unchanged ammonium chromate and sodium protalbinic acid. It was purified to some extent by dialysis.

#### Experimental

Since the properties of precipitated hydrous chromic oxide vary with the method of preparation, it seemed altogether likely that colloidal hydrous oxides prepared in different ways would show wide variation in properties. This proved to be the case as shown by the following experiments.

*Preparation of Colloids.*—A colloid was prepared by adding  $\text{NH}_4\text{OH}$  to 400 cc of green chromic chloride solution (containing 80 g per liter) until the precipitate first formed just failed to dissolve on standing over night. The solution was filtered, diluted to 1200 cc and equal portions placed in two-liter pyrex beakers. One portion was dialyzed continuously for 15 days by the method of Neidle and Barab.<sup>1</sup> Approximately 10 hours each day the solution was kept boiling vigorously. The second portion was dialyzed continuously in the cold for 24 days. The colloid prepared by hot dialysis could be kept only in pyrex vessels since ordinary glass is sufficiently soluble to cause it to gel within a few days.

*Color and Solubility of Precipitated Colloids.*—A quantity of colloid containing 0.15 g  $\text{Cr}_2\text{O}_3$  was precipitated in a short thick-walled test tube by the addition of a few drops of 0.1 N  $\text{Na}_2\text{SO}_4$ . After centrifuging for 5 minutes at 3000 r. p. m., the supernatant liquid was poured off and the precipitate shaken up with 25 cc of acid or alkali. In addition to the two dialyzed solutions mentioned in the preceding paragraph, a third colloid was prepared by adding  $\text{NH}_4\text{OH}$  to a chromic chloride solution just short of precipitation. All the chromium was precipitated from the solution by  $\text{Na}_2\text{SO}_4$  as in the case of the dialyzed colloids. The color of the precipitated

<sup>1</sup> Jour. Am. Chem. Soc., 39, 71 (1917).

oxides and their behavior in the presence of acids and alkalis are given in Table III.

TABLE III  
Properties of Precipitated Colloids

Nature of colloid	Action of precipitated oxide with 25 cc of			Color of precipitate
	N H <sub>2</sub> SO <sub>4</sub>	N/5 HCl	N NaOH	
Freshly prepared	Dissolves rapidly	Soluble	Peptized at once	gray blue
Dialyzed in cold	Dissolves very slowly	Soluble	Peptized	green blue
Dialyzed at boiling point	Insoluble	Soluble	Not peptized	dark green

From the results shown in Table III it is clear that hydrous chromic oxides of widely varying properties may be obtained in the colloidal state by suitable variations in the conditions of preparation. Just as with hydrous ferric and aluminic oxides, there is a pronounced difference between the colloids prepared at room temperature and at the boiling point.

*Precipitation Values of Electrolytes.*—The colloids prepared by peptization of hydrous chromic oxide with CrCl<sub>3</sub> or by hydrolysis of chromic salts, are positively charged and so move to the cathode under electrical stress.<sup>1</sup> Biltz<sup>2</sup> showed that colloidal chromic oxide was precipitated by negative colloids but he did not investigate the precipitating power of different anions. I have determined the precipitation values of the potassium salts of several common anions for a well-dialyzed colloid containing 3.65 g Cr<sub>2</sub>O<sub>3</sub> per liter. This was so instable that it was necessary to carry out all experiments in vessels of pyrex glass. The procedure was as follows: In a 25 cc thick-walled test tube was placed 10 cc of colloid; and in a second tube, a suitable amount of electrolyte diluted to 10 cc. The solutions were mixed by pouring from one tube

<sup>1</sup> Picton and Linder: Jour. Chem. Soc., 71, 572 (1897).

<sup>2</sup> Biltz: Ber. deutsch. chem. Ges., 35, 4431 (1902); 37, 1095 (1904).



to the other with intermediate shaking; after which the mixture was transferred to one tube that was corked and set aside for exactly one hour. To determine whether precipitation was complete, the contents of the tube was shaken and centrifuged for 1 minute at 3000 r. p. m. By this procedure it was possible to determine the precipitation values of the salts with multivalent anions to within 0.02 cc of N/100 solution in 20 cc and of the salts with univalent anions to within 0.05 cc of N/10 solution in 20 cc. The electrolytes were measured with a 2 cc Ostwald pipette. In Table IV are given the precipitation values of a number of salts both in milliequivalents per liter and in millimoles per liter. In the last column of the table is given the nature of the precipitate formed by each electrolyte after standing quietly for an hour.

TABLE IV  
Precipitation Values of Salts

Salt	Precipitation value		Nature of precipitate
	Milliequivalents per liter	Millimoles per liter	
Potassium ferricyanide	0.485	0.162	Firm jelly
Potassium chromate	0.525	0.263	Firm jelly
Potassium dichromate	0.535	0.268	Firm jelly
Potassium sulphate	0.550	0.275	Firm jelly
Potassium iodate	0.635	0.635	Firm jelly
Potassium oxalate	0.660	0.330	Firm jelly
Potassium bromate	19.0	19.0	Jelly
Potassium chloride	30.0	30.0	Jelly
Potassium bromide	33.0	33.0	Jelly
Potassium chlorate	33.8	33.8	Jelly
Potassium iodide	37.5	37.5	Jelly

From the precipitation values of the electrolytes expressed in milliequivalents per liter, we can arrange the anions in the order of their precipitating power beginning with the greatest, thus: ferricyanide > chromate, dichromate > sulphate > iodate > oxalate > bromate > chloride > bromide, chlorate > iodide. If the precipitation values are expressed in millimoles per liter the only change in the order is that iodate fol-



lows instead of precedes oxalate. As has been noted before<sup>1</sup> iodate behaves like a multivalent ion in having a very high precipitating power. It is not known why this should be since the evidence seems to show that in dilute solution iodic acid behaves like a monobasic acid.<sup>2</sup> It is particularly interesting that the conditions at the precipitation concentration are favorable for the formation of a jelly. This point will be considered in a later section. The jellies can be broken up by shaking, yielding a gelatinous precipitate that is readily thrown down with the centrifuge.

### B. The Negatively Charged Colloid

If an excess of alkali hydroxide is added in the cold to a chromic salt solution, the precipitate formed is peptized completely with the formation of a clear green colloidal solution. In this respect hydrous chromic oxide differs from hydrous aluminum oxide which dissolves in alkali hydroxides with the formation of aluminate. As evidence that the solution of hydrous chromic oxide in excess alkali is due to peptization and not to the formation of chromite, Fischer and Herz<sup>3</sup> call attention to the spontaneous precipitation of the hydroxide and point out "that the solution in alkali (particularly in  $\text{Ba}(\text{OH})_2$ ) can be precipitated by electrolytes, that the conductivity of the solution is not changed after precipitation of chromic hydroxide by warming; and that a solution prepared from chromic chloride with  $\text{NaOH}$  is not dialyzable against pure water."<sup>4</sup> From similar work Kremann<sup>5</sup> concluded that alkali chromite was formed since the chromium moved to the anode under electrical stress and dialyzed through a membrane if the latter was surrounded by alkali. Fischer<sup>1</sup> pointed out that Kremann's evidence was inconclusive since chromium in a negative colloidal oxide will move to the anode under elec-

<sup>1</sup> Weiser and Middleton: *Jour. Phys. Chem.*, 24, 51 (1920).

<sup>2</sup> Miolati and Mascetti: *Gazz. chim. ital.*, 31, I, 93 (1901); *Atti Accad. Lincei*, (5) 14, I, 217 (1905).

<sup>3</sup> *Zeit. anorg. Chem.*, 31, 352 (1902); Herz: 28, 344 (1901); 32, 454 (1902).

<sup>4</sup> Fischer: *Zeit. anorg. Chem.*, 40, 39 (1904).

<sup>5</sup> *Ibid.*, 33, 87 (1903).

trical stress. He pointed out further, that Kremann started with chrome alum and that the diffusion of chromium through his dialyzing membrane was due to a chrome-sulphuric acid. Attention was called by Bancroft<sup>1</sup> to the fact that there must be some change in conductivity when hydrous chromic oxide is precipitated from colloidal solution since the precipitate is known to adsorb salts and alkali; but that this relatively slight change was not detected on account of the high initial conductivity. Bancroft showed however, that Fischer and Herz were right in their conclusion that the hydrous oxide is peptized by alkali since all the oxide can be filtered from solution with an ultrafilter.

Further evidence of the colloidal nature of an alkaline solution of hydrous chromic oxide is given by its action with other hydrous oxides. Thus Northcote and Church<sup>2</sup> observed that certain amounts of oxides that are insoluble in caustic potash alone, are soluble in the presence of hydrous chromic oxide. "It was found that complete solution takes place when the chromium as sesquioxide is associated with 40 percent of iron as sesquioxide; with 12.5 percent of manganese, 20 percent of cobalt or 25 percent of nickel as protoxides; and that complete precipitation takes place when the chromium as sesquioxide is associated with 80 percent of iron as sesquioxide, 60 percent of manganese, 50 percent of cobalt or 50 percent of nickel as protoxide. When cobalt and nickel however are thus rendered soluble the result is not permanent and ultimately not only does the oxide of cobalt or nickel become insoluble but it carries down with it some of the oxide of chromium. The other metallic oxides soluble in caustic potash were not found to be influenced in their relations with caustic potash by the presence of sesquioxide of iron or to exert any influence upon that oxide."

Similarly, Prud'homme<sup>3</sup> found that hydrous cupric oxide and hydrous ferric oxide dissolve in the green alkali solution

<sup>1</sup> Chem. News, 113, 113 (1916).

<sup>2</sup> Jour. Chem. Soc., 6, 54 (1854).

<sup>3</sup> Bull. Soc. chim. Paris, (2) 17, 253 (1872).

of hydrous chromic oxide. From the alkali solution of chromium and cupric oxides a precipitate of red cuprous oxide is formed by standing or by heating and sodium chromate appears in the solution. Kreps<sup>1</sup> showed further that mixtures of chromium salts with salts of barium calcium or magnesium in suitable proportions give no precipitate in the presence of alkali.

The observations of Northcote and Church, Kreps and Prud'homme are readily explained in view of the colloidal nature of the alkaline solution of hydrous chromic oxide. Nagel<sup>2</sup> working in Bancroft's laboratory showed that hydrous chromic oxide is peptized by alkali and that the peptized oxide adsorbs to a limited degree and so carries into colloidal solution the hydrous oxides of iron, manganese, cobalt, nickel copper and magnesium. The latter oxides likewise adsorb chromic oxide and so tend to take it out of colloidal solution in alkali. Accordingly if they are present in sufficient amount they will decolorize practically completely the green colloidal solution of chromic oxide. As previously noted the behavior of ferric acetate in the presence of violet chromic acetate can not be accounted for in this way.

Although the evidence given in the preceding paragraphs all seems to indicate that hydrous chromic oxide is peptized completely by alkali, recent investigations by Wood and Black<sup>3</sup> led them to conclude that alkali chromite is formed. These investigators precipitated chromic oxide at 100° with ammonia and treated the thoroughly washed precipitate with NaOH solutions varying in concentration from 0.2 N to 2.0 N. They found that the action was very slight but after two months appreciable quantities of chromate were formed. It is claimed that chromite is the intermediate product and hence that chromic hydroxide possesses a certain degree of acidic character. "In the opinion of the authors, therefore, it seems to be undoubtedly established that chromites do exist in an alkaline solution

<sup>1</sup> Thesis: Berlin (1893).

<sup>2</sup> Jour. Phys. Chem., 19, 331 (1914).

<sup>3</sup> Jour. Chem. Soc., 109, 164 (1916).

of chromic hydroxide; when the solution is freshly prepared and is kept a little time, part of the dissolved hydroxide separates out in a less soluble form and probably does during this period of transition, exist for a time in the colloidal condition, but when all such precipitation has taken place, a small amount of chromite will still be present in the solution." Although some chromate may be formed after a time when hydrous chromic oxide and sodium hydroxide are brought together in the presence of air, this by no means justifies the conclusion that the original solution in alkali is all chromite which gradually decomposes. In this connection it should be pointed out, however, that the spontaneous precipitation of hydrous chromic oxide from the green solution in alkali is not *prima facie* evidence that a colloidal solution is formed, since a solution of alkali aluminate prepared in the same manner as colloidal chromic oxide decomposes on standing and precipitates hydrous alumina. Moreover, the contention is not justified that the aging of hydrous chromic oxide in the alkali solution is unexplainable under the assumption that alkali chromite is formed;<sup>1</sup> since the hydrous oxide that precipitates spontaneously from alkali aluminate is aged in the sense that it is quite insoluble and much less hydrous than the oxide freshly precipitated from an aluminum salt.

#### Experimental

*The Peptization of Hydrous Chromic Oxide by Different Alkalis.*—Fischer and Herz determined the relative peptizing power of sodium and potassium hydroxide by adding chromic chloride solution drop by drop to the solution of alkali until a permanent precipitate just formed. By this procedure it was found that the peptizing action of KOH was greater than that of NaOH. No experiments were made with Ba(OH)<sub>2</sub> but the authors speak of the colloid formed by peptization with this hydroxide.

The method of procedure followed by Fischer and Herz in determining the peptizing action of alkalis is not entirely

<sup>1</sup> Abegg's Handbuch der anorganischen Chemie, (1) IV, 118 (1920).

satisfactory on account of the rapidity with which hydrous chromic oxide ages. It would seem to be more satisfactory to determine the amount of alkali which will just cause complete peptization of the hydrous oxide when added all at once to a definite amount of chromic salt. Accordingly the following method of procedure was followed: The rapid mixing of the solutions was accomplished by means of the mixing apparatus frequently employed in this laboratory.<sup>1</sup> In the inner compartment of this apparatus was placed 5 cc of a chromic chloride solution containing 40 g  $\text{Cr}_2\text{O}_3$  per liter; and in the outer compartment varying amounts of 0.6 N alkali together with enough water to make 20 cc. By inverting and shaking the vessel vigorously, a rapid mixing was obtained. The contents of the mixture was transferred to a large test tube and examined for complete peptization of the

TABLE V  
Peptization of Hydrous Chromic Oxide by Alkalis

Alkali	Solutions mixed (total volume 25 cc)			Observation	Nature of precipitate
	Alkali 0.6 N	$\text{CrCl}_3$	$\text{H}_2\text{O}$		
NaOH	10.0	5.0	10.0	Peptization in- complete	Gelatinous
NaOH	11.5	5.0	8.5	Peptization in- complete	Firm jelly
NaOH	11.75	5.0	8.25	Peptization almost complete	Firm jelly
NaOH	12.0	5.0	8.0	Peptization complete	Firm jelly
KOH	10.0	5.0	10.0	Peptization in- complete	Firm jelly
KOH	10.75	5.0	9.25	Peptization almost complete	Firm jelly
KOH	11.0	5.0	9.0	Peptization complete	Firm jelly
$\text{Ba}(\text{OH})_2$	20.0	5.0	0.0	No peptization	Gelatinous
$\text{Ba}(\text{OH})_2$	24.0	1.0	0.0	No peptization	Gelatinous

<sup>1</sup> Weiser and Middleton: *Jour. Phys. Chem.*, 24, 48 (1920).

hydrous oxide. This determination can be made with a high degree of accuracy by comparison with a tube containing the same amount of  $\text{Cr}_2\text{O}_3$  peptized with a large excess of alkali. After making a number of preliminary trials to determine the approximate amount of alkali required, the experiments recorded in Table V were carried out.

From the results given in Table V it is evident that the peptizing action of KOH is slightly greater than that of NaOH as observed by Fischer and Herz. On the other hand, hydrous chromic oxide is not peptized at all even by a saturated solution of  $\text{Ba}(\text{OH})_2$ , at least in the presence of  $\text{BaCl}_2$ . If an amount of alkali just short of complete peptization is employed, a firm green jelly is formed within an hour. With somewhat higher concentrations of alkali the jellies are formed more slowly.

Peptization experiments were next carried out on the hydrous oxide precipitated from chloride solution with ammonia and washed: Five cubic centimeter portions of chromic chloride were diluted to 20 cc in a 50 cc thick-walled test tube and precipitated in the cold with ammonia. Each mixture was centrifuged 3 minutes at 3000 r. p. m. after which the supernatant liquid was poured from the precipitate matted in the bottom of the tube. The oxide was washed by shaking thoroughly with 25 cc of water. After centrifuging again for three minutes the wash water was poured off and the precipitate treated with 20 cc of 0.6 N alkali. Some peptization was observed with both NaOH and KOH but it was far from complete although the quantity of alkali used was in excess of that necessary to peptize the newly formed oxide completely (see Table V). Since the time required for washing the precipitates was not more than 10 minutes, this experiment illustrates again the rapidity with which hydrous chromic oxide "ages." As might be expected from the previous experiments, no peptization whatsoever resulted with saturated  $\text{Ba}(\text{OH})_2$ .

*The Effect of the Concentration of Alkali on its Peptizing Power.*—Fischer and Herz record a series of experiments which

is offered as proof that the peptizing power of NaOH and KOH depends on the absolute amount present and not on the concentration. This conclusion did not seem reasonable and so I have carried out some experiments to determine its accuracy. The procedure followed was identical with that outlined in the preceding section except that enough water was added to make up the total volume of solutions mixed to 50 cc instead of 25 cc as previously. The results are given in Table VI.

TABLE VI  
Peptization of Hydrous Chromic Oxide by Alkalis (2)

Alkali	Solutions mixed (total volume 50 cc)			Observation	Nature of precipitate
	Alkali 0.6 N	CrCl <sub>3</sub>	H <sub>2</sub> O		
NaOH	13.5	5	31.5	Peptization almost complete	Soft jelly
NaOH	13.75	5	31.25	Peptization complete	Soft jelly
NaOH	14.0	5	31.0	Peptization complete	Soft jelly
KOH	11.5	5	33.5	Peptization incomplete	Soft jelly
KOH	12.0	5	33.0	Peptization almost complete	Soft jelly
KOH	12.25	5	32.75	Peptization complete	Soft jelly
KOH	12.50	5	32.50	Peptization complete	Soft jelly

By comparing the results recorded in Table VI with those in Table V, it will be noted that the concentration of alkali necessary for complete peptization of a given amount of hydrous oxide is greater the greater the dilution. For example, 12 cc of 0.6 N NaOH causes complete peptization of approximately 0.2 g Cr<sub>2</sub>O<sub>3</sub> in a total volume of 25 cc; while 13.75 cc of 0.6 N alkali is required to peptize the same amount of oxide in a total volume of 50 cc. This is exactly what one should expect.

*Precipitation Values of Electrolytes.*—If hydrous chromic oxide is in colloidal solution in alkali, it should be possible to coagulate it by the addition of salts. This was suggested by Fischer and Herz<sup>1</sup> but their observations along this line are

<sup>1</sup> Zeit. anorg. Chem., 31, 352 (1902).

not very enlightening. They point out that KCl and NaCl must have comparatively little precipitating action otherwise no colloid would be formed by adding alkali to chromic chloride. They could not use salts of other metals since most of them are precipitated by OH' ion. Speaking of the colloids prepared with NaOH and KOH they say: "A particularly strong effect on the precipitation could not be demonstrated. On the other hand, the precipitation by alkali salts of an analogous chromic hydroxide solution in barium hydroxide can be readily observed."<sup>1</sup> Fischer and Herz give no experimental data; and in view of the fact that hydrous chromic oxide is not peptized by alkali, the last sentence above quoted has little meaning.

Some preliminary experiments showed that the colloidal oxide was readily precipitated by salts; and that the precipitation values could be determined providing a definite method of procedure was followed. The colloid used in the experiments was prepared by mixing 5 cc of the chromic chloride solution used in earlier experiments with 15.0 cc of 0.6 N KOH and 30 cc of water. Since alkali was in considerable excess, the colloid did not start to precipitate for some time unless treated with salts. Ten cubic centimeters of the colloid so prepared was mixed with a definite amount of electrolyte diluted to 10 cc. The precipitation value was taken as that concentration of electrolyte which will just cause complete

TABLE VII  
Precipitation Values of Salts

Salt	Precipitation value (milliequivalents per liter)	Nature of precipitate
Barium chloride	5.15	Gelatinous
Potassium chloride	500.0	Gelatinous
Sodium chloride	210.0	Gelatinous
Lithium chloride	51.0	Gelatinous
Sodium sulphate	315.0	Gelatinous
Sodium acetate	220.0	Gelatinous

<sup>1</sup> Zeit. anorg. Chem., 31, 355 (1902).



coagulation in 10 minutes. After determining the approximate precipitation values the exact values were found for each electrolyte with a freshly prepared colloid. The values for a number of salts are given in Table VII.

From the results shown in Table VII we find that the precipitating power of the cations follows the usual order: barium > lithium > sodium > potassium; and that the stabilizing action of the anions is: sulphate > chloride, acetate.

*The Formation of Chromate.*—Reference has been made to Wood and Black's observation that the prolonged action of KOH on precipitated chromic oxide in the presence of air, yields chromate. These experiments were repeated with different concentrations of alkali and their results confirmed. Since alkalis attack the precipitated oxide, it seemed likely that the effect would be more marked when the oxide was in the colloidal state. To determine whether such was the case an excess of KOH was added to a  $\text{CrCl}_3$  solution and the mixture set aside for 2 months. Most of the colloid had precipitated in this time leaving a greenish yellow supernatant liquid. The yellow color was due to chromate which was present in considerable amount as proven by acidifying a portion of the solution and adding a dilute solution of potassium iodide and starch. The results of these experiments show that hydrous chromic oxide possesses a slight acidic character that may be detected by its prolonged action with alkali and air under suitable conditions. This does not mean that the solution of hydrous chromic oxide in alkali is all chromite as Wood and Black imply. On the contrary, it is extremely doubtful whether any chromite at all is formed in a reasonable time in the presence of slightly more than enough alkali to cause complete solution. The following experiment bears on this point: A colloidal solution was prepared by adding 20 cc of 0.6 N KOH to 30 cc of a chromic chloride solution that yielded 0.2 g  $\text{Cr}_2\text{O}_3$ . Through this solution was passed a rapid current of air for 30 minutes, after which it was tested for chromate as previously described.

The failure to get any test for chromate indicates the absence of chromite in the alkali solution. This is not proven absolutely by the experiment since it is possible although not probable that the oxidation of chromite in a current of air is too slow to give any chromate in 30 minutes; however, the results are in line with the other experiments, all of which show that hydrous chromic oxide is peptized by alkali and that no appreciable amount of chromite is formed within a reasonable time.

#### Chromic Oxide Jellies

Attention has been called to Reinitzer's observation that a solution of chromic salt boiled with sodium acetate and rendered alkaline with caustic alkalis or ammonia, sets to a jelly. Bunce and Finch<sup>1</sup> confirmed this observation and showed further that a jelly was formed by adding excess NaOH or KOH to chrome alum and allowing the solution to stand. They were unable to obtain a jelly from chromic sulphate, nitrate or chloride; but Nagel<sup>2</sup> showed that a jelly could be formed with sulphate if the alkali concentration was not too great. From these observations it was logical to conclude that acetate or sulphate ions are necessary for the formation of a chromic oxide jelly.<sup>3</sup> As I have shown in a preceding section, such is not the case since jellies were obtained by adding a suitable concentration of alkali to chromic chloride. The results recorded in Tables V and VI show that good firm jellies were obtained containing approximately 1 mole  $\text{Cr}_2\text{O}_3$  and 1000 moles of  $\text{H}_2\text{O}$ ; and soft jellies containing 1 mole  $\text{Cr}_2\text{O}_3$  and 2000 moles of  $\text{H}_2\text{O}$ . No jellies were formed when too little or too much alkali was used.

From the results of experiments on the formation of chromic oxide jellies, we get a pretty clear idea of the factors that influence the formation of jellies in general: A jelly would be expected to form if a suitable amount of a highly hy-

<sup>1</sup> Jour. Phys. Chem., 17, 269 (1913).

<sup>2</sup> Ibid., 19, 331 (1914).

<sup>3</sup> Bancroft: "Applied Colloid Chemistry," 244 (1921).

drous substance is gotten into colloidal solution and allowed to precipitate at a suitable rate. If the concentration of the hydrous substance is too low, no jelly or only a very soft jelly can result. If the precipitation from colloidal solution is too rapid, contraction is likely to occur with the formation of a gelatinous precipitate; if too slow, the particles are likely to grow and settle out in a granular or sandy mass. The effect of the presence of salts on jelly formation<sup>1</sup> is determined by the agglomerating and stabilizing action of ions, in so far as these affect the rate of precipitation. As previously stated, the results of the experiments with chromic oxide bear out these general conclusions: The rapid addition of a slight excess of alkali to a chromic chloride solution produces a negative colloidal oxide that is instable and precipitates slowly forming a jelly (Tables V and VI). If this precipitation is hastened by heating or by the addition of a suitable amount of electrolyte, the precipitate forms so rapidly that it is gelatinous and not a jelly (Table VII). Since the colloid is negatively charged, it will require the addition of more  $\text{Na}_2\text{SO}_4$ , say, than of  $\text{NaCl}$  to get a gelatinous precipitate on account of the stabilizing action of  $\text{SO}_4$  ion (Table VII). Finally, if the hydrous oxide has been peptized by too great a concentration of alkali the precipitate comes down very slowly and is almost granular in character.

The results of the experiments on the formation of jellies from negative colloidal hydrous chromic oxide suggested that the positive colloid could be precipitated under conditions favorable for the formation of a jelly. This proved to be unexpectedly easy to do. All that was necessary was to add just enough electrolyte to cause complete coagulation in an hour or two. It was found that if too little electrolyte were used, precipitation was incomplete and the results were unsatisfactory; while if too great an excess was added the precipitation was so rapid that a gelatinous precipitate was

---

<sup>1</sup> Holmes and Arnold: *Jour. Am. Chem. Soc.*, **40**, 1014 (1918); Holmes and Fall: *Ibid.*, **41**, 763 (1919).

formed. Under the conditions given in Table IV, good jellies were obtained in every case; but those formed with multivalent precipitating ions were the firmer. The following observations give some idea of the nature and stability of the jellies formed by precipitation of the colloid with multivalent precipitating ions: Twenty cubic centimeters of a jelly was prepared containing approximately 1 mole  $\text{Cr}_2\text{O}_3$ , 0.002 mole  $\text{K}_2\text{CrO}_4$  and 4700 moles of  $\text{H}_2\text{O}$ . This jelly stood in a test tube for a week without undergoing noticeable syneresis; and was not broken down by centrifuging for 1 minute at 3000 r. p. m. On shaking, the jelly was destroyed<sup>1</sup> giving a gelatinous precipitate that was thrown down by the centrifuge. A soft jelly was prepared containing 1 mole  $\text{Cr}_2\text{O}_3$ , 0.001 mole  $\text{K}_2\text{CrO}_4$  and 9400 moles of  $\text{H}_2\text{O}$ . It seems to me that firm jellies containing so much water without any supernatant liquid must be of the honeycomb rather than the sponge structure.

#### Summary

The results of this paper may be summarized briefly as follows:

(1) No definite hydrates of chromic oxide are formed by precipitation of a chromic salt with alkali. The numerous so-called hydrates described by earlier investigators were hydrous oxides dried under such conditions that the composition happened to approach that of a definite hydrate. The evidence that the specially prepared pigment, Guignet's green, is a definite hydrate is altogether inconclusive.

(2) Hydrous chromic oxide freshly precipitated in the cold is readily soluble in acids and readily peptized by alkalis; but it "ages" on standing or heating, becoming quite insoluble. The soluble and insoluble hydrous oxides are not definite isomers or allotropic modifications. Between the two extremes of solubility it is possible to prepare an indefinite number of hydrous oxides each differing slightly from the others in water content, in size of particles, in structure of the mass and consequently, in reactivity with acids and alkalis.

<sup>1</sup> Cf. Bunce and Finch: *Loc. cit.*

(3) When precipitated hydrous chromic oxide is heated rapidly to 500°, it evolves enough heat to raise its temperature to incandescence. The loss of heat does not accompany the change from one isomeric form to another but it is due to a sudden decrease in the very large surface of the oxide formed by precipitation.

(4) By precipitating hydrous chromic oxides at temperatures varying between 0° and 225°, substances have been prepared that vary in color from gray blue to bright green. The evidence indicates that the different colors are due not to different isomers but to a difference in the size of particles, the structure of the mass and the amount of water enclosed under the different conditions of formation. Very slow precipitation at low temperature gives an oxide with properties similar to that precipitated rapidly at higher temperature.

(5) Positively charged colloidal hydrous chromic oxide may be prepared by peptization of the hydrous oxide with chromic chloride and by hydrolysis of the chloride or nitrate but not of the acetate. Hydrous chromic oxides that vary widely in color and in their reactivity with acids and alkalis have been obtained in the colloidal state by suitable variation in the conditions of formation.

(6) The precipitating action of the potassium salts of several of the common anions on the positive colloid has been determined. The order of anions beginning with the one of greatest precipitating power is: ferricyanide > chromate, dichromate > sulphate > iodate > oxalate > bromate > chloride > bromide, chlorate > iodide.

(7) Negatively charged colloidal hydrous chromic oxide is prepared by peptization of the hydrous oxide with sodium hydroxide or potassium hydroxide. The peptizing power of potassium hydroxide is slightly greater than that of sodium hydroxide. Contrary to the observations of Fischer and Herz it was found (a) that the peptizing power depends on the concentration of alkali and not on the absolute amount present and (b) that hydrous chromic oxide is not peptized by barium hydroxide.

(8) Like the positive colloid the negative colloid is readily precipitated by electrolytes. From the precipitation values of a number of salts, we find the precipitating power of cations follows the usual order: barium > lithium > sodium > potassium; and the stabilizing action of anions is: sulphate > chloride acetate.

(9) Hydrous chromic oxide peptized by alkali adsorbs to a limited degree and so carries into colloidal solution the hydrous oxides of iron, manganese, cobalt, nickel, copper and magnesium which are not peptized by alkali alone. A precipitate of hydrous ferric oxide is not formed when ferric acetate is boiled in the presence of an excess of violet chromic acetate. This is probably due to the formation of a complex chromium iron acetate and not to the adsorption of hydrous ferric oxide by colloidal hydrous chromic oxide.

(10) Hydrous chromic oxide possesses a slight acidic character as evidenced by the formation of a small amount of chromate by the prolonged action of alkali on the precipitated or colloidal oxide in the presence of air. This property is so slight however, that it is extremely doubtful whether any chromite at all is formed within a reasonable time in the presence of slightly more than enough alkali to cause complete peptization.

(11) Chromic oxide jellies are formed by precipitation of either the positive or negative colloid under suitable conditions. The presence of sulphate or acetate ion is not essential.

(12) Factors that influence the formation of jellies in general, are: A jelly may be expected to form if a suitable amount of a highly hydrous substance is gotten into colloidal solution and allowed to precipitate at a suitable rate without stirring. If the concentration of the hydrous substance is too low, no jelly or only a very soft jelly can result. If the precipitation from colloidal solution is too rapid, contraction is likely to occur with the formation of a gelatinous precipitate instead of a jelly; if too slow, the particles are likely to grow and settle out in a granular or sandy mass. The effect of the presence of salts on jelly formation is determined by the

agglomerating and stabilizing action of ions, in so far as these affect the rate of precipitation. The results of the experiments on the formation of chromic oxide jellies are in accord with these general conclusions.

*Department of Chemistry  
The Rice Institute  
Houston, Texas*

## THE OXIDATION OF OXALIC ACID IN THE ABSENCE OF OTHER ACIDS

BY J. C. WITT

In connection with some work on the various direct and indirect methods for the determination of calcium in cement raw mixtures,<sup>1</sup> occasion arose to study in some detail the precipitation of calcium as the oxalate, and the titration of oxalic acid and its salts with potassium permanganate. Some phases of the work were suggested by a previous study of oxidation-reduction reaction without the addition of acid.<sup>2</sup> In determining calcium by the permanganate titration method, the calcium is precipitated from an ammoniacal solution by adding an excess of ammonium oxalate. The calcium oxalate is collected, dissolved in an excess of dilute sulphuric acid, and the oxalic acid thus liberated titrated with standard permanganate solution.<sup>3</sup> Another procedure is to precipitate calcium with a standard oxalate solution, and after filtering out the calcium oxalate, acidify the filtrate with sulphuric acid and titrate the oxalic acid present.<sup>4</sup> In either case, the reaction is represented by the equation:



$\text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 10\text{CO}_2$ . It is generally believed that this reaction can only take place in the presence of a strong acid. Hydrochloric acid is avoided because of its action on permanganate and nitric acid should not be present because it is an active oxidizing agent. Consequently sulphuric acid has come into general use.

*Oxidation of Oxalic Acid by Potassium Permanganate in the Presence of Acetic Acid.*—Acetic acid may be substituted for sulphuric acid in the reaction. As a preliminary qualitative test, some ammonium oxalate solution was acidified with acetic

<sup>1</sup> Philippine Jour. Sci., 15, 107 (1919).

<sup>2</sup> Jour. Am. Chem. Soc., 37, 2360 (1915); 38, 47 (1916); 40, 1027 (1918).

<sup>3</sup> Mohr: "Titrimethode," p. 239.

<sup>4</sup> Kraut: Chem. Centr., 1, 316 (1856).



acid and the mixture was warmed to about 80° C. A small amount of potassium permanganate was then added and the mixture was stirred vigorously for some seconds. No change in color was observed, and the result was recorded as negative. The beaker was set aside. Some hours later when the beaker was about to be emptied and washed, it was noted that the permanganate color had completely disappeared. Quantitative measurements revealed that satisfactory titration can be made, and that the stoichiometric relations are the same as when sulphuric acid is present. However, the procedure, and the color of the solution when the end-point is reached are somewhat different.

It is a common experience that in the presence of sulphuric acid the color of the first portion of permanganate fades slowly and considerable stirring is necessary. After this, the reaction is practically instantaneous, and the titration proceeds as rapidly as the permanganate is added. The temperature of the solution being titrated constantly decreases by radiation, and because a cooler liquid is being mixed with it.

When the titration is made in the presence of acetic acid, the temperature must not be allowed to fall—otherwise the velocity of the reaction decreases to such an extent that it is impossible to finish the titration in a reasonable time, if at all. The longer the end of the titration is delayed, the greater is the decrease in temperature (as the titration is ordinarily carried out) and of course this causes a still greater loss of time, and so on. It is therefore necessary to keep the mixture heated almost to the boiling point during the entire titration. This was done at first by placing the beaker, containing the solution being titrated, on the hot plate several times for reheating. This was not completely satisfactory. Later an electric hot plate about six inches in diameter was placed on the base of the burette stand. The contents of a beaker were first heated to boiling on a gas hot plate and then transferred one by one to the electric hot plate and the titrations made while the liquid continued to boil. When not actually in use, the burette was raised several inches, and the current turned

off so that there was no error due to expansion of the solution in the burette. There was no appreciable error from volatilization of oxalic acid. Under these conditions, the titration was almost as rapid as in the presence of sulphuric acid. The electric hot plate was used in the same manner in all the titrations subsequently discussed in this paper.

There is a difference in the end-point, however. The permanganate color does not fade directly to colorless but there is an intermediate brown color. As the titration proceeds, this becomes more and more apparent, and longer time and more vigorous stirring is necessary to dissipate it. The end-point is sharp but the color at this stage is not the characteristic pink. It is rather a rose color caused by a blending of the pink of the excess permanganate and the brown of a colloidal solution of manganese compounds.

*Oxidation in the Absence of Other Acids.*—Neutral ammonium oxalate is not oxidized by potassium permanganate, at least under ordinary conditions of concentration, temperature, and the like. However, the fact that the necessary hydrogen ion concentration could be supplied by a weak acid such as acetic suggested that it should be possible to titrate oxalic acid alone with permanganate, the necessary hydrogen ion concentration being supplied by the oxalic acid itself. It has been shown that oxalic acid alone, may be completely oxidized to water and carbon dioxide by permanganate;<sup>1</sup> and Neidle and Crombie<sup>2</sup> found that ferrous salts may be completely oxidized by permanganate, without the additions of acid, though the reaction is not suitable for a method of titration because the end-point is masked by colloidal substances.

Preliminary tests showed that in starting to titrate oxalic acid alone with permanganate, the behavior is identical with that observed in the presence of sulphuric acid. The color caused by the first addition is slow to fade, but after this the color produced by additional permanganate disappears rapidly.

<sup>1</sup> Moranski and Stingl: *Jour. prakt. Chem.*, **18**, 83 (1878).

<sup>2</sup> *Jour. Am. Chem. Soc.*, **38**, 2607 (1916).

However, considerably before the equivalent amount has been added, the solution becomes turbid, and then becomes clear on stirring. As the titration proceeds the turbidity appears with smaller additions of permanganate, and more stirring is necessary to dispel it. Finally a point is reached at which the solution does not become clear on continued stirring. It remains turbid when boiled for 20-30 seconds. At the end of this time the colloid coagulates and a slight permanent precipitate is formed. A further addition of permanganate immediately produces a dense chocolate-colored precipitate. The formation of the first permanent precipitate is taken as the end-point of the titration. To avoid confusion in the discussion that follows, the true end-point, obtained by titrating with permanganate in the presence of sulphuric acid and completely oxidizing the oxalic acid, is termed the "acid" end-point, and the end-point just described, obtained in the absence of any acid other than oxalic is termed the "non-acid" end-point. The reaction was studied further to determine whether or not the non-acid end-point could be obtained with sufficient regularity and accuracy to find out the mechanism of the reaction, and obtain a formula for calculating the acid end-point from the non-acid end-point.

Solutions of potassium permanganate, oxalic acid and calcium chloride (each, 0.2 N) equivalent to each other were prepared. The calcium chloride solution was prepared by dissolving Iceland spar in a small amount of hydrochloric acid and diluting to volume. The concentration of this solution was such that the calcium in 1 cc combined with the oxalate ion in 1 cc of the oxalic acid solution, and 1 cc of the potassium permanganate solution was required to oxidize the calcium oxalate thus formed, when dissolved in dilute sulphuric acid.

Portions of 5, 10, 15, 25, 35, 45 and 50 cc, respectively, of the oxalic acid were placed in beakers and diluted to approximately 100 cc. Each portion was then titrated at the boiling point, with permanganates until the non-acid end-point was reached. The results are shown in Table I (column C).

TABLE I

The Titration of Oxalic Acid with Potassium Permanganate in the Absence of Sulphuric Acid

(A) Cc 0.2 N oxalic acid taken	(B) Cc 0.2 N KMnO <sub>4</sub> re- quired for acid end-point (theo- retical) V <sub>0</sub>	(C) Cc 0.2 N KMnO <sub>4</sub> re- quired for non- acid end-point V <sub>1</sub>	(D) $\frac{V_1}{V_0}$
0			
5	5	3.31	0.662
10	10	6.58	0.658
15	15	9.85	0.657
25	25	16.43	0.657
35	35	22.76	0.650
45	45	29.34	0.652
50	50	32.67	0.653
(E) 0.625 V <sub>0</sub>	(F) $\frac{V_1 - V_0}{0.625 V_0}$	(G) $\frac{V_1}{K}$ or, V <sub>0</sub> <sup>1</sup>	(H) V <sub>0</sub> <sup>1</sup> - V <sub>0</sub>
3.13	0.18	5.06	0.06
6.25	0.33	10.06	0.06
9.38	0.47	15.06	0.06
15.62	0.81	25.12	0.12
21.87	0.89	34.80	-0.20
28.13	1.21	44.86	-0.14
31.25	1.42	49.95	-0.05

The non-acid titrations bear an approximately constant ratio to the acid titrations (column D). Referring to the equation for the oxidation of oxalic acid in the presence of sulphuric acid, it will be noted that for every 5 molecules of oxalic acid oxidized, three molecules of sulphuric acid are required. That is, five of the eight equivalents, of acid accounted for in the equation, or 0.625 of the total amount, is oxidized. Multiplying the values in column B by this factor, we find that the results differ only slightly, and in a regular manner, from the results obtained by titration (column F). Dividing the sum of the terms in column F by the sum of the terms in column A, we obtain the quantity 0.029 which we shall

call  $k$ . Now we may derive a formula for the value of the non-acid titration as follows:

$$V_1 = 0.625 V_0 + kO$$

In which,  $V_0$  = cc of potassium permanganate necessary completely to oxidize a given volume of oxalic acid solution in the presence of excess sulphuric acid (acid end-point)

$V_1$  = cc of potassium permanganate necessary to produce the non-acid end-point.

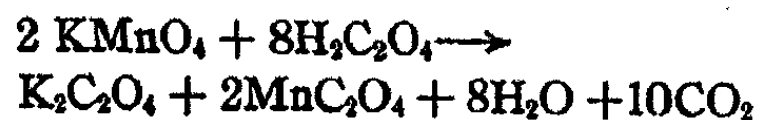
$O$  = cc of oxalic acid titrated.

Now the oxalic acid and the permanganate were taken as equivalent. Therefore we may substitute  $V_0$  for  $O$ . Substituting the value of  $k$  and collecting we have,

$$V_1 = 0.654 V_0.$$

Considering the coefficient of  $V_0$  as a constant, we may write  $V_1 = K V_0$ .

Substituting the successive values of  $V_1$  and dividing by  $V_0$ , we obtain the values given in column G, designated as  $V_0^1$ . The values of  $V_0^1 - V_0$  are shown in column H. The average numerical value of the terms in this column is 0.099 cc. That is, we can calculate the amount of oxalic acid present from the value of the non-acid titration within practically the experimental error. Also on this basis we may consider that  $k$  and  $K$  are constants. However  $k$  must be determined for each series of titrations as will be shown later. The results indicate that the value 0.625 does not vary. Consequently the reaction between oxalic acid and permanganate may be represented by the equation:



The oxalic acid is reduced by the permanganate and as long as there is a sufficient concentration of hydrogen ion, present, the manganese compounds resulting from the reduction of the permanganate are dissolved by the excess of oxalic acid. The hydrogen ion concentration decreases during the titration until a point is reached at which the manganese com-

pounds are no longer dissolved and further addition of potassium permanganate results in the formation of a precipitate. At the end of the titration, the solution is no longer acid—in fact, in most cases it shows a faintly alkaline reaction.

In Figure 1 curve A shows the volume of potassium permanganate that is required completely to oxidize oxalic acid; curve C, the theoretical amount necessary to produce the non-acid end-point; and curve B, the non-acid titration value obtained. The area between B and C is determined by the constant  $k$ .

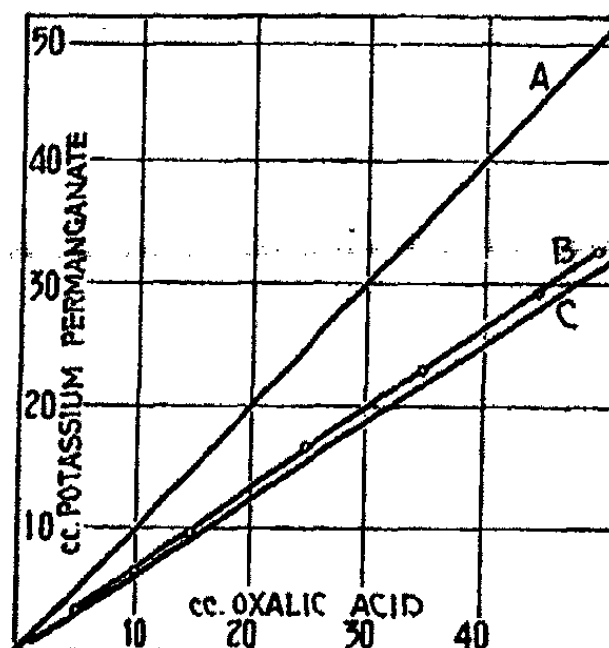


Fig. 1

*Effect of Certain Variables on the Non-acid End-point.*—In making a series of titrations it is necessary to keep constant as many factors as possible if concordant results are to be obtained. Results are affected by the temperature, the total volume of the liquid titrated, the presence of other electrolytes and probably by other factors.

TABLE II  
Effect of Total Volume

Cc 0.2 N oxalic acid	Water added	Cc 0.2 N potassium permanganate to obtain non-acid end-point
50	0	31.83
50	50	32.67
50	150	32.80

In obtaining the results shown in Table I, the temperature was kept nearly constant since the titration was made at the boiling point—though the concentration of the mixture changed during the titration owing to evaporation and to the addition of permanganate, which of course affected the boiling point.

The same solution of potassium permanganate and oxalic acid were used for all the titrations. The total volume of the solution titrated was approximately the same in every case.

The effect of total volume was determined by making three titrations in which every other factor was kept constant.

As the total volume increased (within the limits observed) the excess of permanganate necessary to produce the non-acid end-point increased.

The reaction is affected by the presence of salts of sulphuric, hydrochloric, and acetic acid. The following results were obtained by neutralizing a given volume of the concentrated acid as closely as possible with sodium hydroxide solution using phenolphthalein as an indicator, and then making just acid by adding 1% acetic acid from a burette. Usually only a drop or two of acetic acid was required. To this solution was then added 25 cc of the oxalic acid solution and water to make 100 cc.

TABLE III  
The Effect of Several Neutral Salts on the Reaction

Cc 0.2 N oxalic acid	Other acid added (after neutralizing with sodium hydroxide)	Cc potassium permanganate to give non-acid end-point
25	None	16.34
25	5 cc H <sub>2</sub> SO <sub>4</sub>	15.15
25	5 cc HCl	15.80
25	1 cc HCl	16.26
25	5 cc CH <sub>3</sub> COOH	—

Sodium acetate practically prevents the reaction. Large amounts of sodium sulphate and of sodium chloride decrease the titration values. That is, before the amount of potassium permanganate necessary to produce the non-acid end-point under normal conditions is added, a colloid is precipitated by the high concentration of electrolytes present. When sodium chloride equivalent to only 1 cc of concentrated hydrochloric acid is present, the effect is negligible.

*The Addition of Sulphuric Acid to Complete the Reaction.—*

The effect of several concentrations of sulphuric acid on the reaction was studied. Since the non-acid end-point depends on the diminution of the hydrogen ion concentration, it was thought that possibly the oxidation could be carried to completion by adding the theoretical amount of some other acid necessary to supply the hydrogen ion needed.

Approximately 0.1 N potassium hydroxide and 0.1 N sulphuric acid were prepared. Portions of the hydroxide were titrated with the oxalic acid and like portions were titrated with the sulphuric acid. It was found that 1 cc of the sulphuric acid was equivalent to 0.4836 cc of the oxalic acid (in acidity). Now in tritrating 25 cc of the oxalic solution with permanganate, 0.625 of the total amount present was oxidized and the remaining 0.375 was neutralized by the products of the first reaction. Therefore, the acid equivalent of  $0.375 \times 0.375 \times 25$  cc (=3.52 cc) of oxalic acid would be required to provide for the solution of the products of reaction from the remainder of the original portion of oxalic acid. This is equivalent to  $3.52 \div 0.4836$  cc of the standard sulphuric

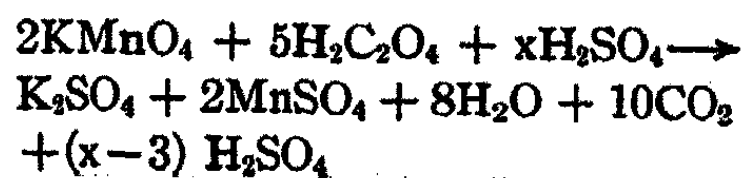
TABLE IV  
The Effect of Small Amounts of Sulphuric Acid

Cc 0.2 oxalic acid	Sulphuric acid present	Cc potassium permanganate
25	Large excess	25.00
25	None	16.25
25	15 cc of approx. 0.1 N	19.77
25	25 cc of approx. 0.1 N	23.87
25	50 cc of approx. 0.1 N	25.00

acid (=7.24 cc). Therefore, 25 cc of the oxalic acid plus 7.24 cc of the sulphuric acid should give the regular acid end-point with permanganate. A number of trials showed this was not the case. Titrations were made with increasing amounts of sulphuric acid, as shown in Table IV. In each



case, water was added to make the total volume titrated 100 cc. Between 25 and 50 cubic centimeters of the sulphuric acid was needed, or approximately 4 to 7 times as much as the theoretical. With 50 cc, the liquid, when the end-point was reached, was not a clear pink but slightly brownish and turbid, resembling the non-acid end-point. The equation for the oxidation of oxalic acid in the presence of sulphuric acid is more properly written:



*Theoretical Considerations.*—When oxalic acid or one of its salts, is titrated with potassium permanganate, there is a question of equilibrium between what may be termed oxidation and acid agencies. The effect of the latter may be divided into solution and precipitation. On the basis of this, the various phases of the reaction that have been studied will be discussed, including (a) the presence of excess sulphuric acid, (b) a limited amount of sulphuric acid, (c) oxalic acid alone (d) the effect of electrolytes, volume, temperature, etc.

*Excess Sulphuric Acid.*—When an excess of this strong acid is present, the manganese compounds formed are dissolved at once, producing a clear nearly colorless solution, and the first drop of permanganate added after the reaction is complete is easily seen. Because of the high hydrogen ion concentration, the reaction is almost independent of temperature, concentration, and the presence of other electrolytes (so long as the latter do not have any oxidizing or reducing power).

*Acetic Acid.*—Even with a large excess of acetic acid, the hydrogen ion concentration is not high, and as the titration proceeds, the concentration is diminishing both by neutralizations and on account of the formation of acetates and the consequent common ion effect. The result is that while the titration can be made and the same values obtained as with sulphuric acid, the temperature must be kept at or near the boiling point, and a longer time is required.

*Limited Amount of Sulphuric Acid.*—The titration starts in the normal manner but the solution of the manganese compound becomes slower and slower as the hydrogen ion concentration diminishes, and a colloid is formed. When this first appears it may be dissolved by continued stirring. Long before the hydrogen ion concentration reaches zero, the precipitating power of the ions present in the mixture (principally the sulphate ions) is sufficient to throw down manganese compounds. Further addition of permanganate produces more of the precipitate according to the so-called Volhard reaction. Various investigators disagree as to the composition of this precipitate. It is probably a hydrous oxide of manganese, and may vary in composition, with the condition under which the precipitation is made. Indeed Orloff<sup>1</sup> says there are thirty-three possible intermediate oxides or combinations of oxides in the reduction of  $Mn_2O_7$  to  $MnO$ .

*Effect of Electrolytes, Volume, and Temperatures.*—When conditions are favorable, the titration of oxalic acid alone with potassium permanganate produces no precipitation until all the oxalic acid has either been oxidized or neutralized. However, changes in volume or temperature may cause a premature precipitation. When neutral electrolytes are added, the precipitating power is increased without increasing the hydrogen ion concentration—consequently the equilibrium is upset and a precipitate forms.

We are now in a position to discuss the constant  $k$ , or why slightly more than the theoretical amount of permanganate is necessary to produce the non-acid end-point. The theoretical amount is required to remove the last of the oxalic acid from the solution, and then a slight excess is required to produce the colloid, which is later precipitated either by heating or by adding still more permanganate. Further, it has been shown that oxidation-reduction reactions in the absence of acids are not instantaneous, and that an excess of one of the reacting substances may be required to drive the reaction to completion.

<sup>1</sup> Zeit. phys. Chem., 80, 230 (1912).

**Summary**

Oxalic acid may be titrated with potassium permanganate without the addition of any other acid. The oxalic acid serves as both reducing agent and as acid, and there are two distinct reactions although they proceed simultaneously. Of 8 equivalents of oxalic acid present, (a) 5 are oxidized by permanganate, and (b) the other 3 equivalents combine with the products of (a). When this point has been reached the further addition of permanganate solution produces a colloidal manganese compound which is precipitated on boiling for a few seconds. The appearance of turbidity followed by a slight permanent precipitate marks the end-point.

The end-point is affected by (a) the temperature at which the titration is made, (b) the concentration and (c) the presence of electrolytes in solution.

When the solution of an oxalate is titrated in the presence of sulphuric acid, the colloid precipitating power of the sulphate ion in a sense acts in opposition to the tendency of the hydrogen ion to keep the products of the reaction in solution. The former is sufficiently powerful to produce a precipitate in the presence of a fairly high concentration of the hydrogen ion. For this reason, the quantity of sulphuric acid actually required is much greater than the theoretical.

*Chicago, Ill.*

## MORDANTS. I

BY WILDER D. BANCROFT

### Introduction

In 1875 Napier<sup>1</sup> wrote: "If the various colouring matters used in dyeing had an affinity for the fibre the process would be very simple: it would only be necessary to make a solution of the dye-drug, and immerse the goods in it to ensure their being dyed. But so far from this being the case, if we except indigo and safflower, there is scarcely a dye-stuff that imparts its own colour to goods; nay, the greater part of the dye-drugs used have so weak an affinity, especially for cotton goods, that they impart no colour sufficiently permanent to deserve the name of a dye. The cause of this is obvious. If, for example, we take a decoction of logwood, the colouring matter is held in solution by the water; by putting a quantity of cotton into this solution the fibres become filled with the coloured solution, but if the cotton has no power to render that colouring matter insoluble, and retain it within its fibres it is plain that, by taking out the cotton and putting it into water, the colouring matter within and upon it will be diffused in the water—in other words, the dye, having no attraction for the fibre, is washed out. This want of affinity makes dyeing sufficiently intricate, and renders it more dependent upon science; indeed, it is only by the nicest arrangement of a few chemical laws that the dyer is enabled to turn to advantage the various colouring matters of which he is in possession. When the dyer finds that there is no affinity between the goods and any colouring substance which is put into his possession, he endeavours to find a substance which has a mutual attraction for the cloth and colouring matter, so that by combining this substance with the cloth, and then passing the cloth through the dyeing solution, the colouring matter combines with the

<sup>1</sup> "A Manual of Dyeing," 186 (1875).

substance which is upon the goods, and constitutes a dye. This third substance used, which acts as a mediator, combining two inimical bodies, is termed a mordant, from the French *mordre*, to bite—from an idea which the old dyers had that these substances bit or opened a passage into the fibres of the cloth, giving access to the colour. And although the theory of their action is now changed, the term is still continued and perhaps further investigation will prove the term not altogether inapplicable.”

In the first English book on dyeing, Bancroft<sup>1</sup> distinguished between substantive and adjective colours.<sup>1</sup> “To me, however, colouring matters seem to fall naturally under two general classes; the first including those matters which, when put into a state of solution, may be fixed with all the permanency of which they are susceptible, and made fully to exhibit their colours in or upon the dyed substance, without the interposition of any earthy or metallic basis; and the second, comprehending all those matters which are incapable of being so fixed, and made to display their proper colours, without the mediation of some such basis. The colours of the first class I shall denominate ‘substantive;’ using the term in the same sense in which it was employed by the great Lord Verulam, as denoting a thing solid by, or depending only upon itself; and colours of the second class I shall call ‘adjective,’ as implying that their lustre and permanency are acquired by their being adjected upon a suitable basis.”

Bancroft’s views on mordants<sup>2</sup> are practically those held many years later by Napier. “Adjective colouring matters are generally soluble, in a great degree at least, by water; though some of them derive their solubility from an intermixture of what has been called ‘extractive’ matter; which being separated in the dyeing process, after the adjective colour has been applied to the dyed substance, their union becomes thereby more intimate and permanent. But in

<sup>1</sup> *Philosophy of Permanent Colours*, 1, 118 (1813).

<sup>2</sup> Bancroft: *Philosophy of Permanent Colours*, 1, 341 (1813).

other respects, adjective colours owe their durability, as well as their lustre, to the interposition some earthy or metallic basis; which, having a considerable attraction, both for the colouring matter and the stuff to be dyed, serves as a bond of union between them, and obviates that disposition to suffer decomposition and decay, which naturally belongs to such colouring matters when uncombined. These earthy and metallic bases, having been commonly employed in a state of solution or combination with acids, were from that circumstance denominated mordants (biters or corrodors) by the French who, indeed, began to employ the term long before anything like a true theory of dying had been conceived; whilst even alum was supposed to act by its sulfuric acid, and not by the pure clay upon which its usefulness depends, and whilst in truth all the other matters called mordants were supposed to be useful only by their solvent or corroding powers; and the term, having been thus employed, has been since adopted in other countries. The ingenious Mr. Henry, of Manchester, has, however, lately objected to it, with great reason, and proposed in its stead to employ the term 'basis,' which seems defective only, inasmuch as it does not express the particular affinity, or power of attraction, manifestly subsisting between these earthy and metallic substances, and the several adjective colouring matters, as well as between the former and the fibres of wool, silk, cotton, etc. I confess, however, that no other more suitable term has occurred to me; and being unwilling to propose new terms, without some cogent reason, I shall some times employ that of mordant as well as that of basis; though not indiscriminately in all cases; since I shall generally use the former to signify earthy and metallic substances when actually dissolved by some acid, alkaline, or other solvent, and when of course they will commonly prove more or less corroding or biting, according to the original meaning of the term. But the denomination of basis will be most frequently used to designate the same earthy and metallic substances, distinctly and separately from any acid or other solvent, when actually fixed in the

pores or fibres of wool, silk, etc., or when it is not intended to notice any property in them, which may more immediately result from their combinations with any particular menstruum. M. Berthollet, indeed, gives the term mordant a much more extensive signification, as meaning all the different chemical agents capable of serving as *intermedia* between the several colouring particles and the stuffs so dyed with them, either for the purpose of assisting their union, or of modifying it. This last effect (of modification) may, however, be produced by a variety of matters besides those which are of the earthy or metallic kinds, and indeed by everything capable, not of fixing, but of merely varying the shades of adjective colouring matters. These, therefore, I think it more proper to designate, not as mordants or bases, but as 'alterants' whose use and application may in this respect be extended to substantive as well as to adjective colours."

A mordant is thus a substance which is adsorbed strongly by the fibre and which adsorbs the dye strongly. If one is a purist, it is necessary to say that adjective colours dye the mordant and not the fiber; but nobody does this because the difference can only be detected by careful microscopic observation.<sup>1</sup>

The word mordant has prevailed over Bancroft's word, basis, so far as the dyeing industry is concerned; but the latter term has survived in the paint trade, where we speak of the carriers for lakes as bases,<sup>2</sup> this having nothing to do with the chemist's use of the word to denote an oxide or hydroxide. In fact a particular precipitated barium sulphate<sup>3</sup> has been given the trade name of Lake Base because it was "of great value as a base upon which to precipitate lakes."

At the present time we distinguish acid and basic mordants the tannins and the so-called oils being the acid mordants<sup>4</sup> while the hydrous oxides of the heavy metals are classed as the

<sup>1</sup> Minajeff: *Zeit. Farben-Ind.*, 6, 233 (1907).

<sup>2</sup> Thorpe: *Dictionary of Applied Chemistry*, 3, 236 (1912).

<sup>3</sup> Toch: "Chemistry and Technology of Paints," 117 (1916).

<sup>4</sup> Knecht, Rawson and Lowenthal: "A Manual of Dyeing," 5 (1910).

basic mordants. This distinction is a comparatively recent one, for the basic mordants used to be considered as practically the only ones.<sup>1</sup>

"All the mordants, with one or two exceptions, are found among the metallic oxides. It may be supposed from this that, as metals are the most numerous class of elements, mordants are also very numerous; it is not so, however. In order that the substance may act as a mordant, it must possess certain properties: it must have an attraction for the colouring matter, so as to form with it an insoluble coloured compound; and it must be held easily in solution in order to enter within the fibre. It may also have an affinity for the fibre, a tendency to unite with it, but this property is not essentially necessary; only the two first properties are so, and they limit the mordants almost wholly to what are termed the insoluble bases—that is, substances which are not by themselves soluble in water.

"The bases or oxides which are in general use as mordants, and which appear to succeed best, are alumina and the oxides of tin and iron; the two first are colourless, and the peroxide of the latter is brown, and imparts to white goods a buff or nankeen colour; which in many cases affects to a considerable extent the colour of the cloth, a circumstance which must also be attended to by the dyer. Indeed, the principal part of all dyeing operations is the proper choice and application of mordants; there being a chemical union between them and the colouring matter, a new substance is formed, not only differing in properties, but differing in colour, from any of the originals, consequently a very little alteration in the strength or quality of a mordant gives a decided alteration in the shade of colour. However, this gives the dyer a much wider field for variety of shades, and at the same time a less number of colouring substances are required; as, for example, logwood alone gives no colour to cotton worthy the name of a dye; yet by the judicious application of a few different kinds of

<sup>1</sup> Napier: "A Manual of Dyeing," 186, 192 (1875).



mordants, all the shades from a French white to a violet, from a lavender to a purple, from a blue to a lilac, and from a slate to a black, are obtained from this substance."

"The property which the fibre possesses of fixing portions of the dye-stuff within its pores will have to be often referred to, as it bears a very important relation to mordants. What are termed astringent substances have a strong action in this way in combining with the fibres of cotton goods. A piece of cotton put into a hot solution of sumach, and remaining in it until cool, there is a quantity of the astringent principle, probably gallic or tannic acid, fixed upon the fibre which no washing will remove. We have seen goods thus treated passed afterwards through all the regular operations of bleaching, and still retaining so much of these substances as was sufficient to impart a black tint on passing them through protosulphate of iron. Hence the astringent matters in many vegetable dyes act a very important part in the dyeing operations. Whether such substances as galls and sumach, which are used only for their astringent principle, may be termed mordants, is a question we need not discuss; but they are essentially necessary for fixing within the fibre such quantities of the metallic base or mordant as are required to give depth and permanency to the colour; and as these astringent matters produce tints with the bases, they give a wider scope for variety of colour. Thus, if we pass a piece of cotton through a solution of protochloride of tin, and then wash it in water, we will have a great quantity of oxide of tin fixed within the fibre by the operation of washing; and by passing this cloth through a decoction of Brazil-wood, and then 'raising' with a little spirits, there is a fine though not permanent, rose-red produced. If we pass the cotton through bichloride of tin, and then wash, there is very little of the oxide of tin fixed; for the bichloride is not decomposed, as the protochloride is, by water. If, then, it is passed through the Brazil-wood in the same manner as the other, a colour of less depth is produced; but if the cloth be previously steeped in sumach, and be then passed through the tin solution, even the bichloride, the astrin-

gent principle of the sumach combines with the tin, and forms an insoluble compound; and there is thus fixed a great quantity of the metallic base within the fibre, which gives the colour with the Brazil-wood, so that, when immersed into the wood decoction, there is obtained a colour of great depth and permanency. But the compound formed between the tin and sumach gives a yellow, and thus peculiar tints of the colour are obtained; instead of having a rose colour, as was obtained without the sumach, a deep rich red, between rose and scarlet, is produced. Thus sumach, galls, etc., are extensively used, in connection with metallic bases, to fix, modify, and impart depth to colours for which these bases are applied. The nature of these astringent substances will be given under the distinctive names of the matters which contain them."

While the oxides of aluminum, tin, and iron were practically the only basic mordants in use in Napier's time, chromic oxide is probably today the most important of all the mordants, unquestionably so for wool. Nearly all possible oxides have been studied at one time or another. Liebermann<sup>1</sup> reports on experiments with the oxides of aluminum, antimony, beryllium, bismuth, cadmium, cerium, chromium, cobalt, copper, iron, lead, manganese, nickel, thorium, tin, uranium, yttrium, zinc, and zirconia. Titania<sup>2</sup> is used as mordant on leather hat-bands. Alumina was the first mordant used, and in the old days the oxides of aluminum and tin were the most important, with iron oxide a poor third because people were interested in obtaining bright colours. Nowadays the oxides of chromium and aluminum are the important ones, with the oxide of iron a fair third and the oxide of tin a poor fourth. The possibility of using other oxides had been considered more than a century ago, for Bancroft<sup>3</sup> says: "It will be ascertained hereafter, by my own particular experiments, that all the metals, properly so called, as far as they have been tried, are capable of attracting adjective colouring

<sup>1</sup> Ber. deutsch. chem. Ges., 35, 1493 (1902).

<sup>2</sup> Barnes: Jour. Soc. Dyers and Colourists, 35, 59 (1919).

<sup>3</sup> Philosophy of Permanent Colours, 1, 392 (1813).

matters in some degree, and of serving as bases to them; and this is also true of most of the earths; though none of them is so efficacious and useful in this way as alumine; indeed this and the oxide of tin, seem to be the only bases suited, by their perfect whiteness, to reflect the rays of light so as to exhibit adjective colours with their utmost lustre and brightness, every other falling short of these in that respect, and almost all of them appearing to sadden or darken the colours which they serve to fix. Probably, the oxides of zinc and antimony do this less than any of the others: the former, however, (zinc) does not appear, by my experiments, capable of giving much stability and permanency to any colour dyed with it."

Until near the end of the fifteenth century the alum used for dyeing in Italy came from the Turks, there being an alum works near Constantinople and a famous one near Smyrna.<sup>1</sup> "About the year 1460, Bartholomew Perdix (by some called Pernix) a Genoese merchant, who had become acquainted with the preparation of alum in Syria, when returning thence to Italy, happened, at the island of Aenaria, now called Ischia or Hiscla to observe large alum stones among the substances which had been thrown up, more than one hundred years before, in consequence of the eruption of a destructive volcano there; and, having calcined some of these stones in a furnace, he extracted from them excellent alum." Pure alum was apparently given the additional appellation in Italy of *rocca* or *roccha*, whence come the French name of *alum de roche* and the English one of roach alum.

A few years after Perdix had begun to produce alum from the stones which he found at Ischia, the famous deposit at Tolfa near Civita Vecchia was discovered by John di Castro. The account of this throws such a light on the trade in the heavy chemicals in those days that it is worth quoting<sup>2</sup> in spite of its having nothing to do with the theory of mordants.

"This John di Castro, being fond of travelling, had re-

<sup>1</sup> Bancroft: *Philosophy of Permanent Colours*, 1, xxxi (1813).

<sup>2</sup> *Ibid.*, 1, xxxiii (1813).

sided some time at Constantinople, and acquired much wealth by dyeing cloth made in Italy, which was transported thither and committed to his care, on account of the abundance of alum in that neighborhood. Having by these means an opportunity of seeing daily the manner in which alum was made, and from what stones, or earth, it was extracted, he soon learned the art. When, by the will of God, that city was taken and plundered, about the year 1455, by Mahomet II, Emperor of the Turks, he lost his whole property; but, happy to have escaped the sword of these cruel people, he returned to Italy, after the assumption of Pius II, to whom he was related, and from whom he obtained, as an indemnification for his losses, the office of commissary-general over all the revenues of the Apostolic Chamber, both within and without the city. While in this situation, he was traversing all the hills and mountains, searching the bowels of the earth; he at length found some alum stones in the neighborhood of Tolfa; and having made experiments by calcining them, he obtained alum, and repairing to the pontiff, said to him: 'I announce to you a victory over the Turk. He draws yearly from the Christians above three hundred thousand pieces of gold, paid to him for the alum with which we dye wool of different colours, because none is found here, but a little at the island of Hiscla, formerly called Aenaria, near Puteoli, and in the cave of Vulcan at Lipari, which having been exhausted by the Romans, is now almost destitute of that substance. I have, however, found seven hills, so abundant in it, that they would be almost sufficient to supply seven worlds. If you will send for workmen sufficient, and cause furnaces to be constructed and the stones to be calcined, you may furnish alum to all Europe; and that gain which the Turks used to acquire by this article being thrown into your hands, will be to him a double loss, etc.' These words of Castro appeared to the pontiff as the mere result of idle dreams. He, however, employed skilful people, who found that the stones really contained alum; but least some deception might have been practised, others were sent to the place where they had been found, who met with abun-

dance of the like kind. Artists, who had been employed in the Turkish mines in Asia, were then brought from Genoa; and these, having closely examined the nature of the place, declared it to be similar to that of the Asiatic mountains, which produce alum; and, shedding tears for joy, they kneeled down three times, worshipping God, and praising his kindness in conferring so valuable a gift on our age. The stones were calcined, and produced alum more beautiful than that of Asia, and superior in quality. Some of it was sent to Venice and to Florence; and being tried, was found to answer beyond expectation. The Genoese first purchased a quantity of it, to the amount of twenty thousand pieces of gold; and Cosmo, of Medicis, for this article laid out afterwards seventy-five thousand. On account of this service, Pius thought Castro worthy of the highest honours, and of a statue, which was erected to him in his own country, with this inscription: 'To John di Castro, the inventor of alum;' and he received, besides, a certain share of the profit; immunities and a share also of the gain, were granted to the two brothers, Lords of Tolfa, in whose land the aluminous mineral has been found. This accession of wealth to the Church of Rome was made, by the divine blessing, under the Pontificate of Pius II; and if it escape, as it ought, the hands of tyrants, and be prudently managed, it may increase; and afford no small assistance to the Roman pontiffs, in supporting the burthens of the Christian religion."

"The wealth which the pope obtained from the discovery and working of the mines of Tolfa, encouraged and produced similar undertakings in other parts of Italy, particularly at Volterra, in the district of Pisa, though their success was greatly obstructed by the obstacles which the pope contrived and employed against them, in order that he might monopolize all the benefits to be derived from the manufacture and sale of alum; of which he raised the price so exorbitantly, that alum procured from the Turks was found much cheaper than that of Tolfa, and, therefore, employed. But to obviate this interference, the pope pretended to devote the revenue produced

by his alum works to the defence of Christianity against the Turks, and menaced all who should act so unchristianly, as to purchase or procure, alum from these infidels, with excommunication; which prohibitions were renewed by several of his successors."

"In England the first alum work was that of Gisborough, in Yorkshire, begun near the end of Queen Elizabeth's reign, upon lands belonging to Sir Thomas Chaloner, who secretly procured workmen from the alum works at Tolfa, no person in England then knowing how to produce it. This seduction of his workmen so enraged the pope, as we are told by Pennant, in his *Tour to Scotland*, that his holiness endeavored to frighten and recall them, by curses, or anathemas, in the very form left us by Ernulphus."

Bancroft<sup>1</sup> states that "this alum continues to be known under the name Roman alum and esteemed above all others; principally because it contains about half as much iron as most other alums: the latter, however, may be rendered equally pure and valuable, by calcining, then dissolving, and afterwards recrystallizing them. Stahl, Newman, Pott, and other eminent Chemists consider alumine as a calcareous earth, and not as being an earth, which it is, *sui generis*, nearly related to clay, but differing from it."

According to Bersch,<sup>2</sup> under the name of Roman alum, "or that of 'cubical alum,' a variety of alum is sold, generally at a rather higher price than ordinary alum from which it is distinguished by its crystalline form. Ordinary alum forms octahedral crystals often the size of a child's head, but cubic alum well-formed cubes. The property of crystallizing in cubes may be imparted to any alum solution by the addition of a little potash.<sup>3</sup> Much so-called Roman alum is made in German works in this way. When this alum contains very little iron, it is quite equal in quality to the best Roman alum, for the higher value of the latter is due entirely to its low con-

<sup>1</sup> *Philosophy of Permanent Colours*, I, xxxv (1813).

<sup>2</sup> "The Manufacture of Mineral and Lake Pigments," 46 (1901).

<sup>3</sup> Cf. Napier: "A Manuel of Dyeing," 120 (1875).

tent of iron. The alum prepared in the province of Naples is still better than Roman alum; it contains less iron."

We are so familiar with metallic aluminum and so accustomed to look upon Sir Humphry Davy's preparation of the alkali metals as one of the great discoveries of the period that it is rather a shock to learn that this view was not shared by all of his contemporaries.<sup>1</sup>

"I have in the course of this work, commonly adopted the language, and with a few exceptions, the principles or explanations of modern chemistry, not as being wholly unobjectionable but as according best with known facts, and being most likely to become parts of a more perfect system, when future discoveries shall have laid a sufficient foundation for the construction of one. I have not, however, been convinced of the expediency of adopting some of the opinions promulgated by Sir Humphry Davy; though I hope and believe, that I am properly disposed to admire his extraordinary talents, and acknowledge the important additions made by him to chemical science. This is not the place to discuss, and, therefore, it would be improper to dispute any of his facts; but I hope it may not be deemed improper for me to mention a few of the objections to which some of his conclusions seem liable.

"He supposes himself to have proved that the fixed alkalies (and several of the earths) are metals combined with oxygene, or, in other words, metallic oxides; and that when the oxygene has been separated by the powerful agency of opposite electricities, from the bases of these alkalies, the latter are reduced, each to its proper metallic state, and though the supposed metallic globules so produced, cannot be retained in this state for a single minute without burning, and again becoming potash and soda, and are besides much lighter than water, he has thought it right to consider and arrange them as metals, under the names of potassium and sodium.<sup>2</sup> He.

<sup>1</sup> Bancroft: *Philosophy of Permanent Colours*, 1, vii (1813).

<sup>2</sup> Gay-Lussac and Thenard have supposed these productions to be compounds of potash and soda with hydrogen (or hydrures), and Curadon has thought them to be compounds of charcoal, or charcoal and hydrogen, with potash and soda.



(Sir H. Davy) admits that 'a considerable degree of specific gravity was formerly considered as an essential character of metallic substances, but (he adds) I have discovered bodies lighter even than water, which agree in all other essential qualities with metals, and which consequently must be arranged with them.' See 'Elements of Chemical Philosophy,' p. 319. How it should follow that bodies which agree with metals in all but one essential character, must be arranged with them, I am unable to conceive: for to my understanding, an opposite inference seems the most natural, and indeed, the only allowable one. But is it true that the bodies in question do really possess all the other characters which are deemed essential to the constitution of a metal? Is not the strong propensity of potassium and sodium to burn instantaneously in the air, and as instantaneously to decompose water, without acquiring in either case, the properties of metallic oxides, at variance with all former ideas of the nature and essential characters of a metal? Even the shining quality of these supposed metals, which more than anything else seems to give them a metallic appearance, belongs equally to petroleum, when diffused upon the surface of water, and to indigo when dissolved for topical application by calico-printers, as is hereafter described. Sir. H. Davy has admitted (p. 321 of his Elements) that 'the common metals, in consequence of their fusibility, malleability, hardness, and durability, have been the most important instruments of the arts;' and that 'the uses of them have been essential to the progress of civilization:' after such an admission, it may, I think, be reasonably asked, why they are to be confounded with matters which have none of these characters?

"Surely, if it be expedient (which I do not perceive) to comprehend things so dissimilar, under one common or general denomination, it would be much more convenient to invent a new name for that purpose, and allow us to designate matters of such high importance as the metals, properly so called, by that which has been so long appropriated to them. To confound, by one appellation, substances so unlike each other,



as those commonly called metals, earths, and salts, must be highly inconvenient for the ordinary purposes of life, as well as for the operations of human intellect; and it must be no small addition to the evils of this confounding, to have it extended even to water, and to that fluid of which our atmosphere chiefly consists, nitrogene; both of which, as a consequence of these doctrines, are to be deemed metallic oxides (i. e., of hydrogen). It cannot, I think, be necessary for the advancement of science that we should thus perplex our language and ideas, and subvert those distinctions which have long regulated the actions and opinions of mankind; and I have, therefore, abstained from these innovations in the following pages. There is, indeed, an additional reason for not considering in this work the alkalies as metallic oxides; which is, that their effects in dyeing are as opposite as possible to those of the oxides of metals, properly so called: and in regard to alumina (or the earth of alum), which is supposed to contain a peculiar metal, called by Sir H. Davy 'aluminum,' I must declare that the evidence of probability of its existence, appears to me much more feeble even than that which regards the supposed metals of the alkaline earths; which last, in my judgment, is far from being sufficient to warrant his arrangement of them in the class, and under the denomination, of metals."

It is worth noting that Bancroft uses the word aluminum and not aluminium. Davy<sup>1</sup> says in one place that if he had succeeded in isolating the metal he was going to call it alumium; but he actually does call it elsewhere<sup>2</sup> aluminum. Graham<sup>3</sup> uses the same spelling, while Silliman<sup>4</sup> writes aluminium though adding that "aluminum would seem preferable, but I adopt the orthography already introduced." The truth of the matter seems to be that aluminum is the proper English spelling, analogous to platinum, stannum, and glucinum, while aluminium is a later and German version.

<sup>1</sup> Collected Works, 5, 122, from Phil. Trans., 1808

<sup>2</sup> Ibid., 4, 262; from "Elements of Chemical" Philosophy, 1812.

<sup>3</sup> "Elements of Inorganic Chemistry," 419 (1858).

<sup>4</sup> Elements of Chemistry, 1, 293 (1830).

The earlier experiments on the mordanting of wool and with aluminum sulphate or with alum do not seem at all in accord with what we now find; but the discrepancy is more apparent than real. According to Bancroft:<sup>1</sup> To impregnate wool or woollen cloth with aluminous basis, it is commonly boiled in water, with from one-fourth to one-sixth of its weight of alum, and from one-twelfth to one-sixteenth of its weight of crude tartar, putting the latter first into the water, and, afterwards, the powdered alum: the heat of the water being gradually raised, is kept at the boiling point for an hour and a half, or two hours, during which the cloth is turned through the boiling liquor on a winch, that the mordant may be equally applied; and being afterwards taken out and drained, it is commonly left until the next day, and then rinsed in clean water, for dyeing. In the early collection of recipes, printed in 1605, and already mentioned, sour bran liquor is commonly directed to be employed in this way with alum; and it seems to have answered the purpose of tartar, which, when it came to be generally used in this way with alum, was supposed by the older dyers to do good by softening and correcting the acrimony of the latter: probably, however, the purposes which it answers, are not yet clearly ascertained; one of them seems to be, that of increasing the solubility of alum, and enabling it more completely and intimately to penetrate the fibres of the wool, with which it moreover enters into a permanent union, and thereby contributes efficaciously to modify, vary, and in some cases to brighten the colours with which it is employed, as will be seen hereafter.

"It was until very lately believed, even by those who had most knowledge of the subject, that woollen cloth boiled in this way, with alum, decomposed the latter, in a considerable degree at least, attaching to itself the alumine, though not without a small portion of the sulphuric acid in combination therewith.<sup>2</sup> Very recently, however, MM. Thenard and Roard

<sup>1</sup> *Philosophy of Permanent Colours*, 1, 384 (1813).

<sup>2</sup> Berthollet, tom. i. p. 80, after saying, that in aluming stuffs the latter decompose the alum, and combine with the alumine, whilst the acid, which held it dissolved, separates and remains in the bath, adds, "Mais il ne faudrait pas conclure de là, qu'aucune portion de l'acide ne reste dans la combinaison de l'étoffe où elle peut avoir quelque influence sur la couleur."

(of whom, the latter is director of the dyeing department at the imperial manufactory of the Gobelins at Paris), appear to have acquired more correct ideas on this point, by a series of experiments, of which they have given a minute statement; in a memoir read at the Physical and Mathematical class at the French National Institute (see *Ann. de Chimie* tom., 74, p. 267 [1810]).

"These experiments were principally made with alum, acetate of alumine, tartar, and the solutions of tin, applied to wool, silk and cotton; and by these, it was fully ascertained that alum and cream of tartar do not decompose each other when dissolved in water, and boiled with wool, (a fact which had, indeed, been previously asserted by Berthollet); that in this boiling, the wool combines with the alum, without decomposing it in any degree,<sup>1</sup> and also with the tartar; that equal parts of alum and tartar would dissolve in two-fifths less of water, than would be required to dissolve them separately.

"They found that wool, as it is commonly cleansed for being alumed, was not deprived of the carbonate of lime naturally combined with it; and that this wool being boiled the usual time, with one-fourth of its weight of alum and one sixteenth of its weight of cream of tartar, rendered the bath or water, troubled or muddy, and produced (as is, indeed,

<sup>1</sup> It was completely ascertained that when wool had been so alumed, the alum employed might be all recovered, partly from the bath or liquor in which the aluming had been performed, and partly from the wool itself, by repeatedly washing the latter in pure boiling water: commonly a dozen separate washings were sufficient to remove completely all the alum which had united itself to the wool; and the alum, so separated, was susceptible of a distinct crystallization, as if it had never been so employed. After the last of these washings, the wool or cloth, so washed, was found to be as incapable of receiving colours by dyeing, as if it had not been so alumed; and, indeed, before the last, it was always found, that the colour attempted to be dyed upon it, was feeble, in proportion to the number of washings which had taken place.

It became evident, therefore, from these experiments, that wool or cloth boiled with alum (and tartar) attached to itself the undecomposed alum only, and that a decomposition of the latter does not take place until the subsequent operation of dyeing, when the affinity of wool, being assisted in the dying vessel, by the affinity of the adjective colouring matter, their co-operation separates the alumine, in a great degree at least, from the sulphuric acid.

commonly observed) a copious white sediment, which being collected, washed, and analysed, was found to consist chiefly of a sulphate of lime, and a saturated sulphate of alumine. That when wool had been properly cleansed, and deprived of its carbonate of lime, no sulphate thereof was found. Such wool or cloth, being boiled in pure distilled water, with the proportions just mentioned of alum and tartar, and the bath or liquor with which the boiling had been performed being carefully evaporated, a residuum was found, consisting of alum, cream of tartar, and a compound, difficultly crystallizable, of tartrate of potash and animal matter. The wool itself, when so boiled, afforded, by repeated washings, alum, and a small quantity of cream of tartar, besides a very sour combination of tartaric acid, alum, and animal matter. As the acid of tartar combines so copiously with wool, MM. Thenard and Roard have inferred, that it ought not to be employed in this way with alum, except for colours which acids contribute to raise and improve: and among such colours they rank those of cochineal, kermes, and madder; but those of weld, logwood, and Brasil wood, not resisting acids as they suppose, wool, intended to be dyed from either of these, ought, as they think, to be alumed, without any addition of tartar. The accuracy of these opinions will be tried by facts when the several colouring matters here mentioned shall claim our particular attention."

Napier<sup>1</sup> quotes the following theory of mordants by M. Dumas:

"Cream of tartar, or bitartrate of potash, constitutes by itself a feeble mordant, but which is very often used in dyeing light woollen stuffs, to which we may wish to give a delicate but brilliant shade. It is also employed in the dyeing of ordinary woollen goods, but here it is associated with alum, sulphate of iron, chloride of tin, etc. Its influence, under these circumstances, consists evidently in determining a double decomposition, from which we have produced a sulphate of potash or

<sup>1</sup> "Manual of Dyeing," 200 (1875).

chloride of potassium, whilst the tartaric acid combines with the alumina, the peroxide of iron, or the oxide of tin. Now it is very probable that the colouring matters remove the alumina, the peroxide of iron, or the oxide of tin, more readily from tartaric than from sulphuric acid. Moreover, the presence of free sulphuric acid would certainly prove injurious, as well to the stuff as to the colouring matter, whilst free tartaric acid can exercise no unfavorable action over them.

"The operation of subjecting wool to the alum mordant is always effected at the boiling point; the mixture used in this process is a compound of alum and of cream of tartar. One of the objects of this addition is to free the bath of the carbonate of lime which the water generally retains in solution, and which, acting on the alum, would determine its partial decomposition by producing an insoluble subsulphate of alumina and potash, and this accumulating on the stuff, and becoming unequally fixed upon its surface, would lead to stains or blotches on passing the material through the dye-bath. But, independently of the above effect, which might be produced by any acid, cream of tartar appears to be capable of effecting a further object, by inducing a double decomposition, which transforms the alum into a tartrate of alumina. However this may be, after one or two hours' boiling in the alum-bath, the cloth which should be constantly agitated so as to cause a more equal application of the mordant, is withdrawn from the copper, and, after thoroughly draining, it should be put aside for two or three days, when we wish to dye it with any full-bodied colour. Experience has proved that this repose after the use of the mordant greatly favours the union of the latter with the stuff. In applying the tin mordants we also make use of cream of tartar. It is, moreover, an indispensable addition where we desire to fix the salts of iron previously to dyeing in black.

"Woolen cloth, on being dipped into a cold aqueous solution of alum, appropriates to itself a part of this salt, but without undergoing any very sensible alteration. MM. Thenard and Roard have, indeed, proved that cloth, when thus

treated by a cold solution of alum, gives up this salt to boiling water, and that, after a few washings performed at the boiling point, it will have parted with the whole of the alum which it had received in the cold bath. When, however, cloth is boiled in a solution of alum, it yields to this liquid a portion of its organic matter, which becomes dissolved; but at the same time it absorbs an equal amount of the alum.

"We have now merely to shew the action which wool undergoes when brought into contact with alum and cream of tartar at one and the same time. It is very possible that there may be in this case a simultaneous fixation of alum, as well as of the double tartrate of alumina and potash, and of tartaric acid. The presence of alum in the cloth when taken from the boiling solution is very evident; that of the tartrate of alumina and potash and of free tartaric acid is only presumable.

"Silk, in like manner, unites itself with alum when placed in a cold solution of this salt, and afterwards parts with it to boiling water; it may be reproduced from this liquor by evaporation. The action of silk on acetate of alumina is identical with that of wool. It at first absorbs this salt in its pure form; then, by desiccation it loses some acetic acid, and retains a mixture of the acetate together with alumina in its free state; it gives up a further portion of this acetate to boiling water.

"The alum mordant is always used cold with silk: if employed hot, it would destroy its lustre. The bath should not contain cream of tartar when it is intended for this material; on the contrary, we here have recourse to a variety of alum of as neutral a character as possible.

"The theory of the action of mordants is connected in the closest manner with that of dyeing. It may, in fact, be viewed under two very different aspects. Sometimes we admit that there exists a true combination between the stuff and the colouring matter—a combination which can only be determined by a veritable affinity between these two bodies, and which will present a condition analogous to that which occurs in all chemical combinations—that is to say, a state of saturation,

beyond which the union of these bodies becomes of a very unstable character; at other times, on the contrary we regard the dyeing of stuffs as produced by a nearly mechanical phenomenon, by virtue of which the colouring matters become imprisoned in the meshes of the organic filaments contained in the material to be dyed. This latter opinion is evidently the better founded. It approximates the theory of dyeing to some analogous phenomena which we find manifested by animal charcoal on coloured solutions; for, as the animal charcoal seizes upon the colouring matters contained in an aqueous solution, and renders them insoluble by fixing them in a purely mechanical manner within its own pores: so may the wool, the silk, and the cotton, appropriate the colouring matters held in solution, and, by fixing them in their pores, render them more or less insoluble to water. Experience, however, shews that dyeing thus produced is wanting both in intensity and in fixity—two qualities which it derives by the previous application of a mordant. Now, we can readily see that the mordants themselves may become fixed in the tissues by similar causes to those which determine the fixation of the colouring matters by animal charcoal. We know, in fact, that this latter body possesses the property of removing from water not only the colouring matters, but also certain salts. There will, therefore, be no difficulty in imagining that silk, wool, and cotton may, in their character of porous bodies, purely and simply seize upon the alum, and that this salt, when once imprisoned in the meshes of the tissue, may subsequently react upon the colouring matter according as this latter, in its turn, penetrates the interior of these materials.

"We may then refer the phenomena of absorption, which characterise the fixation of the mordants and the penetration of the colouring principles into the tissues, to the same cause as that which determines the action of animal charcoal on certain soluble salts and colouring matters. But if one of these stuffs be impregnated with alum and then dipped in a bath of soluble colouring matter, it acquires a very deep tint, which appears to be essentially produced by a kind of lac,



formed by means of the colouring matter and the base of the mordant. On the other hand, in a great number of cases, the mixture of the above mordant with the dye-bath fails in producing an insoluble precipitate. Thus, when we mix together alum and a decoction of Brazil-wood, no precipitate is formed, and, to obtain a lac from this liquor, we are obliged to add some alkali or alkaline carbonate, such as ammonia; in a word, we must render the alumina free. While admitting, then, in accordance with the experiments of MM. Thenard and Roard, that the stuffs fix the alum in its natural state, we must acknowledge, at the same time, that, by some special action, the tissue subsequently determines the union of the base of the mordant with the colouring matter. This special action is equivalent to that of the alkali.

“Now, it is certain that the above-mentioned stuffs possess in a high degree the faculty of seizing upon the insoluble colouring matters when these are presented to them in their nascent state. It is thus that cotton becomes dyed of a rose colour in a liquor which contains carthamic acid in suspension, arising from the decomposition of a carthamate of soda by an acid. In like manner we find wool acquires a black colour, when placed in a boiling solution of a salt of iron and tannin, by attracting to itself the black precipitate resulting from their admixture. Consequently, although the dyer generally endeavors to produce the insoluble compound, on which the colouring stuff depends, within the very pores of the tissue, still we may affirm that, in many cases, the cloth or other material, when placed in presence of the nascent precipitate, has the property of seizing upon it, and thus acquiring a shade of greater or less intensity.

“It is to this property (which is due to some hitherto undetermined cause) that we must undoubtedly refer the reaction which takes place between the alum and the soluble colouring matters, as well as some of these more mysterious phenomena which are manifested in dyeing. How else, indeed, are we to account for the fact that wool so readily takes a scarlet colour, while cotton and silk are unable to fix it? How



explain the cause of wool so easily appropriating the black precipitate formed by tannin and the salts of iron, while silk, under the same circumstances, acquires a black colour only by great trouble and expense? How, in one word, can we understand why certain colours should fix themselves better on certain materials than on others, unless it be by virtue of some special action, wrongly designated by the name of affinity, but which does not the less constitute a force, or rather a consequence of diverse forces of which we must take full account during the operations of dyeing? To confound, in fact, a chemical affinity properly so called, such as is evidenced in ordinary chemical combinations when produced in definite proportions, with the phenomena of dyeing, is certainly to mix together two very distinct ideas. The union of silk with Prussian blue, or of wool with indigo, is quite a different thing to the combination of sulphur with lead. But to consider the tissue as a simple filter, capable of retaining in its pores certain principles, and of receiving from them peculiar colours, is to go equally far in an opposite direction; nor would this supposition at all explain the mode in which the coloured lac is formed in most of the operations of dyeing, operations which are effected by an aluminous salt and a colouring bath, altogether incapable of producing any lac, except by the addition of an alkali for the purpose of setting the alumina at liberty, or of a stuff which has the power of taking up the lac, as quickly as it is formed.

“Among the reasons which induce us to regard the insoluble colouring matters and the stuffs as capable of uniting together by virtue of some special force, we must mention the facts elicited by the recent experiments of M. Chevreul, who has found that the stuffs and colours, when once united form products which are endowed with properties differing, according to the nature of the stuff, in the same given colour. The properties of the dyeing matter are, then, greatly modified by the peculiar action of the tissue on the dye. Numerous examples place the truth of this assertion beyond all question. It becomes, therefore, perfectly clear that it is only by an

attentive and systematic study of the specific properties of the stuffs, in their relation to the various dyeing matters which we may desire to fix upon them, that we can hope to direct the future progress of the art of dyeing."

On the other hand<sup>1</sup> "Chevreul denied that the alum could be washed out by water, and Bolby stated that actual decomposition took place; a basic salt being deposited on the fibre, leaving the solution more acid."

Knecht, Rawson and Loewenthal<sup>2</sup> consider that "the mordanting of wool and silk appears to be analogous to the dyeing of these fibres, and to depend upon their acid and basic properties. Thus, wool boiled with a solution of aluminum sulphate fixes both the acid and the basic constituents of the salt; but, being possessed of more pronounced acid than basic properties, it absorbs the basic constituents more energetically than the acid one, and some free acid is left in the solution. By subsequent treatment with boiling water, more acid is extracted, and the alumina becomes more firmly combined with the substance of the fibre. It is noteworthy that only such salts which contain the acid and basic constituents in a comparatively loose state of combination are absorbed by the wool fibre. Thus, whereas the sulphates of aluminum, iron, chromium, and copper are readily taken up from the boiling solution by the wool fibre, sodium sulphate or sodium chloride are not taken up at all. Chromic acid, on the other hand, is readily taken up by wool, and, like the acetates of the heavy metals, is precipitated from its aqueous solution by lanuginic acid."

Thenard and Roard believed that aluminum sulphate or alum is adsorbed by wool unchanged and that the elimination of the sulphate radical takes place when the mordanted fibre is dyed. Most of the work since then has been to the effect that wool does decompose aluminum sulphate more or less. If the recent writers had read the original paper by Thenard and Roard, there would have been no discrepancy to explain.

<sup>1</sup> Dreaper: "The Chemistry and Physics of Dyeing," 61 (1906).

<sup>2</sup> "A Manual of Dyeing," 20 (1910).

Havrez<sup>1</sup> showed that when relatively concentrated solutions of alum are used in mordanting wool, the mordant washes out readily and the wool is not dyed so deeply as when more dilute solutions of alum are used. He recommends not going above ten percent alum, referred to the amount of wool. It has been found by von Georgievics<sup>2</sup> that from relatively dilute solutions of alum, more alumina than sulphate is taken up by wool while the reverse is true for relatively concentrated solutions. At twenty-four percent alum, referred to wool, the two are taken up in equivalent quantities. Thenard and Roard used twenty-five percent alum, referred to the wool, so that their results are absolutely in accord with the most modern data. The whole trouble arose from their using a more concentrated solution of alum than is now customary.

*Cornell University*

---

<sup>1</sup> Dinger's Polytech. Jour., 205, 491 (1872).

<sup>2</sup> Jour. Soc. Chem. Ind., 14, 653 (1895).

## THE RELATION BETWEEN LIGHT-ABSORPTION AND LIGHT-SCATTERING FOR LIQUIDS\*

BY W. H. MARTIN

Water is well known to exercise selective absorption on light in the yellow and red part of the spectrum and also in the extreme ultra-violet. Between 2000 Å and 5000 Å however is a region in which water is extremely transparent. If now it be assumed that in this region of very slight absorption all the energy lost by the primary wave appears as scattered light, we are led at once to a value for the ratio of incident to scattered light for water or other liquid.

Such an assumption has been made by various authors. Lacking until recently any measurements of the light scattered by liquids, they have used in their stead absorption measurements for testing out various light-scattering formulas. It is the purpose of this article to review somewhat critically the measurements of absorption of water previously made and to present some measurements on dust-free water and benzene made in this laboratory.

Hufner and Albrecht,<sup>1</sup> Ewan,<sup>2</sup> and Aschkinass<sup>3</sup> all give results which are not at all in good agreement in the region of the spectrum with which we are concerned. Kreuzler<sup>4</sup> examined the transparency of water in the ultra-violet and violet region. It is clear that, although all the above workers carefully distilled the water, they did so in the presence of air and must certainly have had a great deal of dust in the water.

Fowle<sup>5</sup> has used the results of these experimenters to evaluate  $N$ , the number of molecules of water per cubic centi-

\* Received April 21.

<sup>1</sup> Wied. Ann., 42, 10 (1891).

<sup>2</sup> Proc. Roy. Soc., 57, 127 (1894).

<sup>3</sup> Wied. Ann., 55, 401 (1895).

<sup>4</sup> Ann. Phys., [4] 6, 412 (1901).

<sup>5</sup> Smith: Mis. Coll., 69, No. 3 (1918).

metre, by means of the Rayleigh formula:<sup>1</sup>

$$\epsilon = \frac{32 \pi^3 (\mu - 1)^2}{3N\lambda^4}$$

and has obtained a value of  $N$  in most excellent agreement with the accepted value. The author believes this agreement to be entirely fortuitous, and has shown in an earlier paper<sup>2</sup> that the measured value of the light scattered by water is only about one tenth of that used by Fowle in his calculation. Moreover Rayleigh distinctly states that his formula is not quantitatively applicable to liquids.

C. V. Raman<sup>3</sup> has recently and very successfully applied the Einstein-Smoluchowski<sup>4</sup> relation

$$\epsilon = \frac{8\pi^3}{27} RT\beta_0 \frac{(\mu^2 - 1)^2 (\mu^2 + 2)^2}{N\lambda^4}$$

to the scattering of light by liquids, and has shown that the observed values for several liquids are in excellent agreement with those calculated from the above relation. This equation is evidently more general than the Rayleigh equation since:

- (1) it reduces to the Rayleigh equation for gases which obey Boyle's law;
- (2) it fits fairly well the observed results for liquids;
- (3) it accounts for the remarkable opalescence of liquids near the critical conditions.

Raman has assumed that all the light absorbed by water in the neighborhood of 5000 Å is scattered. He has favored the absorption measurements of Aufsess<sup>5</sup> who took considerable care to free the water from motes, following Spring's method of removing the dust by precipitation of gelatinous precipitates in the water, and no doubt removed all the dust.

The extinction-coefficients measured by Aufsess are much smaller than those of other experimenters—in fact he could

<sup>1</sup> Phil. Mag., 47, 375 (1899).

<sup>2</sup> Martin and Lehrman: Jour. Phys. Chem., 26, 75 (1922).

<sup>3</sup> "Molecular Diffraction of Light, University of Calcutta," 1922. See also Proc. Roy. Soc., 101A, 64 (1922).

<sup>4</sup> Ann. Phys., [4] 33, 1275 (1910).

<sup>5</sup> Ibid., [4] 13, 678 (1904).

detect no absorption for "optically empty" water for wavelengths shorter than 5200 Å. The reason for this is apparent however on reviewing his method. He passed the light through a tube 5.5 metres long and compared the emergent light with a standard. By filling the tube first with air and then with water he found the absorption due to the water. Regarding the reflection of the glass plates at the end of the water-tube he says: "The reflection on the passage of the light to a different medium had, as I persuaded myself, no appreciable influence on the measurement."

Now it is well known that for perpendicular incidence the fraction of light reflected is approximately  $\left(\frac{\mu - 1}{\mu + 1}\right)^2$ ,

which for an air-glass surface is four percent, whereas for a water-glass surface it is negligibly small. Therefore emptying out water from the tube is equivalent to decreasing the intensity by about eight percent. Presuming that he used glass of refractive index 1.5, I have recalculated his results and found that they are in fair agreement with the results given later in this paper.

Since the matter of the absorption of water has been so much in dispute, and is of considerable interest to those concerned with the theory of light scattering, some measurements have been made with water carefully freed of dust.

#### **Measurement of the Absorption of Light by Water**

The water used in the measurements was contained in a pyrex-glass tube 90 cm long and 2.5 cm in diameter. Optically flat end-plates of pyrex glass were sealed into the tube by the method described in a former paper,<sup>1</sup> and the water was rendered free from dust by the method of distillation in vacuum without ebullition. The source of light was a Cooper-Hewitt mercury lamp and the three lines 4358, 5461 and 5780 were isolated by Wratten light-filters placed in front of the observer's eye. Two pieces of white paper A and B, illumi-

<sup>1</sup> Jour. Phys. Chem., 26, 75 (1922).

nated by the mercury lamp were seen side by side through a Lummer-Brodhun cube. The paper B was seen through the tube of water, and the paper A was made to match it in intensity by adjustment of an optical wedge. The tube of water was then replaced by two pieces of pyrex glass cut from the same piece as the end-plates of the tube and having a thin film of water between them. Any loss of light due to reflection at the ends of the tube was thus compensated for. From the two readings of the wedge with the tube in place and with the tube replaced by the reflection-compensator the absorption of the water is given. A telescope was used in making the photometric comparison and several diaphragms were so placed that the field was limited as desired and all parasite light was excluded.

The optical wedge used, though supposedly a good neutral grey, was found to exercise some selective absorption and was calibrated for the three wave-lengths used by comparison with a whirling disc with variable sector.

The actual absorption was very small so that the extinction-coefficients  $\epsilon$ , given below, are subject to considerable error. The probable error is as great as 25 percent for the blue line 4358 Å, and less for the other lines. The blue line is particularly difficult to measure since there is apparently no light filter obtainable which is transparent to this line and quite opaque to the other mercury lines. On the other hand very transparent monochromatic filters are obtainable for 5461 Å and 5780 Å.

The results of the measurements of the coefficients of extinction per centimetre of water are given below.  $\epsilon$  is defined by the relation

$$\epsilon = -\frac{1}{d} \log_e \frac{I}{I_0}$$

$d$  is the length of the column of water in centimetres.  $\frac{I}{I_0}$  is the ratio of the intensity of light transmitted by water to that which was transmitted by air. (The slight absorption

of the air was neglected, the laboratory being rather isolated and the air fairly dust-free.)

The same experiments were repeated with ordinary laboratory distilled water and with dust-free benzene prepared by distillation in vacuum.

Wave-length	$\epsilon$ Ordinary dis- tilled water	$\epsilon$ Optically empty water	$\epsilon$ Ewan's results	$\epsilon$ Dust-free benzene
4358Å	.00087	.00012	.00042	.00056
5461	.00072	.00034	.00051	.00024
5780	.00095	.00064	.00090	.00045

It appears from the table that the dust-free water prepared by the method of distillation in vacuum in pyrex glass (an extremely insoluble glass) is much more transparent than the water used by Ewan. Aufsess is the only experimenter whose results are lower than ours, and the reason for this seeming discrepancy has been suggested above.

#### The Relation of Absorption to Scattering

Recently Martin and Lehrman have measured the light scattered by water. Let us then consider the extinction-coefficient  $\epsilon$  as consisting of two parts  $\epsilon_1$  and  $\epsilon_2$ ,  $\epsilon_1$  being that part of  $\epsilon$  accounted for by the scattering and  $\epsilon_2$  the remainder.

The ratio  $\frac{Ir^2}{EV}$  for  $\lambda$  4358 Å is known.

$I$  is the intensity of the scattered light at a distance,  $r$ , in a direction perpendicular to that of the exciting beam,

$E$  the intensity of the exciting beam,

$V$  the volume of liquid under observation.

Since the intensity of the scattered light varies inversely as the fourth power of the wave-length, we can find this ratio for any wave-length. By summing all the light scattered in every direction, that is, by integrating the scattered light over a sphere, it follows that

$$\epsilon_1 = \frac{16\pi}{3} \frac{Ir^2}{EV}$$



## For dust-free water

$\lambda$	$\frac{I_r^2}{E_V}$ (measured)	$\epsilon_1$	$\epsilon$ (measured)	$\epsilon_2 = \epsilon - \epsilon_1$
4358	$1.77 \times 10^{-6}$	$3.0 \times 10^{-6}$	$1.2 \times 10^{-4}$	$0.9 \times 10^{-4}$
5461	$7.2 \times 10^{-7}$	$1.2 \times 10^{-6}$	$3.4 \times 10^{-4}$	$3.3 \times 10^{-4}$
5780	$5.7 \times 10^{-7}$	$9.6 \times 10^{-6}$	$6.4 \times 10^{-4}$	$6.3 \times 10^{-4}$

## For dust-free benzene

4358	$2.6 \times 10^{-6}$	$4.4 \times 10^{-4}$	$5.6 \times 10^{-4}$	$1.2 \times 10^{-4}$
5461	$1.1 \times 10^{-6}$	$1.8 \times 10^{-4}$	$2.4 \times 10^{-4}$	$0.6 \times 10^{-4}$
5780	$8.4 \times 10^{-6}$	$1.4 \times 10^{-4}$	$4.5 \times 10^{-4}$	$3.1 \times 10^{-4}$

4358 Å lies in the region where it has been assumed that all the absorption is due to scattering. How far this assumption is from the truth appears from the above table. Of light of this wave-length absorbed by water only one-fourth is scattered. We presume the rest of the absorbed light goes to heat up the water. The absorption is much greater towards the red—all experimenters agree that considerable selective absorption is met with beyond 5000 Å.

In benzene we have a liquid which for  $\lambda$  4358 and  $\lambda$  5461 scatters almost three-fourths of the light which it absorbs.

It would appear then to be very unsafe to draw conclusions regarding the light scattered by liquids from absorption experiments. Possibly some hypotheses might be made by which the scattered radiation might be related to the total absorption.

#### Summary

The transparency of dust-free water and benzene has been measured for three wave-lengths of light.

The absorption of the dust-free water is considerably less than that found by other experimenters.

The absorption is however still much too great to be accounted for by scattering alone.

Some conclusions regarding light-scattering, made by various authors who based their calculations on absorption measurements, are discussed.

*Chemical Laboratory  
University of Toronto  
April 1922*

### EFFECT OF GRINDING UPON THE APPARENT DENSITY OF LEAD OXIDES

BY O. W. BROWN, S. V. COOK AND J. C. WARNER

The apparent density of lead oxides is recognized as an important factor in their use in the manufacture of storage battery plates. It has been noted in a previous article by Brown and Nees<sup>1</sup> that grinding in a pebble mill has an effect on the apparent density of lead oxides. An oxide which is worthless for use in the manufacture of plates, if ground in a pebble mill under such conditions that its apparent density is increased, can be used in the production of very satisfactory storage battery plates.

The influence of grinding is not the same upon all oxides. Coarse crystalline oxides, on grinding, at first show a decrease in apparent density, but with further grinding again show a greater apparent density. A light amorphous oxide steadily increases in apparent density when subjected to grinding in a pebble mill.

In this investigation, the Abbe Trojan Mill was used for the grinding. The outside measurements of the porcelain jar were 8.75 by 9.75 inches. The flint pebbles ranged approximately, from one-half to one inch in diameter, and had a combined weight of 1,033 grams. The mill was

adjusted so as to revolve 50 times a minute. In order to obtain equal grinding in all parts of the load, the mill was stopped every two hours and the contents scraped down from

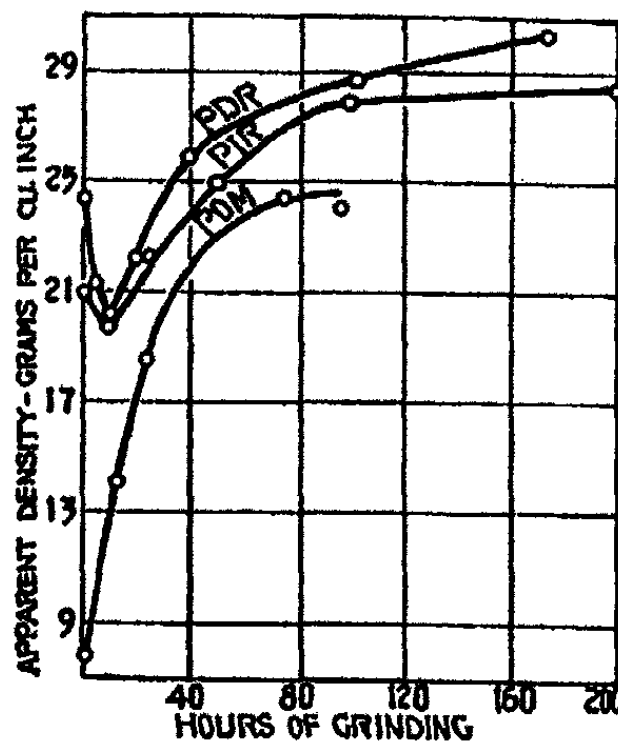


Fig. 1

<sup>1</sup> Jour. Ind. Eng. Chem., 4, Dec. 1912.

the walls of the porcelain jar with an aluminum spoon. The load consisted of about 1800 grams of the oxide except when an extremely light oxide was being ground.

The apparent density of the oxides was determined before grinding and after various intervals of grinding. The Scott Volumeter was used in all apparent density determinations. The results obtained were plotted using hours as abscissae and grams per cubic inch as ordinates. The lead oxides used in this investigation were obtained through the courtesy of the Picher Lead Co.

The first oxide investigated was a red lead (Sample P. D. R.) which, by microscopic examination, was shown to be of a coarse crystalline nature. It was made from yellow litharge and had an apparent density of 24.34 grams per cubic inch before grinding. The results of experiments showing the effect of grinding on the apparent density of this oxide are given in Table I.

TABLE I  
Sample P. D. R.

Hours of grinding	Apparent density grams per cubic inch
0	24.34
5	21.33
10	20.10
20	22.22
40	25.88
102	28.77
173	30.45
234	31.68

The results from Table I are shown graphically in the accompanying figure.

From the results of these experiments, it can be seen that the apparent density of the oxide first decreases with grinding and passes through a minimum after ten hours. Further grinding causes a steady increase in apparent density until a practically constant value is reached after 234 hours.

The next oxide (Sample P. I. R.) subjected to grinding

was a crystalline oxide made from "red" litharge. Its apparent density, before grinding, was 20.96 grams per cubic inch. The effect of grinding upon the apparent density of this oxide is shown by the results of the experiments given in Table II.

TABLE II  
Sample P. I. R.

Hours of grinding	Apparent density grams per cubic inch
0	20.96
5	21.71*
10	19.77
25	22.33
50	25.01
100	27.95
200	28.52

From the results in Table II, it is evident that the apparent density of this oxide was affected by grinding in a manner very similar to Sample P. D. R. A minimum apparent density was obtained after 10 hours of grinding. Further grinding caused a regular increase in apparent density as the period of grinding was lengthened up to between 100 and 200 hours, after which, grinding had practically no effect upon the apparent density of the oxide.

The third oxide (Picher Orange Mineral) was a very light amorphous oxide made from "sublimed" litharge. Its ap-

TABLE III  
Picher Orange Mineral.

Hours of grinding	Apparent density grams per cubic inch
0	7.81
13	14.15
24	18.53
74	24.52
96	24.12

\*This value is probably too high due to excessive packing of the oxide when falling through the volumeter and is not plotted on the curve by which the results from this table are graphically shown.

parent density, before grinding, was 7.81 grams per cubic inch. The results of experiments showing the effect of grinding upon the apparent density of this oxide are given in Table III.

The data from this table are also shown graphically in the figure. The light amorphous oxide, used in these experiments does not pass through a minimum apparent density upon grinding as the heavy crystalline oxides do, but shows a regular increase in apparent density until a practically constant value is reached with between 74 and 96 hours of grinding.

The apparent densities of the oxides, before grinding and after various periods of grinding were also determined in a packed condition by the use of a jolting machine. Under these conditions, the apparent densities of the oxides show a similar variation upon grinding, but the results obtained are not in all cases as consistent as the results obtained by the use of the Scott Volumeter.

#### Conclusions

The apparent density of a heavy crystalline oxide, first becomes less upon grinding, but with further grinding increases.

After the minimum point is reached, the apparent density of a lead oxide increases rapidly at first, but gradually approaches a constant value.

The apparent density of a light amorphous oxide increases with grinding from the start.

*Laboratory of Physical Chemistry,  
Indiana University  
Bloomington, Indiana*

# THE FORMATION OF A WATER-IN-OIL TYPE EMULSION BY THE CONCENTRATION OF THE OIL PHASE

BY RABINDRA PRASAD SANYAL AND  
SHRIDHAR SARVOTTAM JOSHI

Newman's results obtained in the laboratory of Bancroft<sup>1</sup> seem to throw doubt on the formation of a Water-in-Oil Type Emulsion by the mere increase of the Oil Phase. There is however some evidence in favour of the possibilities of the formation of both the types by changing the volume ratio of the phases in the experiments of Robertson<sup>2</sup> and in the more recent pronouncements of Roon and Oesper<sup>3</sup> from experience in pharmaceutical chemistry. Bhatnagar<sup>4</sup> has also shown that in very low concentrations of the emulsifying agents, the phase ratio alone can determine the formation of one type or the other in case of viscous oils like B. P. paraffin and olive oil and not in the case of light oils like kerosene. These observations have been doubted by Bancroft.<sup>5</sup> Many cases of the formation of Water-in-Oil emulsion by churning an excess of oil with water are known to chemists interested in the Industry of Paint and Margarine. It was therefore considered desirable to investigate the conditions governing the formation of type by merely changing the volume ratio of the two phases.

## Experimental

The experiments were performed in wide-mouthed test tubes; varying amounts of the oil and soap solutions were used, the total volume of the two liquids being always 20 cc. The soap used was a pure sample of sodium oleate prepared in this laboratory from Merck's pure chemicals. The oils tried

<sup>1</sup> Jour. Phys. Chem., 18, 34 (1914).

<sup>2</sup> Koll. Zeit., 7, 7 (1910).

<sup>3</sup> Jour. Ind. Eng. Chem., 9, 156 (1917).

<sup>4</sup> Jour. Chem. Soc., 117, 542 (1920).

<sup>5</sup> Cf. Clayton: Nature, 108, 586 (1921).

were castor oil, olive oil and benzene. The emulsions were examined for type by the Briggs' Drop method. The creaming of an emulsion is not considered as instability. All emulsions in which the density of the two phases are different must cream sooner or later. An emulsion which separates into three layers namely water, oil and emulsifying agent layers, is considered unstable. In the creaming of a water-in-oil emulsion, soap is found to be with the oil phase, in the case of oil-in-water with the water phase. The emulsions have been observed for stability for at least twenty-four hours. The results are shown in Tables I-IX.

### Results

TABLE I  
Concentration of Sodium Oleate Solution 0.02%  
Olive Oil

No. of tubes	Amount of soap soln., cc	Amount of oil, cc	Type	Remarks
1	1	19	Water in Oil	Stable
2	2	18	Water in Oil	Stable
3	3	17	Water in Oil	Stable
4	5	15	Water in Oil	Stable
5	8	12	Oil in Water	Stable & Creams
6	10	10	Oil in Water	Foams & Creams
7	15	5	Oil in Water	Foams & Creams

TABLE II  
Concentration of Sodium Oleate Solution 0.05%  
Olive Oil

No. of tubes	Amount of soap soln., cc	Amount of oil, cc	Type	Remarks
1	1	19	Water in Oil	Stable
2	2	18	Water in Oil	Stable
3	3	17	Water in Oil	Stable
4	5	15	Water in Oil	Stable
5	8	12	Oil in Water	Stable
6	10	10	Oil in Water	Creams & Foams
7	15	5	Oil in Water	Creams & Foams

**TABLE III**  
Concentration of Sodium Oleate Solution 0.075%  
Olive Oil

No. of tubes	Amount of soap soln., cc	Amount of oil cc	Type	Remarks
1	1	19	Water in Oil	Stable
2	2	18	Water in Oil	Stable
3	3	17	Water in Oil	Stable
4	5	15	Water in Oil	Stable
5	8	12	Oil in Water	Unstable
6	10	10	Oil in Water	Creams
7	15	5	Oil in Water	Creams & Foams

**TABLE IV**  
Concentration of Sodium Oleate Solution 0.1%  
Olive Oil

No. of tubes	Amount of soap soln., cc	Amount of oil cc	Type	Remarks
1	1	19	Water in Oil	Stable
2	2	18	Water in Oil	Stable
3	3	17	Water in Oil	Stable
4	5	15	Water in Oil	Stable
5	8	12	Oil in Water	Stable
6	10	10	Oil in Water	Creams & Foams
7	15	5	Oil in Water	Creams & Foams

**TABLE V**  
Concentration of Sodium Oleate Solution 0.5%  
Olive Oil

No. of tubes	Amount of soap soln., cc	Amount of oil cc	Type	Remarks
1	1	19	Water in Oil	Stable
2	2	18	Water in Oil	Stable
3	3	17	Water in Oil	Stable
4	3	15	Oil in Water	Stable
5	5	15	Oil in Water	Stable



TABLE VI  
Concentration of Sodium Oleate Solution 0.75%  
Olive Oil

No. of tubes	Amount of soap soln., cc	Amount of oil cc	Type	Remarks
1	1	19	Water in Oil	Stable
2	2	18	Water in Oil	Stable
3	3	17	Oil in Water	Stable

TABLE VII  
Concentration of Sodium Oleate Solution 1.0%  
Olive Oil

No. of tubes	Amount of soap soln., cc	Amount of oil cc	Type	Remarks
1	1	19	Water in Oil	Doubtful
2	2	18	Inversion Point	Unstable
3	3	17	Oil in Water	Stable
4	5	15	Oil in Water	Stable

Similar results were obtained with castor oil. The emulsions of the Water-in-Oil type were of increased stability in this case.

Two typical results are appended below:

TABLE VIII  
Concentration of Sodium Oleate Solution 0.1%  
Castor Oil

No. of tubes	Amount of soap soln., cc	Amount of oil cc	Type	Remarks
1	1	19	Water in Oil	Stable
2	2	18	Water in Oil	Stable
3	3	17	Water in Oil	Stable
4	5	15	Water in Oil	Stable
5	8	12	Oil in Water	Stable
6	10	10	Oil in Water	Creamed & Foamed

TABLE IX  
Concentration of Sodium Oleate Solution 0.2%  
Castor Oil

No. of tubes	Amount of soap soln., cc	Amount of oil cc	Type	Remarks
1	1	19	Water in Oil	Stable
2	2	18	Water in Oil	Stable
3	3	17	Water in Oil	Stable
4	5	15	Oil in Water	Stable
5	10	12	Oil in Water	Creamed & Foamed
6	15	10	Oil in Water	Creamed & Foamed

The Water-in-Oil type emulsions were unstable with Benzene. The Oil-in-Water type was formed when soap solutions of concentration about 1% were used.

#### Discussion of Results

From the results shown in Tables I-IX, it is evident that the Water-in-Oil type emulsion can be formed by simply shaking large quantities of viscous oil with soap solutions. The formation and the stability of these emulsions is dependent upon a low interfacial tension and a viscous continuous medium. That the viscosity of the oil plays a great part in the stability of the Water-in-Oil type is evident from the fact that in light oils like kerosene and benzene, the Water-in-Oil type is not stable, when large quantities of oil are churned with small quantities of soap solutions. On increasing the concentration of soap solution to about 1% the nature of the emulsifying agent is more effective than the volume ratio effect and Oil-in-Water emulsions only, are stable with a soap like sodium oleate. It is interesting to note that on decreasing the concentrations, the inversion point is shifted towards the degree of closest packing. Similar results were also obtained by Bhatnagar.<sup>1</sup> Also Clayton<sup>2</sup> has shown that by churning large quantity of oil with water containing emulsifying agents, a Water-in-Oil emulsion is formed but is poorer in texture and

<sup>1</sup> Loc. cit.

<sup>2</sup> "Symposium on Colloids." Faraday Soc., Oct., 1920.

can be stabilised by increasing the viscosity of the continuous medium by sudden chilling.

In a preliminary paper, Bhatnagar (Loc. cit.) used sodium hydroxide and olive oil containing fatty acids, as the results were intended only to test the electrical method of determining the inversion point of emulsions. In later contributions (Bhatnagar Part III Thesis for the Degree of Doctorate of Science, London University, July, 1921) Bhatnagar used pure soaps and the results obtained by him agree with ours. Bhatnagar has also pointed out there that "The stability of the Water-in-Oil emulsion obtained by simply increasing the amount of oil is less than that obtained when the very nature of the emulsifying agent helps its stability."

There is no doubt however as to the formation of a Water-in-Oil emulsion, when the concentration of the emulsifying agent is smaller than 1% and the oil used is viscous. In these cases the volumes of the two phases become important factors in determining the formation of type.

Such emulsions can well be classified with the mechanical emulsions of McLewis & Ellis, because their formation is mechanical and they remain unexplained like the Water-in-Oil emulsions described here, on Bancroft's hypothesis.

We desire to express our thanks to Professor S. S. Bhatnagar, D.Sc., for suggesting this work.

*Department of Chemistry  
Hindu University  
Benares*

## NEW BOOKS

**Atomic Theories.** By F. H. Loring. 22 × 14 cm; pp. v + 218. New York: E. P. Dutton and Co., 1921. Price: \$5.00.—The object of this book as stated by the author, is to give the leading facts and theories which relate to the atom, particularly those which have not yet been treated at any length in text-books owing to their newness. The subject is presented under the following heads: introduction; atomic weights and whole-number isotopes; electrons and atomic nuclei; co-ordinating the electrical properties of the atom; K and L series of lines by X-ray analysis; a note on crystal structure; radio-activity and crystal structure as clues to atomic structure; Rutherford's nuclear theory of the atom with detailed experimental evidence; the quantum theory; the Bohr-Rutherford atom; Sommerfeld's extension, and Epstein's studies of the Stark effect; the photo-electric effect; the Zeeman effect, gaseous ionization, ionization potentials, and views concerning radiation; the Lewis-Langmuir atomic theory; the octet theory; co-ordinating the Rutherford and Lewis-Langmuir theories; the Lewis-Langmuir octet theory of valence applied to organic nitrogen compounds; the octet theory as a clue to certain types of molecular instability, and a few remarks; a note of caution; the possible complexity of hydrogen and its position in the Periodic Table; the energy of the atom, elements in the sun and their ionization, atomic energy and solar radiations, sun-spots and magnetic storms, high temperatures; atomic and molecular magnitudes determined by the Brownian movement; magnetic susceptibilities of the elements; Sir. J. J. Thomson's views of matter, mass, and radiation.

On p. 14 is given Aston's list of isotopes and on the next page is the statement that "the fractional irregularities of the atomic weights may be attributed to the existence of isotopes." On p. 45 is the account of Rutherford's work on the production of hydrogen from nitrogen. "Thus it will be seen that the previous 1919 experiment is in general confirmed, and for the first time the disintegration of the nitrogen atom by swift  $\alpha$ -particles is placed on record as an accomplished fact. While the effect is small [since] only one  $\alpha$ -particle in 300000 gets near enough to the nucleus of the nitrogen atom to displace a hydrogen sub-atom, it is of far-reaching theoretical consequence."

The statement in regard to light emission and to the photo-electric effect, p. 69, is refreshingly definite. "When light emission takes place, it is supposed to be due to the electron striking inwards towards the positive nucleus of the atom, and according to Bohr's theory of the hydrogen atom an electron jumps from an outer to an inner orbit, and during its passage monochromatic radiation is emitted. In the photo-electric effect, the electron is caused to fly out of the atom, or out of its inter-nuclear position, by high-frequency light falling on it. Ultra-violet light incident on a clean metallic surface causes the emission of electrons from the metal. This is the photo-electric effect. With the alkali metals, sodium and potassium for example, visible light, i.e., light of lower frequency than the ultra-violet, and of longer wave-length, causes this electronic emission."

It is stated that a substance only emits its characteristic spectrum when it is subjected to intense ionization, p. 73. "It seems probable that an electron

on recombining with an ionised atom does not fall immediately into the atom but, owing to its velocity, describes a series of orbits round it, in the same way that the planets describe orbits round the sun. Each of these orbits will be described in a definite period, and will give rise to a single line in the spectrum. A single electron in passing successively through each of these orbits will thus emit in succession each of the lines in the spectrum. If the process was one of gradual collapse, so that the electron described circles of gradually diminishing radius, the light emitted would of course contain vibrations of every possible period—that is to say, it would be white light. It can, however, be shown that the number of orbits in which it is possible for the electron to move with the periodic motion necessary for the production of light is not definite, but that their number and radii depend on the arrangement of electrons in the atom. They are thus as characteristic of the atom as the periods of its own electrons, while at the same time the light of corresponding frequency is only emitted when the atom is undergoing recombination. Bohr on the assumption that the difference in the energy of the electrons describing two successive orbits is equal to the 'quantum of energy' . . . has succeeded in accounting numerically for some of the lines in the hydrogen spectrum."

On p. 80 there is a quotation from Millikan. "The appearance of  $h$  in connection with the absorption and emission of monochromatic light (photo-electric effect and Bohr atom) seems to demand some hitherto unknown type of absorbing and emitting mechanism within the atom. This demand is strikingly emphasized by the remarkable absorbing property of matter for X-rays, discovered by Barkla (*Phil. Mag.*, 17, p. 749), and beautifully exhibited in De Broglie's photographs opposite p. 197. It will be seen from these photographs that the atoms of each particular substance transmit the general X-radiation up to a certain critical frequency and then absorb all radiations of higher frequency than this critical value. The extraordinary significance of this discovery lies in the fact that it indicates that there is a type of absorption which is not due either to resonance or to free electrons. But these are the only types of absorption which are recognised in the structure of modern optics. We have as yet no way of conceiving this new type of absorption in terms of a mechanical model. There is one result, however, which seems to be definitely established by all of this experimental work. Whether the radiation is produced by the stopping of a free electron, as in Duane and Hunt's experiments, and presumably also in black-body experiments, or by the absorption and re-emission of energy by bound electrons, as in the photo-electric and spectroscopic work, Planck's  $h$  seems to be always tied up in some way with the emission and absorption of energy by the electron.  $h$  may therefore be considered as one of the properties of the electron."

Whetham's remarks on the lines of force, p. 83, are also interesting. "Faraday's tubes, it is clear, give a powerful and convenient method of studying the phenomena of the electromagnetic field, and indications are not wanting that they represent something more than a useful mathematical fiction. If the structure of the electric field be discontinuous in reality, as our tube-picture of it indicates; if the electric and magnetic effects of a charge of electricity are in reality exerted throughout the surrounding space by means of discrete tubes of force-vortex filaments in the aether, or whatever they may actually be; an advancing wave of light must be discontinuous also. Could we look at such a wave

from the front and magnify it millions of times we should see not a uniform field of illumination, but a number of bright specks scattered over a dark ground. Each tube of force would convey its own tremors and these would constitute light, but between them would lie undisturbed seas of aether."

On p. 154 is given a summary of the author's views in regard to hydrogen. "Hydrogen appears to be unique in not being a whole-number atom. The fractional part of its mass is relatively great. Hydrogen does not find a proper place at the heads of Groups I and VII. Its chemical activity is evidently such as not to enable it to form stable polymerides answering to known elements. There is a gap at the end of Group I that does not accommodate any radio-active element. Similarly, there are gaps below manganese which seem difficult to fill, and one of these would have to be filled by a radio-active element which seems improbable. On the hypothesis that all elements are polymerides of hydrogen, a difficulty arises owing to the fractional value, suggesting that the fundamental unit has a mass of 1 exactly. Considering hydrogen as a complex atom composed of mass parts  $a = 1.0000$ ,  $b = 0.0077$ , and  $c$  (an electron) = 0.00055,  $a$  and  $b$  could possibly be more properly placed at the heads of Groups I and VII respectively, and thus account for the very strong affinity between these parts, and thereby explain the stability of the hydrogen complex ( $ab$  or  $abc$ ), whilst the respective parts alone might have very great affinity, especially  $a$ , which could polymerise and form the whole-number elements as revealed by Aston's recent experiments. Moreover, constructing a modified Langmuir Periodic Table, the absence of elements in Groups I and VII would suggest a shortage of elementary material, so to speak; but this shortage would be made up at the heads of these groups by introducing the entities  $a$  and  $b$  at these places. This procedure reveals a numerical regularity, as will be seen by the additions in Table XII. The complexity of hydrogen thus indicated would account for the fact that it is not fully eligible for a position at the head of either of the above-mentioned groups. The question of atomic numbers to be assigned to these hypothetical parts is of interest but cannot be discussed here. The fact that ordinary hydrogen is not known to polymerise to form the elements would be expected if it carries an auxiliary part which deprives it of this property."

On p. 161 there are a couple of paragraphs in regard to the behavior of elements in the sun. "In studying the chemical elements in the sun, Saha observes that since there is no direct spectroscopic evidence of nitrogen in the sun, nitrogen being a light element, and also of thorium, thorium being a heavy element, there may be a reason for these and other apparently missing elements not giving spectroscopic evidence of the solar existence. In other words, atomic weight cannot be directly associated with the absence of these elements in the sun's spectrum; therefore, some other cause is to be sought. It is suggested that all the elements are really present in the sun, but only those which are stimulated into activity by the high temperature prevailing therein emit radiation.

"It is suggested that the cause of this variation in the sun is due, not to a temperature variation, but to differences in the internal structure of the atoms.

"In order to test this view, the elements are classified or studied according to their ionisation potentials. Thus the most strongly ionised elements appearing in the high-level chromosphere would be Ca, Ba, Sr, Sc, Ti and Fe; while in the lower layers such atoms are mixed with neutral ones. Hydrogen ( $H_2$ )

is completely dissociated into atoms throughout the solar atmosphere as there is no evidence of a secondary spectrum due to hydrogen molecules. This would be expected as the temperatures of the chromosphere and photosphere are respectively about 8000° and 7500° abs."

The reviewer was not familiar with the work done recently in obtaining very high temperatures, p. 171. "It is important to investigate stellar phenomena in the laboratory, as thereby a better understanding of stellar physics is obtained. To this end, J. A. Anderson has investigated the light from electrically exploded wires with the object of imitating high-temperature absorption spectra. When this method is fully developed it is hoped to reproduce stellar absorption spectra of the solar type. The experiments are, moreover, of interest in showing the possibility of obtaining very high instantaneous temperatures; for in probing the atom it is important to consider high temperatures and any effects arising therefore in connection with atomic structure—in particular the study of the problem from the energy side.

"In these experiments a large condenser charged to 26,000 volts was discharged through a fine wire (5 cms long, weight 2 mgrms) in about  $10^{-5}$  seconds. It was shown that about 30 calories were dissipated during this short interval of current flow. The wire was volatilised in a confined space. If all the energy involved had been dissipated as heat in the wire itself, its temperature should have been about 300,000° C. When the wire exploded the flash intensity, however, corresponding to a temperature of about 20,000° C, was about one hundred times greater in brilliancy than that of the sun.

"When the wire was exploded within a tube or slot under a bell jar exhausted to 20 mm pressure a line emission spectrum was obtained, and as the pressure was increased the continuous background increased in intensity and the spectra became more an absorption one. The spectrograms showed clearly a pressure shift of the lines. Pressures up to 50 atmospheres can easily be obtained.

"Using an iron wire, an absorption spectrum was produced which extended to 0.66  $\mu$ , and this spectrum includes all classes of lines except pronounced enhanced lines. It is hoped to reproduce stellar absorption spectra of the solar type by this method."

*Wilder D. Bancroft*

*Within the Atom.* By John Mills. 19 × 13 cm; pp. xiii + 215. New York: D. Van Nostrand Co., 1921. Price: \$2.00.—As the author says in the preface, "the volume is intended for readers who wish to obtain a familiarity with the basis of modern physical science. Without mathematical formulation it deals with modern theories as to matter and energy, emphasizing the granular structure and electrical nature of matter and the apparently corpuscular character of energy. The reader need have no previous knowledge of electricity, mechanics, or chemistry."

The subject is presented under the following headings: atomic structures; satisfied and unsatisfied systems; the periodic table of atomic systems; mass and inertia of atomic systems; radioactive disintegrations; conduction of electricity through gases; conduction through solids and other electrical phenomena; the proof for the existence of an electron; isolating a proton; X-rays and atomic numbers; photo-electric effects and the quantum of energy; light radiation and atom-models; more evidence for the quantum hypothesis; energy and its availability.



Some parts of the book are extraordinarily good. Speaking of X-rays, p. 124, the author says that "orderly reflection, to which we are accustomed in the case of polished mirrors and light rays, does not occur. Such reflection is possible only if the surface irregularities of the reflecting body are negligible in comparison to 'the wave-length,' so-called, of the incident radiation. . . . For X-rays this distance is just about half the diameter of an ordinary diatomic molecule. No surface, therefore, can be smooth to X-rays and reflecting in the ordinary sense. For this reason the re-radiation of X-rays is usually irregular and disorderly."

On page 165, after a discussion of the Bohr atom, we read: "For the basic ideas involved in the Bohr atom-model there is a large amount of evidence. It will be noticed, however, that it does not conform to the picture of atom structure which was given in our early chapters, where the electrons were assumed to occupy relatively fixed positions in the atom. The concept of definitely localized electrons is highly satisfactory to the chemists who have found it to explain not only valence in chemical combinations but also many phenomena like the miscibility of different liquids, tendencies to vaporize, and hence melting and boiling temperatures. In such matters molecules which are believed to have like shells of electrons are found to have similar properties.

"Between the chemists who are interested in molecular combinations and such physicists as are concerned with radiation there is at present established a gulf. Each finds his own atom-model most convenient and satisfactory. The chemical model is due to a number of scientists, chief of whom are Lewis, who first suggested its general features, and Langmuir, who has elaborated and extended it. It requires that the electrons effective in valence relations should be relatively fixed. The Bohr atom requires that some, at least, of the electrons shall be in rotation.

"It seems quite probable, nevertheless, and indeed more or less inevitable, that the two conditions are not hopelessly conflicting and mutually impossible. According to the chemists' construction the valence electrons in all except a few of the atoms are in external shells within which are other shells of electrons. Perhaps these inner shells contain the rotating electrons which determine the radiation of the ionised atom. In the case of the elements between lithium and argon, however, all except two electrons are in a single shell. It is possible, therefore, that future investigations of these elements will lead to evidence upon the basis of which a reconciliation may be possible, and the salient features of both models may be retained."

Especially good are the two paragraphs on p. 168. "In the preceding chapters there have been mentioned two types of emission spectra, line and continuous. Of these the line spectrum is the more interesting. It is emitted by elementary substances which are in the state of a gas or a vapor, when the electrons have been displaced to new orbits or completely detached from the atoms. The return of an electron is accompanied by a radiation of which the frequency is characteristic of the element and the energy equal to one quantum. Line spectra are due to the natural vibrations of electrons and atomic nuclei.

"A continuous spectrum, on the other hand, is a phenomenon of substances in the solid or molten-liquid state where the atoms are packed relatively close together. The atomic systems no longer function as untrammelled individuals but as members of a large and unorganized crowd. Each is limited in the ex-



pression of its tendencies (line spectrum) by the inter-relations and reactions with the other systems of its milieu. Energy, imparted to the atomic systems under these conditions, results in chaotic motions on the part of all, which then proceed to jostle and crowd each other. Instead of a clear individual expression, which is characteristic of the atomic type there arises a roar of notes, expressive only of conflict and chaos. No longer are types easily distinguishable by characteristic lines for the spectra are continuous. Of this phenomenon all incandescent solids are examples."

The reviewer is not quite certain about the statement on p. 182 "that reflection is really re-radiation. Any reflected radiation must then include most prominently those radiations which are of the same frequency as the oscillators would themselves naturally emit. The phenomenon is one of resonance so-called—that is the phenomenon of greatest response when the appeal strikes the proper personal note." If reflection is really re-radiation, it should be made clear why there is not radiation in all directions. That point may be clear to the physicist; but it is not to the layman.

On a much lower plane is the paragraph on p. 58. "Suppose two dissimilar substances are brought into close relations by rubbing. In general there will be an appreciable difference between the substances in the matter of what constitutes a satisfactory configuration for the electrons of their molecules, for one may have a greater need for electrons than the other. Although the surfaces may appear smooth, the structure of their atoms is such that the act of rubbing two bodies together is really the act of crowding one planetary system into another or causing one to pass through the other. There is every opportunity for some of the electrons to be displaced from their own planetary systems and to join those of other nuclei. The molecules of the system which has the greater need for electrons will gain or that which would more willingly assume a configuration with fewer electrons will lose. The net results when the substances are separated is that one has more than its normal number and the other less; the first is negative and the second positive in charge. The classical substances are glass and silk, or cat's fur and sealing wax. The first of each pair acquires a positive charge and the second a negative charge."

There is nothing wrong about this; but it is not helpful and it is not convincing. The paragraph is merely a collection of perfectly respectable words and sentences which constitute a study in circumlocution.

On p. 68 is the only actual mistake which the reviewer is qualified to detect. In the electrolysis of sulphuric acid it is not true that the sulphate ion delivers two electrons to the positive plate and then reacts with water to form sulphuric acid and oxygen. The sulphate ion does carry practically all the current to the positive plate; but it is the hydroxyl or the oxygen ions of water which discharge there and not the sulphate ion. That point was cleared up by LeBlanc over thirty years ago.

The author has kept to his promise to avoid mathematics and the book is a praiseworthy attempt, perhaps the best that could be made. In places it attains success; but the task which the author set himself was a very difficult one and the reviewer feels that the author has not scored an unbroken string of bull's-eyes.

*Wilder D. Bancroft*

**Elektrochemie wässriger Lösungen.** By Frits Foerster. Third edition. 25 X 18 cm; pp. xx + 900. Leipzig: Johann A. Barth, 1922. Price: paper 200 marks, cloth 230 marks.—In the preface to this edition the author says: "The second edition of this book appeared during the World War in the first quarter of 1915, at the time when it was a question in Germany whether it was really possible to solve the problem of providing continuously the supply of munitions needed to defend the Fatherland. The problem was solved in a way to surpass all expectations. Electrochemistry had its share in the work. The things that technical ability, supported and guided by scientific research, had started earlier were developed to the limit of production and new factories were started on the largest scale. These years were therefore years of harvest and growth. What was learned then will prove a weapon in the bitter struggle necessary to make profits in spite of the completely disorganized conditions that have resulted from the war."

The chapters are entitled: electrical energy and direct current in general; Faraday's law and its practical consequences; theoretical consequences of Faraday's law and electrolytic dissociation theory; applications of the electrochemistry of the metals; electrolytic reduction; special electrochemistry of the halogens; electrolytic oxidation.

The second edition was a good book (19, 791) and the third edition is also good; but there is not the progress that one hoped to find. It would have been a great deal better if the author had rewritten the book practically completely, chapter by chapter. It is not so much that new material should have been put in as that the material should have been presented more logically and less chronologically. In 1915 the author was ahead of his readers; today he is behind them because his point of view has not changed much in six years and ours has. The chapter on electrical endosmose is as good as it was; but it ought to be much better. Instead of a series of somewhat disconnected paragraphs, it should have been a clear and consistent presentation of the subject.

In the discussion of over-voltage, practically no advance has been made and it is much more evident now than it was six years ago that the author's general point of view is wrong. Instead of adopting frankly the view of Tafel, of Lewis, and of Bennett that hydrogen over-voltage is due to monatomic hydrogen, he slurs this over and lays great stress on hydrogen alloys, p. 316. "It seems natural to refer the varying effects of different cathodes on the electrolytic evolution of hydrogen to the fact that the hydrogen atoms set free at these cathodes pass through the stage of hydrogen alloys before becoming hydrogen gas. The varying stability of these alloys is the reason for the varying ease with which the evolution of hydrogen takes place at cathodes of different metals. Under hydrogen alloys is to be understood alloys of the metal with atomic hydrogen and also metallic hydrides, which then stand in equilibrium with definite concentrations of atomic hydrogen. At present it is impossible to distinguish between these two possibilities and we will therefore class both, for the sake of brevity, under the heading of hydrides. We must consider these 'hydrides' as the primary products of increased free energy."

In the first place, there is no evidence that any hydrides are formed at all and, in the second place, hydrides cannot account in themselves for over-voltage. If the hydrides are stable, they will lower the voltage at which hydrogen is set free. If they are instable, they cannot form unless there is over-voltage and we have got

to have a primary product having a stronger reducing power than the hydrides. So far as we can see, the only possible thing is electrically neutral, monatomic hydrogen. Foerster postulates monatomic hydrogen but makes no use of it and digresses to the question of possible hydrides, which are secondary products at best and which are useful only in accounting for the form of the discharge curve. Similarly, one may concede the existence of  $\text{PtO}_2$  without that helping us in any way towards a theory of over-voltage.

The question of passive iron is not discussed clearly. On p. 227 and elsewhere it seems to be admitted that iron is passive because of an adsorbed, and thereby stabilized, oxide, though there is no discussion of its possible composition. That is a pity, for Bennett has shown that it must contain more oxygen than  $\text{Fe}_2\text{O}_3$  and cannot contain more than  $\text{FeO}_2$ . On p. 430 however Foerster swings back to a possible adsorption of oxygen and to the formation of a negative catalyzer.

It would be a very desirable thing if somebody were to translate this book because it is quite in a class by itself; but it would be still better if the translator should give a free translation, rearranging and rewriting so as to make it a logical presentation.

*Wilder D. Bancroft*

**Inorganic Chemistry for Schools and Colleges.** By James Lewis Howe. Second edition, revised. 23 × 16 cm; pp. viii + 443. Easton: The Chemical Publishing Company, 1920. Price: \$3.00.—In the preface to the first edition (1907) the claim was made for the book that it was the first of its kind to take the Periodic System for its guiding principle throughout. In the preface to the present edition Mr. Howe says that "the experience gained in using previous editions of this book has served to convince the author of the advantages of its general plan especially as to the sequence of topics."

Fifteen years of experience should be a good test and yet it does not seem to the reviewer to follow that the best way to remember a subject is necessarily the best way to present it to students beginning the subject. To the reviewer—who is speaking without any real knowledge of the subject—it would seem wiser when discussing the elements to group the metals together and to put the non-metals in another group at least temporarily. It cannot be helpful to the student to discuss manganese and bromine together for instance. As the author puts the noble gases in the eighth group instead of in a zero group, consistency would require him to discuss iron and krypton together, which of course nobody would do. The truth of the matter is that concessions have been made.

The author begins with hydrogen, oxygen, and water, and then takes up salt, sodium, and chlorine. As sub-divisions he includes the phase rule, osmotic pressure, electrolytic dissociation, and neutralization of bases by acids, all of which has nothing to do with the periodic system. He then takes up the elements consistently, discussing manganese immediately after fluorine, and calling the noble gases the inert series and the iron and platinum metals the active series of the eighth group. When it comes to the compounds, the treatment varies. The hydrogen compounds start with the seventh group and end with the fourth, while the halides and oxides begin with the first group and end with the eighth.

It seems to the reviewer that the merit of the book is probably due more to the contents than to the arrangement. The author does tell about buffaloes and

deer at salt licks, about pottery, and about alloys. There is a distinctly human touch about the book, which is lacking in some standard text-books. On the other hand one must ask the question whether elements and compounds, the law of definite and multiple proportions, atomic theory and chemical affinity should come in the introduction. The historical treatment of a subject is apt to be long-winded and obscure; but it can easily be made interesting. The extremely logical and deductive method of presentation is concise and clear but usually dull. The reviewer believes that one should use the deductive method for research and the inductive method for teaching, whereas his colleagues, with very few exceptions, hold the opposite view on both points.

There are one or two statements of fact that grieved or puzzled the reviewer. On p. 29, is the statement that the motion of the molecules may be so great that the substance remains in the gaseous state in spite of any increase of pressure. The student will probably gather from this that the motion of the hydrogen molecule is enormously greater than that of the carbon dioxide molecule and that the motion of the carbon dioxide molecule is enormously greater than that of the water molecule. Also, the author's presentation inculcates the idea that one can only have gas at temperatures above the critical temperature, whereas all we mean is that we cannot differentiate between gas and liquid above that temperature.

On p. 30 it is doubtful whether the student will grasp the relation between sublimation and fusion. On p. 89 is the statement that when fused sodium chloride is electrolyzed, small metallic globules of sodium are obtained at the negative pole, which seems improbable in view of the fact that sodium boils at 878°. On p. 145 is the statement that aluminum is now obtained by the electrolysis of bauxite dissolved in an artificial mixture of double chlorides. On p. 341 the account of the behavior of chromated gelatine is badly confused. So far as the reviewer knows, light has no action on a mixture of gelatine and chromium hydroxide and a mixture of gelatine and chromate is not insoluble. The word cation is misspelled consistently.

*Wilder D. Bancroft*

*Alchemy, its Science and Romance.* By J. E. Mercer. 20 × 13 cm; pp. iv + 245. New York: The Macmillan Co.; London: S. P. C. K., 1921. Price: \$3.50.—In Part I "General History" (60 pp., Myth and Early History, Arabian Alchemy, Mediaeval Alchemy, Decadence, Transition to Science) the author sketches the lives and times of a dozen representative alchemists, describes the spread of the art and its invasion of medicine, and finds the chief cause of decadence in "the confusion of objective fact and subjective notions."

In Part II "The Idea of Transmutation" (60 pp., Suggestions from Natural Processes, Philosophy and Transmutation, Alchemy and Animism, Magic and Astrology) the reasonableness of the alchemists' aim is insisted on: "the inference from observations of external happenings to the possibility of transmutation was warranted; indeed, the supposition may be granted the rank of 'scientific.'" The analogies noted by the alchemists between chemical processes, those of life, growth and death in the vegetable and animal worlds, and those of spiritual and moral experience, are discussed at length; and the influence of Plato's philosophy on the operations of the laboratory is traced from the time of Psellus to the days when alchemy was discredited and discarded.

In Part III "The Object of the Quest" (38 pp., The Philosopher's Stone

The Stone and Mysticism, Credulity and Imposture, Life of Bernard of Trèves) examples are given of the extravagant language employed by the alchemists when writing of the Stone; "nevertheless we recognize throughout the influence of philosophical presuppositions which supply a rational basis for even the most rhapsodical and mystical of these speculations." Examples are given also of the fraudulent exploitation of alchemy, "yet the art has to its credit a long list of discoveries; it has advanced to a considerable extent our knowledge of nature; many of its speculations have a future before them. If we are fair to it, we shall, while laughing at or condemning the charlatans, acclaim the successes won by the genuine adepts."

In Part IV "Alchemy and Science" (77 pp., Difficulties of Interpretation, The Materials, The Laboratories, Advances and Discoveries, Transition to Modern Chemistry, The Outlook) an attempt is made to summarize the chemical knowledge of the alchemists, to sketch the dawn of the scientific spirit, and to describe the discoveries which have led to the chemistry of today.

The author thinks that his book "may perhaps claim to be an apology for Alchemy." He "lays no claim to detailed research throughout the whole vast range of the literature of the subject," but has "consulted the works of representative alchemists, especially of the earlier periods." Throughout the book are numerous quotations from Zosimas, Psellus, Valentine, Paracelsus, van Helmont, and a dozen other alchemists; also from Plato, Dante, Chaucer, Addison, Ben Jonson, and the Book of Enoch. Indebtedness is acknowledged to Berthelot, Figuier, Pattison Muir, and Thorpe; Hofer's *Histoire de la Chimie* is quoted, but no mention is made of Kopp.

The writer of this sympathetic account of a stage in the evolution of modern science is not a chemist by profession, but a clergyman, doctor of divinity, and sometime Bishop of Tasmania. A far country, Tasmania; very far, apparently, from Kentucky and even from Nebraska.

W. Lash Miller

**The Physical Properties of Colloidal Solutions.** By E. F. Burton. *Second edition.* 22 × 15 cm; pp. biii + 221. New York and London: Longmans Green and Co., 1921. Price: \$4.25.—The first edition was reviewed six years ago (20, 543). In the preface to the second edition the author says that "the book has been thoroughly revised for this new edition. Certain parts, particularly the chapters on introduction to the subject and on the coagulation of colloids have been almost entirely rewritten in the light of recent work."

The author is definite in saying, p. 183, that "in the light of the experimental results quoted above, the Schulze-Linder-Picton law cannot be upheld in its simple form to which Whetham's explanation was applied. The coincidence, nevertheless, is remarkable enough to convince one that there is fundamentally some truth in the Whetham view." One interesting thing is the section on the limitations of Perrin's distribution law, p. 86, in which the author shows how the introduction of another term may reconcile Perrin's theory with the facts.

At other times he is unwilling to put his foot down hard. On p. 182, he discusses Loeb's view on gelatine solutions as though it were a possible variant of other views. "According to recent work by Loeb, the preceding point of view is entirely wrong, and he makes out a very good case for explanation of the phenomena resulting from the addition of neutral salts on the basis of classical chemi-

cal action. For example, Loeb shows that gelatine in solution is in a critical state when the hydrogen ion concentration is a certain definite amount, *viz.*  $pH = 4.7$ , which he calls the isoelectric point. At this point the gelatine is non-ionized and does not show cataphoresis.

"On the more acid side of this point, the gelatine forms a compound in which the gelatine fills the rôle of a positive (metal) radical in combination with such negatively charged radicals as chlorine or hydroxyl; when ionized the gelatine ion is positively charged. On the more basic side of the isoelectric point, the gelatine acts the part of a negative (acid) radical in combination with such positively charged radicals as hydrogen or sodium, and, when ionized, the gelatine ion in this case is negatively charged. Loeb maintains that the whole action is in agreement with ordinary chemical reactions and that when a neutral salt is added to either of these solutions the gelatine units in solution react with only one ion of the neutral salt; on his view, it is useless to try to balance up adsorptive effects of anions and cations in a way attempted by the colloidal chemists.

"McBain classifies these protein solutions with soaps and dyes, such as congo red, under a class which he has called colloidal electrolytes. These he defines as 'salts in which one of the ions has been replaced by a heavily charged, heavily hydrated ionic micelle (particle) which exhibits equivalent conductivity which is not only comparable with that of a true ion but may even amount to several times that of the simple ions from which it has been derived. The ionic micelle is a typical but very highly charged colloidal particle of very great conductivity. In a sense this is in line with Loeb's ideas, if the latter's protein ion is replaced by the ionic micelle suggested by McBain."

The reviewer feels that this is inadequate. It should have been brought out clearly that there is no possible compromise, so far as we can now see, between Loeb and the colloid chemists. Loeb has burned his bridges behind him and stands or falls on the explicit assumption that gelatine does go entirely into true solution. We have got to take up his challenge and there is nothing to be gained by pussy-footing. It would have been better if the author had stated clearly where he stands.

*Wilder D. Bancroft*

**Patents and Chemical Research.** By Harold E. Potts. 21 × 14 cm; pp. ix + 198. Liverpool: The University Press, 1921. Price 8 shillings, six. In the preface the author says that "progress in industrial chemical research and invention is intimately dependent on the efficiency of the patent system. Patent law deals with such complex problems that a heavy responsibility is thus cast upon practitioners of the law. Therefore it is most desirable that chemists should familiarise themselves with the leading principles of patent law; first, to enable them to co-operate with the patent agent and thus contribute to the object of obtaining secure protection for their inventions, and, second, so that their criticism will stimulate patent agents to maintain the highest level of professional skill. In this way, better work will be done, and the greatest possible benefits will be derived from the patent system."

The headings of the chapters are: patents as an element of business policy—the business problem; a short general account of patent procedure; obtaining maximum protection for an invention—the theoretical problem; accuracy of experimental data and theory in patent specifications—the experimental prob-



lem; validity of patents—the historical problem; the definition of an invention—the problem of language; patents in other countries.

The book is written in an interesting way and is well worth reading. What the author has to say on the subject of ownership of patents, p. 49, is worth quoting. "There has been much discussion as to whether patents should belong to the employer or the employee. In this connection it may be useful to draw a broad distinction between the invention made by a routine worker, which is outside the ordinary range of his duties, and should be substantially remunerated, and the invention made by the research worker, who is definitely employed to make improvements or inventions. If the remuneration of the research worker is to be contingent on the patents taken out in his name, there may be a tendency for work to be concentrated on the immediately profitable problems rather than on the fundamental research which may be all-important for future development. Further, team-work will not be helped if there is a feeling of secretiveness arising from each worker trying to monopolise his own ideas. There is much to be said, therefore, for the policy of paying the research worker adequately without reference to the patents resulting from his work, which would then become the property of the employer. It must be remembered that the lucrative patents must carry the overhead expense of the whole of the research work, all of which will not be financially successful."

"Possibly the main advantage of the patent system to the research worker is not the immediate cash remuneration per patent, but the fact that the existence of a series of patents earmarks his contributions to the knowledge of the firm, and increases his standing both with the firm and with the public. The financial part of the reward is probably best given in the form of increases of salary and status, which will naturally follow the appearance of important patents."

*Wilder D. Bancroft*

**Tables of Physical and Chemical Constants.** By G. W. C. Kaye and T. H. Laby. Fourth edition. 25 X 17 cm; pp. 161. New York and London: Longmans, Green and Co., 1921. Price: \$4.00.—The first edition appeared in 1911. In this latest edition, matter relating to the figure of the earth, the absolute determination of the acceleration of gravity, and more extended tables of the relative value of that constant have been added. "The chemical data have been recalculated, using the international atomic weights. Some seven hundred additions and alterations in the physical constants of chemical compounds have been made. The published values of these constants have been critically examined, and what appear to be the more accurate values for the chemical compounds included in these pages have been used. Through the kind co-operation of Dr. Ezer Griffiths of the National Physical Laboratory, many of the heat tables have been revised and amplified. Among other additions and changes are tables of atomic numbers, spark-gap voltages, X-ray wave lengths and terrestrial magnetic constants. The effect has been slightly to increase the size of the book."

The data are grouped in the following subdivisions: general physics, astronomy, etc.; heat; sound; light; electricity; magnetism; rays, radioactivity and gaseous ionization; chemistry; mathematical tables. From this it appears that the strictly chemical part is relatively small, about one eighth of the whole. The chemical tables include: formula weight, density, melting-point, and boiling-

point, for a number of inorganic and organic substances, arranged alphabetically; two pages of data in regard to solubilities; the density and hardness of some minerals; and factors for gravimetric analysis.

This is not really a fair statement of the case because elsewhere are given: data for electrical conductance, migration velocities, etc.; data for latent heats, heats of combustion, etc.; data for melting-points and boiling-points of the elements; data for surface tensions and compressibilities; data for densities of solutions, etc. There is very little in the book that the chemist will not want to refer to at some time or other.

*Wilder D. Bancroft*

**Colorimetric Analysis.** By *F. D. Snell*. 20 × 14 cm; pp. xiii + 150. New York: *D. Van Nostrand Company*, 1921. Price: \$2.00.—The book is, in essence, an attempt to combine, for ready reference, all the colorimetric tests which experience has shown to be at all practical. The chapters are entitled: conditions of use of colorimetric methods; apparatus used and methods of using it; figuring of results; determination of iron; determination of copper; carbon in steel; lead, bismuth and arsenic; aluminum and chromium; nickel, cobalt, manganese and zinc; potassium and magnesium; gold; titanium, vanadium, and tungsten; fluorine, chlorine and perchlorates; nitric and nitrous acids, and ammonia; phosphorus, silica and boron; oxygen and hydrogen peroxide; sulphur, hydrogen sulphide and selenious acid; salicylic acid and cyanides; color of water, oils and dyes; nephelometry.

On p. 3 the author says: "Colorimetric tests may be classified into two classes according to the reason for their use. Some find their popularity because they are fast, and the accuracy of the test is sacrificed for speed in obtaining the final result. The second class finds use because they furnish a method of determination of small amounts of substances with greater accuracy than is possible by gravimetric or volumetric methods. The first class may all be made in a short time but it may often happen that the method of preparation of the second class of tests may take hours to insure the accuracy desired."

On p. 145 the author says that "the use of the colorimeter for determination of the strength of solutions of dyestuffs is very limited in extent, inasmuch as it is not reasonably accurate in practice in a majority of cases. It is however useful as a method of preliminary classification and may then be followed by the longer and more accurate test necessary after this preliminary has given a clue to the concentration to be expected."

The reviewer is not competent to speak as to the accuracy of the details; but the author has certainly written an interesting book and it is the kind of book that we want.

*Wilder D. Bancroft*

**Handbuch der Mineralchemie.** By *C. Doelter*. Vol. II. Part 3. 26 × 19 cm; pp. 161–320. Dresden and Leipzig: *Theodor Steinkopff*, 1920. Price: \$1.00.—If one treats desmin with ammonium chloride solution, the interchange of cations can be represented fairly satisfactorily by an exponential formula, p. 169. The data for the dehydration and hydration of heulandite are quite conclusive that no definite hydrates occur over the range studied, p. 183, and Weigel comes to the very proper conclusion, p. 184, that the water in the zeolites is present as a solid solution, though either he or Doelter rather obscures matters



by saying that "it cannot be told whether the water in this solution reacts with the solvent forming a close compound with the silicate, or whether the molecule takes its place in the space lattice after decomposing into atoms or ions."

For good and sufficient reasons the Geophysical Laboratory decided that sodium anorthite was not a satisfactory name for the triclinic form of  $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$  which they had made synthetically and they therefore called it carnegieite. Apparently everybody agreed that sodium anorthite was an unsatisfactory name and apparently nobody objected to the reference to Mr. Carnegie and yet a protest was made that it was outrageous for the Geophysical Laboratory to give what should have been the name of a mineral to a compound which had been made in the laboratory and which probably did not occur in nature, p. 291. It probably never would have occurred to a chemist that such a thing would stir a mineralogist to wrath.

Most of this number is taken up with analyses of minerals, data which are doubtless of great importance to those working in this field; but which are not especially interesting to the casual reader.

*Wilder D. Bancroft*

35. 4001

## MORDANTS. II

BY WILDER D. BANCROFT

### ALUMINA

#### Hydrolysis of Aluminum Salts

Over a century ago, Gay-Lussac<sup>1</sup> found that if one heats a solution of aluminum acetate, it soon becomes turbid and a large amount of alumina precipitates. If the solution is allowed to cool, the precipitate dissolves slowly and becomes transparent. On the reheating and recooling these changes repeat themselves and this can be kept up indefinitely. With a dilute solution of aluminum acetate the turbidity begins at about 50° and a precipitate forms at a little higher temperature. The precipitate must change gradually because it dissolves more slowly, when the solution is cooled, the longer the heating has lasted. With a more concentrated solution of aluminum acetate the temperature must be raised somewhat higher before turbidity occurs; but this solution also clears up when cooled.

"To determine the amount of alumina precipitated from an acetate solution by heating and the variation with the temperature, there were taken two equal portions of aluminum acetate made by mixing in the cold two solutions of alum and of lead acetate. One of these portions was raised to the boiling-point and filtered at once, while the other portion was precipitated by ammonia. The two precipitates were washed and dried; after which it appeared that the first weighed about half as much as the second.

"These observations may be very important for the makers of dyed fabrics for they use the hot solutions of alum and lead acetate in order to get as concentrated solutions of the mordant as possible. A great deal of alumina must precipitate, and the loss will be considerable if the solution is filtered at once. To

<sup>1</sup> *Annales de Chimie*, 74, 193 (1810).

avoid this it is necessary to let the solution cool completely before filtering or decanting off the mother liquor, and it is also necessary to stir vigorously so as to be certain that all the alumina redissolves. Unless these precautions are taken, the aluminum acetate will be very acid, which is probably the reason for usually adding chalk. It is nevertheless easy to prevent the precipitation of alumina when an aluminum acetate solution is heated, by adding alum. As is well known, alum dissolves alumina and therefore keeps the solution of aluminum acetate from becoming turbid. A large excess of acid will accomplish the same result."

"The precipitation of alumina on boiling and the redissolving at a lower temperature are facts which are of interest to the general theory of chemistry and which are rather exceptional. If the precipitation were due to volatilization of the acetic acid, the alumina would not redissolve when the temperature is lowered. As a matter of fact similar changes can be observed in a strongly acid solution or in hermetically sealed flasks. Since the precipitation does not depend on the volatilization of the acid, it is evident that it is due to the heat which wrenches apart the molecules of acid and alumina, carrying each out of the sphere of action of the other, and causing their separation. With less heat the same molecules come within each other's sphere of activity and combine."

Gay-Lussac is practically saying in other words what we now designate as reversible hydrolysis. In 1854 Crum<sup>1</sup> prepared colloidal alumina from a weaker and more basic solution than that used by Gay-Lussac. "By the continued action of heat on a weak solution of binacetate of alumina,  $\text{Al}_2\text{O}_3 \cdot (\text{CH}_3\text{CO}_2)_4(\text{OH})_2$ , a permanent separation of the constituents of the salt takes place, although no acid escapes and no alumina is precipitated. The properties of the alumina are at the same time materially changed. A solution of binacetate of alumina diluted so as to contain not more than one part of alumina in two hundred of water, was

<sup>1</sup> Jour. Chem. Soc., 6, 225 (1854).

placed in a closed vessel which was immersed to the neck in boiling water, and kept in that state day and night for ten days. It had then nearly lost the astringent taste of alum, and acquired the taste of acetic acid. Being afterwards boiled in an open capsule, acetic acid was freely given off, and when the boiling had continued about five hours (the loss of water being continually restored), the liquid was found to have retained not more than one-eleventh of its original quantity of acetic acid, or about one equivalent to five and a half of alumina."

The theory of this is very simple. Water will hydrolyze any salt until the product of the concentrations of the hydrogen and hydroxyl ions reaches a value of about  $10^{-14}$ . If either base or acid is very sparingly soluble, the hydrolysis will run farther than if both are strong electrolytes. Equilibrium will be reached much more rapidly if the solution is heated. Whether the insoluble base precipitates or remains in colloidal solution will depend on the conditions of the experiment. That hydrolysis has taken place can be shown in a number of different ways. Gay-Lussac deduced it from seeing the precipitated alumina and Crum from the change in the taste of the solution. One could measure the change in acidity in other ways than by the sense of taste. Debray<sup>1</sup> showed that if a dilute solution of ferric chloride is heated to 70° it no longer reacts with potassium ferrocyanide to form Prussian blue. The reason for this is that there is no more ferric salt in solution, it having been converted completely into colloidal ferric oxide. Colloidal ferric oxide is not blackened by hydrogen sulphide. On the other hand it is precipitated from apparent solution either by sodium sulphate or by sulphuric acid, a behavior which is distinctly not characteristic of ferric chloride. Wiedemann<sup>2</sup> has used the magnetic properties as a means of following the hydrolysis, because the atomic magnetism of the iron in colloidal ferric oxide is only one-fifth that of the iron in a strongly acid

<sup>1</sup> Comptes rendus, 68, 913 (1869).

<sup>2</sup> Pogg. Ann., 135, 218 (1868); Wied. Ann., 3, 45 (1878).

solution of ferric chloride. Colloidal solutions of the hydrous oxides can be obtained by hydrolysis of the acetates, nitrates, or chlorides; but not in general by hydrolysis of sulphates, because sulphuric acid precipitates the colloidal solutions more readily than does hydrochloric, nitric, or acetic acid.

In 1883 Liechti and Suida published some work on the hydrolysis of solutions of aluminum salts. Their original paper is not in the John Crerar Library, the Library of Congress, or the Library of the Franklin Institute. I have therefore made use of the lengthy abstract by J. J. Hummel.<sup>1</sup> With aluminum sulphate ( $\text{Al}(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , 200 g per liter) there was no visible hydrolysis on heating or on diluting. With  $\text{Al}_2(\text{SO}_4)_2(\text{OH})_2$  made from 200 g  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} + 31.82$  g  $\text{Na}_2\text{CO}_3$  per liter, there was no visible change on heating; but a precipitate formed when the solution was diluted fourteenfold. With a solution three-quarters as concentrated, there was no visible change on heating, but dissociation took place on diluting tenfold. Since three-fourths of fourteen is ten and a half, this shows the error in determining the beginning of visible hydrolysis. With  $\text{Al}_4(\text{SO}_4)_3(\text{OH})_6$ , made from 200 g  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} + 45.7$  g  $\text{NaHCO}_3$  per liter a jelly was formed on heating and a precipitate remained on cooling. Diluting to one-half caused a precipitate to appear in the cold. With  $\text{Al}_2(\text{SO}_4)(\text{OH})_4$ , made from 300 g  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} + 151.3$  g  $\text{NaHCO}_3$  per liter, the solution kept only a short time. The general results are that hydrolysis takes place more readily on heating and on diluting, the more basic the solutions. The statement is made that sodium sulphate accelerates the dissociation. If this is true, it must be because the sodium sulphate decreases the hydrogen ion concentration by reacting with the sulphuric acid to form acid sodium sulphate. Since sodium sulphate coagulates colloidal alumina, it may be that it has practically no effect on the hydrolysis; but causes the precipitate to become visible sooner. In other places Liechti

<sup>1</sup> Jour. Soc. Chem. Ind., 2, 537 (1883).

and Schwitzer<sup>1</sup> say that they have proved that sodium sulphate retards the decomposition. There must be a misprint somewhere. A retarding of the decomposition would be more in line with the observation by Schmid<sup>2</sup> that sodium sulphate retards the precipitation of alumina by sodium carbonate.

With what they call a sulpho-acetate,  $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)_4$ , made from 200 g  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  + 227.6 g  $\text{Pb}(\text{CH}_3\text{CO}_2)_2$  per liter, a precipitate formed on heating to  $90^\circ$  and a jelly on heating to  $100^\circ$ . The solution cleared up on cooling. There was no precipitate on diluting sixtyfold. On adding sodium bicarbonate to this so-called sulpho-acetate, Liechti and Suida obtained solutions of what they called basic sulpho-acetates, from  $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)_3(\text{OH})$  down to  $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)(\text{OH})_3$ . There is no real reason for assigning these formulas to these solutions. In the first place there is no obvious reason why the sodium bicarbonate should take acetate rather than sulphate out of the aluminum salt. It would be distinctly more reasonable to consider the basic compounds as varying from  $\text{Al}_4(\text{SO}_4)(\text{CH}_3\text{CO}_2)_4(\text{OH})_2$  to  $\text{Al}_2(\text{CH}_3\text{CO}_2)_3(\text{OH})_3$ . Probably the reason for not doing this was that these solutions did not behave like basic acetate solutions obtained by adding sodium bicarbonate to aluminum acetate; but that does not prove anything because these latter solutions do not contain sodium sulphate. In the second place there is no reason to suppose that Liechti and Suida ever had a sulpho-acetate solution. The so-called sulpho-acetate solution was undoubtedly merely a mixture of  $\frac{1}{3} \text{Al}_2(\text{SO}_4)_3$  and  $\frac{2}{3} \text{Al}_2(\text{CH}_3\text{CO}_2)_6$ . Similarly there is no satisfactory evidence of the existence of any of the alleged basic compounds. They may perfectly well have been aluminum sulphate or aluminum acetate or a varying mixture of both with peptized alumina. Liechti and Suida undoubtedly thought they were dealing with true basic salts because of

<sup>1</sup> Mitt. techn. Gewerbe-Museums in Wien, Sektion für Färberei, 3, 59, 60 (1888).

<sup>2</sup> Jour. Soc. Chem. Ind., 14, 654 (1895).

their getting an apparent solution; but it is quite evident even from the abstract that they know nothing about colloidal solutions. The formulas which are written therefore indicate the relative amounts of sodium bicarbonate which have been added to the original solution and nothing more than that. This point seems to have been overlooked by all the people who have discussed this work.

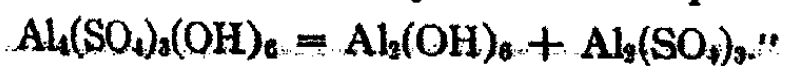
The so-called basic sulpho-acetates all formed jellies on heating and all formed precipitates on dilution, the temperature at which the first turbidity occurred being lower the more basic the solution. Less water had to be added to cause precipitation as the solution became more basic. With straight aluminum acetate, made from 200 g  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  + 341.4 g  $\text{Pb}(\text{CH}_3\text{CO}_2)_2$  per liter, there was no turbidity on heating and no precipitation on cooling. This result does not contradict that of Gay-Lussac because he was working with a more dilute solution. All the so-called basic aluminum acetates formed precipitates or jellies on heating which did not dissolve when the solutions were cooled. The one with the alleged formula  $\text{Al}_2(\text{CH}_3\text{O}_2)_4(\text{OH})_2$  precipitated on dilution; but the more basic ones did not. This may only be a question of a time factor. If not, sodium acetate must peptize alumina strongly.

By adding sodium carbonate to aluminum chloride, solutions were obtained having the analytical compositions,  $\text{Al}_2\text{Cl}_5(\text{OH})$ ,  $\text{Al}_2\text{Cl}_4(\text{OH})_2$ ,  $\text{Al}_2\text{Cl}_3(\text{OH})_3$ ,  $\text{Al}_2\text{Cl}_2(\text{OH})_4$ . None of these solutions become turbid either on heating or on diluting. Liechti and Suida were not able, however, to make these alleged solutions synthetically. "The solubility of aluminum hydrate in aluminum chloride was tested, and the following remarkable results were obtained. To a solution of  $\text{Al}_2\text{Cl}_6$  a quantity of aluminum hydrate was added sufficient to form the basic salt  $\text{Al}_2\text{Cl}_4(\text{OH})_2$ . The alumina dissolved only on heating and the solution remained clear on cooling. To this clear solution a further quantity of aluminum hydrate was added sufficient to form the compound  $\text{Al}_2\text{Cl}_2(\text{OH})_4$ . It was, however, found that no more alumina could be made to

dissolve, the precipitate even increasing, and on filtering it was found that the solution contained equal molecules of normal  $\text{Al}_2\text{Cl}_6$  and of  $\text{HCl}$ . The nascent  $\text{Al}_2\text{Cl}_2(\text{OH})_4$  had apparently decomposed according to the following formula:



In the same way it was proved that, on adding aluminum hydrate to  $\text{Al}_2(\text{SO}_4)_3$  solution sufficient to produce the basic compound  $\text{Al}_4(\text{SO}_4)_3(\text{OH})_6$ , no alumina at all dissolved, the filtrate only containing  $\text{Al}_2(\text{SO}_4)_3$ . Here, too, we must suppose that the nascent basic compound decomposes as follows:



We know that hydrous ferric oxide, if present in excess, will remove from suspension all the chromic oxide<sup>1</sup> peptized by caustic alkali; but nobody has studied the removal from suspension of a substance by an excess of itself, unless perhaps we have such a case in the Bayer process for the purification of alumina. Since Liechti and Suida were obsessed with the idea of basic compounds, they made no experiments to see whether addition of sodium chloride would cause more alumina to go into apparent solution. According to Schmid<sup>2</sup> sodium sulphate retards the precipitation of alumina.

A whole series of so-called basic nitrate solutions were made up by adding sodium bicarbonate to aluminum nitrate solutions. None of these solutions became turbid either on heating or on dilution. The sum total of all these experiments is that basic aluminum acetate solutions hydrolyze very readily because the resulting acetic acid is a weak acid; that basic aluminum sulphate solutions become turbid because of the coagulating action of the sulphates, this more than counterbalancing the effect due to the strength of sulphuric acid; and that basic aluminum chlorides and nitrates do not become markedly turbid because the acids are strong ones having low coagulating powers.

Although Liechti and Suida got no cloudiness with their

<sup>1</sup> Nagel: Jour. Phys. Chem., 19, 331 (1915).

<sup>2</sup> Jour. Soc. Chem. Ind., 14, 654 (1895).



aluminum sulphate solution on heating, that may have been a question of concentration or of time for Naumann<sup>1</sup> reports that "when a solution of potash alum is heated to the boiling point of water, a white precipitate is formed, which, after washing with water, is an amorphous powder, with an admixture of glittering laminae, and dissolves with difficulty in strong hydrochloric acid, but easily in potash. The precipitate contains 31.2-32.6 percent of alumina, about 11 percent of potash, 30-40 percent of sulphuric acid, and water; and is therefore a more or less basic compound of alumina, potash, and sulphuric acid, with water. It was found that with pure alum solutions the decomposition was most rapid at first, gradually becoming less for equal intervals of time, so that a state of equilibrium in the liquid was reached only after a very long time. Dilution of the solutions favored decomposition. Free sulphuric acid, added to alum solutions, prevented the decomposition, partially or entirely, according to the amount added. Neutral potassium sulphate, on the contrary, expedited the decomposition."

There is a good deal of uncertainty as to what compounds are formed when salts of aluminum are boiled or are treated with soda. Cajar<sup>2</sup> states that the action of soda on cold aluminum sulphate solution gives a white precipitate which covers well; whereas a more transparent precipitate is obtained when the soda is added to a hot sulphate solution. Underwood<sup>3</sup> states that alumina precipitated cold with sodium carbonate contains basic sulphate and dries soft and powdery; but that it dries horny when precipitated hot. Jennison<sup>4</sup> says that the hydrate of aluminum,  $Al_2(OH)_6$ , "is produced when caustic soda or potash, ammonium hydrate or carbonated alkalies is added to a solution of an aluminum salt; it is soluble in caustic alkalies, and therefore is usually obtained by

<sup>1</sup> Ber. deutsch chem. Ges., 8, 1639 (1875); Jour. Chem. Soc., 29, 682 (1876).

<sup>2</sup> Zeit. angew. Chem., 27, 793 (1911).

<sup>3</sup> Underwood and Sullivan: "Printing Inks," 81 (1915).

<sup>4</sup> "The Manufacture of Lake Pigments from Artificial Colours," 51 (1900).

means of the carbonates. When produced from cold, dilute solutions, it is of a transparent, gelatinous nature; but, on heating, becomes opaque and more contracted in bulk. With carbonated alkalies it is much denser and is very lumpy, owing to the reaction being incomplete. Aluminum hydrate when dried, forms a hard, white, horny substance, which has the composition of  $\text{Al}_2(\text{OH})_6$ , and only on ignition is the whole of the water driven off, leaving  $\text{Al}_2\text{O}_3$ ."

According to Knecht, Rawson and Loewenthal<sup>1</sup> a crystallized basic sulphate,  $\text{Al}_2(\text{SO}_4)_2(\text{OH})_2$ , has been placed on the market by Messrs. Peter Spence and Co., Ltd. Schlumberger<sup>2</sup> claims that there is one basic sulphate of aluminum. On adding 4.5 mols of caustic potash to a solution containing one mol of aluminum sulphate, the supernatant liquid was still distinctly acid. On adding 5 mols KOH the solution was neutral and contained no aluminum salt. On adding 6 mols KOH the supernatant liquid was alkaline and contained some alumina, presumably as potassium aluminate. The precipitate must therefore analyze for  $(\text{Al}_2\text{O}_3)_2\text{SO}_3 \cdot x\text{H}_2\text{O}$  where  $x$  is not less than six. Actually it came out seven, so Schlumberger writes the formula of the basic salt  $(\text{Al}_2\text{O}_3)_2 \cdot \text{H}_2\text{SO}_4$ . Of course, it will be noticed that he analyzed a precipitate obtained only under one set of conditions. While it may be that he was dealing with a definite compound, there is nothing in his experiments to prove it. He should have analyzed the precipitate after adding three or four mols of caustic potash and have shown that it had exactly this same composition. Then his results could have been accepted as proving something. This is the more necessary because many basic aluminum sulphates are to be found in the books.<sup>3</sup> Böttinger contributes a new one of his own by evaporating repeatedly to dryness a mixture of aluminum sulphate and sodium chloride at  $130^\circ$ - $140^\circ$ . This one analyzes for  $\text{Al}_2\text{O}_3 \cdot \text{SO}_3 \cdot 6\text{H}_2\text{O}$  or

<sup>1</sup> "A Manual of Dyeing," 225 (1910).

<sup>2</sup> Bull. Soc. chim. Paris, [3] 13, 41 (1895).

<sup>3</sup> Böttinger: Liebig's Ann., 244, 224 (1888).

$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  if we adopt Schlumberger's way of writing the formula.

#### Adsorption of Aluminum Sulphate by Wool

Since the different salts of aluminum hydrolyze of themselves under suitable conditions, they should hydrolyze even more readily in presence of a textile fiber which adsorbs the alumina and they do as a matter of fact. In so far as the acid radical is also adsorbed, there may be minor complications and the matter may seem less simple than it really is.

When wool is treated with aluminum sulphate,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , less than about five percent on the wool, the bath is exhausted completely, all the alumina and all the sulphuric acid being taken up.<sup>1</sup> With higher concentrations, more and more aluminum sulphate is left in the bath. There has been some discussion whether the wool takes up aluminum sulphate or alumina and sulphuric acid in the cases when the bath is exhausted completely. When wool mordanted in this way is boiled with water, the wash water is always acid, sulphuric acid being removed slowly and alumina left behind. This has been considered by von Georgievics<sup>2</sup> as a proof that the sulphuric acid is free. While this may be true, it does not follow, because the adsorbed aluminum sulphate might be hydrolyzing. It is much wiser to admit frankly that we have no way at present of deciding this point. In case the acid is not combined in definite proportions, the next problem is whether it is adsorbed by the alumina, by the wool, or by the two in some unspecified ratio.

Ganswindt<sup>3</sup> gives some data by Fürstenhagen and Appleyard<sup>4</sup> on the mordanting of wool by potash alum, which are reproduced and extended in Table I.

<sup>1</sup> Liechti and Schwitzer: Mitt. techn. Gewerbe-Museums in Wien, Sektion für Färberei, 3, 47 (1886).

<sup>2</sup> Chem. Centralblatt, 1895, 402; Binz and Rung: Zeit. angew. Chem., 1908, 628.

<sup>3</sup> "Theorie und Praxis der modernen Färberei," II, 83 (1902).

<sup>4</sup> Jour. Soc. Dyers and Colourists, 1888, 105.

TABLE I  
25.4% sulphuric acid in potash alum.

Potash alum referred to wool Concentration percent	Sulphuric acid referred to potash alum		Sulphuric acid referred to wool	
	Wool percent	Solution percent	Wool percent	Solution percent
5	25.4	0.0	1.27	0.0
10	22.1	3.3	2.21	0.3
15	14.6	10.8	2.19	1.6
20	11.0	14.4	2.20	2.9

In the first column are the amounts of potash alum referred to the weight of wool. In the second and third columns are the percentages of sulphuric acid in the total amount of alum in the wool and the bath respectively. At 5% alum all the sulphate is taken up, but with higher concentrations of alum more of the sulphuric acid stays in the bath. Since determinations on the alumina adsorption are not given, we cannot tell to what extent alumina is adsorbed more than sulphuric acid. Since this method of presentation is not the usual one, I have added two columns to show the percentage of sulphuric acid referred to wool, taken up by the wool and left in the bath respectively. If these figures are to be trusted, the amount of sulphate adsorbed by the wool is practically constant when the bath contains 10%-20% alum referred to the wool. It is probable that this is not strictly true.

Knecht<sup>1</sup> comments on these data as follows: "It is a prevalent opinion that when wool is boiled with aluminum sulphate, for instance, the salt is decomposed by the fibre in such a manner that aluminum hydrate and sulphuric acid are formed, of which the former is assimilated by the fibre, while the latter remains in solution. Others again assume that an insoluble basic sulphate of alumina is formed on or in the fibre. Quantitative determinations, carried out by Fürstehagen and Appleyard, show that when wool is boiled with a solution of alum no free acid remains in solution when the

<sup>1</sup> Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 58 (1910).

amount of alum does not exceed five percent of the weight of the wool. When larger amounts are used, a basic sulphate of alumina is fixed on the fibre. Now it has always been shown that wool possesses a considerable affinity for both acids and bases, and, in its whole behavior it evidences the properties of an amido acid—that is a substance possessing simultaneously basic and acid properties. This would explain in a satisfactory manner the fixation of both the acid and basic constituents of the alum, but in what form these are fixed still remains a matter of conjecture. It is not improbable that the phenomenon is due to actual chemical combination with the fibre or with certain constituents of the latter; just as lead or mercury, when absorbed by the system, enters into chemical combination with the albuminoids in the various organs. That a hydrate is not formed is conclusively shown in mordanting wool with copper salts. The fibre assumes a green color; but copper oxide, when boiled, is at once dehydrated and transformed into black copper oxide. If copper hydrate had been formed, the fibre would be black whereas it is green, and remains so even after prolonged boiling.”

It has already been shown that Fürstenhagen and Appleyard have not proved by quantitative determinations that a basic sulphate of alumina is fixed on the fibre. They have proved that both alumina and sulphuric acid are taken up by the fibre; but nothing more. Knecht seems to realize this unconsciously because he himself admits that it remains a matter of conjecture in what form the acid and basic constituents of the alum are fixed. That is true; but that is quite a different thing from showing that a basic aluminum sulphate is fixed on the fibre. Knecht's argument in regard to the copper hydrate is fallacious because hydrous copper oxide does not necessarily turn black when heated to 100°. Tommasi<sup>1</sup> showed that when a little hydrous manganous oxide is precipitated with the hydrous copper oxide, the latter does not turn

---

<sup>1</sup> Bull. Soc. chim. Paris, [2] 37, 197 (1882); Comptes rendus, 99, 37 (1884).

black when boiled. Blucher and Farnau<sup>1</sup> found that a similar stabilization of the blue color could be obtained by adding hydrous oxides of nickel, cobalt, aluminum, chromium, and magnesium. With zinc there was some stabilization but practically none with mercury. If the blue color is due to the state of subdivision of the copper oxide, anything which will prevent it from agglomerating will keep it blue. Schenck<sup>2</sup> has shown that a mixture of the oxides of copper and alumina containing about five percent copper oxide can be heated in a blast lamp without turning black. Owing to the lower copper content the color is a light grayish blue. With ten percent copper oxide, the blue color was deeper and withstood heating in a Bunsen burner but showed signs of turning black when heated in the blast lamp. During the winter of 1920-21 Mr. R. K. Parsell repeated Mr. Schenck's experiments and, after heating, dissolved out as much alumina with caustic soda as he could without getting any blackening. In this way he was able to get a powder which was a beautiful deep blue and which contained approximately seventy-five percent cupric oxide and twenty-five percent alumina. If one insisted on writing a formula for this, it would be approximately  $(\text{CuO})_4 \text{Al}_2\text{O}_3$  which is rather absurd. There are not only no indications of a definite chemical compound; but, after standing for a year the powder has changed from blue to green. We do not know whether it will go black in time or not.

According to Havrez<sup>3</sup> and to von Georgievics<sup>4</sup> the amount of sulphuric acid taken up by wool from an aluminum sulphate or an alum bath increases relatively to the wool at high concentrations until at twenty-four percent alum referred to the wool, the alumina and the sulphuric acid are taken up in the same relative amounts as they occur in aluminum sulphate.

---

<sup>1</sup> Jour. Phys. Chem., 18, 629 (1914).

<sup>2</sup> Ibid., 23, 283 (1917).

<sup>3</sup> Chem. Centralbl., 1874, 696; Cf. Liechti and Hummel: Jour. Soc. Chem. Ind., 13, 226.

<sup>4</sup> Jour. Soc. Chem. Ind., 14, 653 (1895).

At higher temperatures, relatively more sulphuric acid is taken up. I have never seen the original data and the abstracts are confusing and to some extent contradictory. Havrez<sup>1</sup> claims that with high alum concentration, the peptizing action of the alum on the alumina is so great that less alum is taken up than at lower concentrations. If this is true, the amount of alumina adsorbed passes through a maximum. On the other hand he apparently based his conclusion on the fact that wool mordanted in concentrated alum solutions did not dye to so deep a shade and this may be an effect of the sulphate taken up. Liechti and Hummel, however, "disagree with his assertion that an excess of alum acts like an acid which dissolves the alumina." Dreaper<sup>2</sup> who gets Havrez's name wrong, says that "Harvey pointed out in 1872 that in the case of very concentrated solutions of alum, more sulphuric acid than alumina is absorbed. This has been recently confirmed by von Georgievics. It appears that with a 24 percent solution of alum [referred to wool], and a proportion of water fibre of 30:1 alumina and sulphuric acid are taken up in their normal proportions. The affinity of wool for acid is stronger in dilute solutions and stronger for the alumina in strong solutions. The relative curves cross each other at 24 percent." There must be a misprint in the next to last sentence of this quotation, the words acid and alumina being transposed.

Havrez<sup>3</sup> states, and Liechti and Hummel confirm him that addition of acid (presumably sulphuric acid)<sup>4</sup> is beneficial with such low concentrations of alum as one percent on the wool. Since all the alumina is taken up at these concentrations, the object of adding the acid cannot be to increase the adsorption. The statement is made that with low concentrations of alum the bath becomes alkaline, in which case the

<sup>1</sup> Jour. Chem. Soc., 26, 206 (1873).

<sup>2</sup> "The Chemistry and Physics of Dyeing," 62 (1906).

<sup>3</sup> Jour. Soc. Chem. Ind., 13, 226 (1894).

<sup>4</sup> Cf. Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 237 (1910).

acid is added to counteract this. It is not clear whether the alkalinity is due to lime in the wool reacting with sulphuric acid, to ammonia going out from the wool, or to a partial adsorption of sulphuric acid from the potassium sulphate of the alum. This last hypothesis could be tested by running similar experiments with aluminum sulphate. Liechti and Suida<sup>1</sup> state that alum is not quite as good a mordant as aluminum sulphate, though the difference is not marked. This may seem to contradict their alleged previous statement that sodium sulphate increases the hydrolysis of aluminum sulphate on boiling; but the contradiction disappears if we postulate, which seems reasonable, that the sodium sulphate, though increasing the hydrolysis of the aluminum sulphate, also increases the relative amount of sulphuric acid taken up by the wool. The first would be beneficial and the second harmful and we do not know to what extent the two balance, or even whether this is the true explanation.

One objection to alum or aluminum sulphate as a mordant is that the sulphate coagulates the hydrolyzed salt so readily that very perceptible amounts of alumina or of basic salt are precipitated in the bath or on the wool in such a form that it rubs off. It seems as though this could be got round by heating the solutions more slowly. A simpler method of getting round this difficulty is to use aluminum salts of organic acids, which hydrolyze more readily than the sulphate because the acids are weaker, and yet which keep the colloidal alumina peptized in a finer form.

#### Adsorption of Aluminum Tartrate, etc., by Wool

This was done more than a century ago by adding tartar (acid potassium tartrate) to a solution of alum.<sup>2</sup> "To impregnate wool or woollen cloth with the aluminous basis, it is commonly boiled in water, with from one-fourth to one-sixth of its weight of alum, and from one-twelfth to one-sixteenth of its

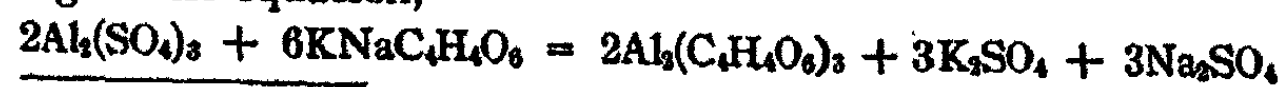
<sup>1</sup> Jour. Soc. Chem. Ind., 5, 526 (1886).

<sup>2</sup> Bancroft: "Philosophy of Permanent Colours," 1, 384 (1813).



weight of crude tartar, putting the latter first into the water, and, afterwards, the powdered alum: the heat of the water being gradually raised, is kept at the boiling point for an hour and a half, or two hours, during which the cloth is turned through the boiling liquor on a winch, that the mordant may be equally applied; and being afterwards taken out and drained, it is commonly left until the next day, and then rinsed in clean water, for dyeing. In the early collection of recipes, printed in 1605, and already mentioned, sour bran liquor is commonly directed to be employed in this way with alum; and it seems to have answered the purpose of tartar, which, when it came to be generally used in this way with alum; was supposed by the older dyers to do good by softening and correcting the acrimony of the latter: probably, however, the purposes which it answers, are not yet clearly ascertained; one of them seems to be, that of increasing the solubility of alum, and enabling it more completely and intimately to penetrate the fibres of the wool, with which it moreover enters into a permanent union, and thereby contributes efficaciously to modify, vary, and in some cases to brighten the colours with which it is employed, as will be seen hereafter."

Liechti and Suida<sup>1</sup> have studied the behavior of aluminum tartrate. Starting with an amount equivalent to eight percent aluminum sulphate,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ , referred to the wool, the whole of the alumina was fixed firmly on the wool. On treating the wool with hot water, the wash water became acid, showing that some tartaric acid was also taken up. The normal tartrate can be replaced without detriment by a mixture of one molecular weight of aluminum sulphate with 1.5-3.0 molecular weights of cream of tartar. If the normal tartrate is prepared by double decomposition, using the normal potassium sodium tartrate (Rochelle or Seignette salt) according to the equation,



<sup>1</sup> Mitt. techn. Gewerbe-Museums in Wien, Sektion für Färberei, 3, 48 (1886); Jour. Soc. Chem. Ind., 4, 526 (1886); Kaecht, Rawson and Loewenthal: "A Manual of Dyeing," 237 (1910).

the results were not as good as those obtained with the pure tartrate or with alum and tartar, in which latter case the bath contains some acid potassium sulphate in addition to the aluminum tartrate. "Since the general practical experience of dyers is that wool is better mordanted in an acid bath, it was thought possible, perchance, to replace the cream of tartar by an acid, sulphuric acid for instance. Experiment showed, however, that although a small addition of sulphuric acid (1 mol) increases slightly the amount of alumina absorbed by the fibre, it cannot replace the cream of tartar. Since the addition of a larger amount of sulphuric acid (3 mols) yields very unsatisfactory colors although it hinders the dissociation of the mordant solution, it is evident that the beneficial action of the cream of tartar cannot be ascribed merely to its retarding the dissociation of the mordant." The explanation undoubtedly is that the use of tartrate cuts down the degree of adsorption of the sulphuric acid.

"An experiment was made accordingly with a view to determining whether the tartaric acid used along with aluminum salts played the rôle of a carrier, so that it might be possible to use any free acid along with only a small quantity of tartaric acid. The result obtained, however, proved that the tartaric acid plays no such intermediary part in mordanting wool with aluminum salts; on the contrary, a considerable amount of tartaric acid must be present (at least half the theoretical amount necessary to form aluminum tartrate) in order to fix on the wool sufficient alumina to yield full, bright colours."

Knecht<sup>1</sup> evidently believes in starting with aluminum sulphate. "The aluminum mordant *par excellence* for wool is aluminum sulphate, either alone or in conjunction with acids or acid salts. In some cases the sulphate is used without any additions. Most generally, however, a mixture of the sulphate with tartar or tartar substitutes is required to obtain full and brilliant colours which do not rub off. These tartar substitutes are mostly sodium bisulphate or oxalates, or they con-

<sup>1</sup> Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 238 (1910).

sist of tartar which has been prepared with sufficient sulphuric acid to convert all the potassium into potassium sulphate. From the foregoing it appears that none of these 'substitutes' can replace the tartar completely because the action of the latter depends on the formation of aluminum tartrate by double decomposition. They have, of course, some effect, as has also sulphuric acid. For a full shade about 6 to 8 percent aluminum sulphate and 5 to 7 percent tartar (of the weight of the wool) are necessary. The quantity of tartar may be reduced to about half this amount, or it may be partly or even wholly replaced by sulphuric, hydrochloric, oxalic acid, bisulphate of sodium, etc., with very good, although not equally fine, results. About 4 percent of sulphuric acid (of the weight of the wool) is used, if the amount of water does not exceed 50 to 60 times the weight of the wool; otherwise more acid must be applied. When sulphuric acid has been used in mordanting it is often beneficial to add about 5 percent sodium acetate to the ultimate dye-bath to neutralize the mineral acid which always remains in the wool fibre (and which otherwise would be converted into potassium sulphate if tartar had been employed). The mordanting bath is prepared with the necessary quantities of aluminum sulphate and tartar (or its substitutes), and the wool is entered at a low temperature. During one and a half hours the bath is heated gradually to boiling, and boiled for half an hour more. When the bath has cooled down, the wool is taken out and thoroughly washed in water; boiling out with water is beneficial. It has been shown that washing is absolutely necessary to remove all loosely adhering mordants and to prevent rubbing of the ultimate colour. The washing, moreover, removes some of the acid, which is absorbed by the wool, and would be injurious in dyeing."

I am inclined to believe that accurate experiments will show that the presence of sulphate in the mordanting bath is probably always detrimental.

Aluminum oxalate behaves very much like aluminum tar-

trate but is not quite so good. According to Knecht<sup>1</sup> aluminum acetate decomposes too readily to be used for wool; but this can hardly be the whole truth. The use of lactic acid instead of tartaric acid has also been suggested.

Matthews<sup>2</sup> has rather a hard time with the theory of mordants, chiefly because he copies with but slight changes from Ganswindt's book published in 1903. "The mordanting of the animal fibres with metallic salts is probably for the most part a chemical process, the metallic salts or oxide forming a chemical compound with the substance of the fibre. It is usually considered in the case of mordanting wool, for instance, with metallic salts, that the metal is precipitated in the fibre as the oxide or hydroxide; in certain methods of printing, this may be the fact, but in the ordinary processes of mordanting wool for dyeing, it cannot be considered that the oxide of the metal is directly precipitated in the fibre. It is possible, for instance, to mordant the wool by boiling in a bath containing a solution of alum, squeezing, and then passing through a bath containing ammonia water; this would cause the precipitation of aluminum hydrate on and in the fibre as an insoluble body. As an actual fact, however, the mordanting is not done in this manner, but is carried out by boiling the wool with a solution of alum and tartar, which it cannot be presumed would lead to the precipitation of aluminum hydrate."

Even with Ganswindt to fall back on in silence, this paragraph is quite extraordinary; but the clue is to be found elsewhere. Matthews<sup>3</sup> has evidently not understood any of the work of Liechti and Suida or of Knecht because he enters into an elaborate explanation that sodium chloride is dissociated electrolytically in water and thereby made more active, giving this as a help in understanding the theory of Knecht, although Knecht<sup>4</sup> himself speaks of hydrolytic dissociation,

---

<sup>1</sup> Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 237 (1910).

<sup>2</sup> "Application of Dyestuffs," 602 (1920).

<sup>3</sup> "Application of Dyestuffs," 588 (1920).

<sup>4</sup> Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 15 (1910).

and the case that Matthews is discussing is the decomposition of rosaniline hydrochloride into the free base and hydrochloric acid, which is not a case of electrolytic dissociation.

#### Adsorption of Alumina by Silk

Silk behaves towards alumina mordants very much as wool does, though less intensely. Knecht<sup>1</sup> states that "in silk dyeing alum has not been replaced yet by aluminum sulphate<sup>2</sup> probably owing to the circumstance that slightly basic alum decomposes more readily than basic sulphate on account of the ammonium or potassium sulphate present. . . . Aluminum sulphate-acetate and nitrate-acetate are used in a similar way. . . . During the steeping process the silk absorbs basic sulphates or basic sulphate-acetates or nitrate-acetates. By the subsequent treatment with water or silicate of soda or soap the basic salts are decomposed and aluminum hydroxide is precipitated in the fibre." Heermann<sup>3</sup> claims to have proved that, with silk, the basic mordants of aluminum, chromium, iron, and tin are present as hydrous oxides and not as basic salts. Heermann<sup>4</sup> has discussed the various theories of mordanting and mentions favorably what he calls the catalytic theory according to which the fibers bring about the hydrolytic decomposition of the mordanting salts catalytically. It is easy enough to see what he has in mind, for the hydrolysis of the aluminum salts is increased by wool or silk; but this cannot properly be called catalytic because the fibre is not in the same condition after the process as before. It is mordanted.

Heermann also advances a theory of his own which he calls the ionatic theory of mordanting. He considers mordanting "as the electrolytic precipitation of certain ion complexes in consequence of the preponderating electro-affinity of the fibres (as opposed to that of the cations of the mordant) and

<sup>1</sup> Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 238 (1910).

<sup>2</sup> Both are used according to Ganswindt: "Theorie and Praxis der modernen Färberei," II, 18 (1903).

<sup>3</sup> Chem. Centralblatt, 1905, I, 128.

<sup>4</sup> Ibid., 1904, II, 674.

in consequence of the [electrolytic?] dissociation of the mordant which is perhaps increased by the catalytic power of the fibres or of the cations of the mordant."

This can mean anything or nothing, so Heermann explains his views in more detail. "There are fibres of greater and lesser electro-affinity<sup>1</sup> and mordants of greater and lesser electrolytic dissociation. The affinity of a mordant to a fibre reaches its maximum when the greatest dissociation of the mordant coincides with the greatest difference between the electro-affinities of the fibre and of the ions of the mordant. The fibre, having the greater electro-affinity discharges successively the ions or ion-complexes of the mordant, since these have a lesser electro-affinity. The ion-complexes of the mordant, when thus discharged deposit themselves, while in the nascent, state, uniformly on the fibre and are at first held there in a labile state along with the acid. Washing removes most of the acid of the mordanting salt and the resulting base is fixed fast to washing." It is perhaps not surprising that no further use has been made of this theory even by the enthusiastic author.

#### Adsorption of Alumina by Cotton

Over a century ago it was pointed out<sup>2</sup> that "the attraction between aluminous basis and the fibres of linen and cotton is much weaker than that which subsists between the same basis and the fibres of wool and silk." The knowledge that alum cannot be used by itself to mordant cotton turns back to a very early period. Bancroft<sup>3</sup> states that "when a solution of alum is applied to calico which has received no impregnation, it will not easily be decomposed; but, on the contrary, a great part of it will again crystallize, so soon as the water which held it in solution has evaporated; and none but feeble colours can be raised upon such a basis. But when calico has been impregnated by such astringent and animal matters as are ob-

<sup>1</sup> [He is referring to Bodländer and Abegg's theory of electro-affinity.]

<sup>2</sup> Bancroft: "Philosophy of Permanent Colours," 2, 148 (1813).

<sup>3</sup> "Philosophy of Permanent Colours," 1, 357; 2, 242 (1813).

tained from myrobalans and buffaloes' milk, the alum will not only be decomposed, but the alumine will combine with the astringent and oily matters so obtained, and a basis will be laid for a colour almost as durable as the 'Turkey red.'

"For the common madder red, linen or cotton, after being boiled in a weak lixivium of potash or soda, and well rinsed and dried, is to be macerated in a decoction of powdered galls, employed after the rate of four ounces to every pound of linen or cotton to be dyed; and being equally impregnated with the soluble matter of the galls and afterwards dried, the linen or cotton is to be alumed, by soaking it thoroughly in a saturated luke-warm solution of alum, employed also at the rate of four ounces to each pound of linen or cotton; after having previously neutralized the excess of its acidity, by adding to the solution one ounce of soda for every pound of alum: this being done, and the linen or cotton moderately and equally wrung or pressed, it is to be well dried, and afterwards alumed a second time, dissolving for that purpose half as much alum as for the first aluming, and adding to it the residue of the former solution. After this second aluming, the linen or cotton is to be again well dried, and then rinsed, to remove any superfluous part of the alum which may not have been united thereto. By substituting the acetate of alumine (formerly described) for the solution of alum, just mentioned, a more beneficial effect might be obtained; but it would be attended with a considerable increase of expense.

"The use of galls, in this operation, will be readily conceived, by recurring to what I have mentioned, at p. 356 and 357 of my first volume, concerning the effect of myrobalans, when employed by the Hindoos, in causing a more copious precipitation, and a more intimate union of the earth of alum, in or with the calico which had previously imbibed their astringent matter. That this is the only use of galls so employed, I presume, because I have found, by repeated trials, that when employed with madder in the dyeing operation, they add nothing to the durability of the colour.



"For every other purpose, except that of decomposing the alum, and increasing the precipitation of alumine, and, perhaps, its closer union with the fibres of cotton, galls appear to do harm rather than good with madder, by diminishing the vivacity of its colour, and giving it a brownish tinge, without the smallest increase of its durability; on the contrary, I have observed, that when calico printed with acetate of alumine was divided, and one half dyed with madder only, and the other with madder and galls, the colour of the latter, besides a considerable degradation, was injured by being boiled with soap and also by being exposed to the weather sooner, and in a degree considerably greater, than the half which had been dyed with madder only."

Napier<sup>1</sup> points out that "alum forms but a weak mordant for cotton goods, owing, probably, to the strong attraction which the sulphuric acid has for the alumina; there are three proportions of acid to every two of alumina. But if we neutralise a portion of the acid, so that no more remains than is necessary to hold the alumina in solution, which, according to experiment is not above a third of the acid contained in the common alum, its properties as a mordant are greatly improved. This may be done by taking a quantity of carbonate of soda in solution, and adding this gradually to the alum solution, stirring all the time: the alumina is at first precipitated but by keeping up the agitation, the precipitate again dissolves: continue until all the precipitate is redissolved. In this state alum is a more powerful mordant for cotton, as the base is held more feebly by the sulphuric acid and is readily detached by the superior affinity of the cloth to form a mordant; and thus prepared, it is perfectly pure—any iron formerly present is precipitated in the process. Alum in this state is known by the name of cubical or basic alum, from the form in which it crystallises. We have already referred to Roman alum being superior to other alums."

---

<sup>1</sup> "A Manual of Dyeing," 120 (1975).



Very recently Tingle<sup>1</sup> has claimed that alumina is not adsorbed by cellulose either from aluminum sulphate or basic aluminum sulphate solution. The first statement is not new and the second is probably not correct as a general one though it may be true for the particular experimental conditions. There is nothing to show that Tingle appreciated the necessity of having peptized alumina in his solution or that he did have it.

Aluminum acetate is usually used for mordanting cotton both in dyeing and printing.<sup>2</sup> "The most common, and we believe the best method of using alumina as a mordant for cotton, is by substituting acetic acid for sulphuric acid in combination with it. The acetate of alumina has several advantages over the sulphate: 1st, the acetic acid is not so hurtful in its action upon the vegetable colouring matters; 2nd, it holds the alumina with much less force than sulphuric acid, and consequently yields it much more freely to the cloth; and 3rd, being volatile, a great portion of the acid flies off during the process of drying. When strong colours are wanted, and the mordant is of such a nature as will admit of being dried, it is better to dry the cloth from the mordant previous to dyeing. This last property of acetic acid is, therefore, very convenient, as it frees the cloth from any superfluous acid which may have been in the mordant; besides, it has been found that during the drying by heat, the soluble acetate is converted into a less soluble subacetate. We may here put the dyer in mind that when goods containing volatile acids are drying, no other kind of goods should be allowed to be in the same apartment, as the acid will be absorbed by them, and will affect almost any colour that either has been or may be put upon them. Many unpleasant and also expensive consequences occur from the neglect of these precautions."

Bancroft<sup>3</sup> gives an interesting account of the early use of aluminum acetate in calico printing. "By thus substituting the acetic for the sulphuric acid, in the aluminous mordant

<sup>1</sup> Jour. Ind. Eng. Chem., 14, 198 (1922).

<sup>2</sup> Napier: "A Manual of Dyeing," 121 (1875).

<sup>3</sup> "Philosophy of Permanent Colours," 1, 365 (1813).

lately described, several considerable advantages are gained. The acetate of alumine being much more soluble in water than common alum, the liquor will contain a much larger proportion of alumine, than could be otherwise suspended in it; and with this advantage, moreover, that it will not be liable to form crystals in or upon the linens or cottons in drying, as would happen with a solution of common alum, the acetate of alumine being incapable of crystallization. I may add also, that the acid of vinegar being volatile, and having a much weaker attraction for its earthy basis than the sulphuric acid has, the former will be speedily separated and carried off, especially by the heat of the stoves employed for drying the pieces printed with it, and will leave behind the alumine which it has dissolved, and which, being no longer encumbered by any other attraction, will yield itself wholly to that, which subsists between it, and the fibres of linen or cotton, and will unite with them more copiously and firmly than it otherwise could do, and be thereby enabled more strongly to attract and fix the colouring matters in the dyeing vessel. This, however, will only prove true, so far as the sulphate of alumine has been really decomposed by the acetate of lead, or so far as the alumine has been combined with the acetic instead of the sulphuric acid.

"As the practice of calico-printing has been but lately introduced into Europe, and as the acetic aluminous mordant does not appear to have been previously known in any other country, we might have expected that its discovery in this, would have been deemed a matter so important, as to have constituted an era in the history of the art; and, therefore, I was not a little surprised in finding that no writer had mentioned, and that no calico-printer, of whom I have inquired, could inform me, at what time, or by whom, this mordant was first employed, as the basis of red and yellow colours in calico-printing. My wonder has, however, ceased on this subject, since I have inspected a considerable number of recipes for making the several mixtures employed as mordants, soon after the business of calico-printing began to be carried on with

some degree of success here, and in other parts of Europe. In one of these which seems to have been the earliest, alum, sal ammoniac, saltpetre, red orpiment, and kelp, were directed to be mixed with water. In another, which probably followed this, it was directed that these ingredients should be dissolved in vinegar. In a succeeding recipe, a little sugar of lead was directed to be employed, but in a quantity too small to be of any considerable use; I mean one ounce of it for every pound of alum. Afterwards, the calico-printers, without any system or reasonable motive, appear in different instances to have added verdigrise, arsenic, corrosive sublimate, blue vitriol, litharge, and white lead. By stumbling upon the two last (which alone were of any use), it happened, where vinegar had been also employed, as it commonly was in some shape, that after a variety of decompositions and recompositions, some portion of acetate of alumine was formed, the good effects of which were experienced, though without any true knowledge of the ways and means by which they have been produced. By degrees, however, the printers seem to have increased the quantity of sugar of lead, and several of them to have suspected that many of the other ingredients usually employed for making their mordants were useless. Some of them, therefore, began to omit one, and some another of these ingredients, until at length all the useless ones were laid aside, though without the aid of any chemical reasoning on the subject, and without any one having ever suspected, as indeed few of them do at this day, that the lead which they continued to employ, occasioned any decomposition of the alum, or that the mordant so produced did not really contain all the lead and other ingredients used to prepare it. Among the useless ingredients before mentioned, corrosive sublimate seems to have been retained the longest, since Mr. Wilson includes it in his recipe, which was published so lately as the year 1786.

"It is not wonderful, therefore, that no particular person or period has been noted, or remembered, as distinguishable for the first invention of the acetated aluminous mordant; since the sugar of lead, or other means of forming it, were at

first used by chance so sparingly, as to have scarcely produced any better effect than would have resulted from the mere solution of alum, and the alterations and improvements by which the mordant afterwards acquired its present form, I had almost said perfection, were made by such impreceptible gradations, and resulted so much from the random additions and omissions of different individuals (no one of whom seems to have been guided by anything approaching to a just theory), that neither the discovery nor any considerable step towards it, can properly be referred to any one person or period.

“Mr. Henry, justly sensible of the superior advantages of the acetated aluminous mordant in calico-printing, and conceiving it to have really been very anciently known and employed in those countries where the art was first practiced, concludes from thence, that it must have resulted from a very advanced state of chemical knowledge in those countries, at some very remote period, which was afterwards lost, whilst the improvements arising from it in this respect continued to be practiced and handed down, through a long succession of ages to the present time. To have invented (says he) the process of printing, in the manner described by Pliny, the inhabitants of India must probably have known how to prepare alum; they must have been acquainted with the manner of dissolving lead in the vegetable acids; they must at least have been acquainted with the component parts of these salts, and they must have had a knowledge of double elective attractions, etc. In truth, however, the inhabitants of India neither had, nor have they at present, any knowledge of the use of sugar of lead, or of any other preparation of that metal which could produce similar effects in calico-printing; a solution of common alum in water being their only aluminous mordant, and the previous application of the soluble parts of myrobalans and of buffaloes' milk, to their calicoes, aided by a very hot sun-shine, and the complete desiccation which it produces, enabling them, without anything like an acetate of alumine, to give equal durability to their colours. This fact I have learned, not only from all the accounts published,

or transmitted to Europe respecting this point, but from the positive verbal informations of eye-witnesses to the practice of calico-printing in that part of the world, and particularly of a gentleman of great veracity, as well as knowledge on this subject, who formerly carried on the business of calico-printing very extensively in Bengal (principally for account of the East-India Company): and indeed sugar of lead is so far from being used for this purpose there, that within a few weeks I have received a letter from Mr. John Adie (successor to the gentleman last mentioned) dated, "Gondelpara, near Chandernagore, the 10th of February, 1792," and mentioning, that he had some little time before been obliged to pay twenty shillings the pound for sugar of lead, in order to prepare a particular colour which I had formerly recommended; so far was this ingredient from being in use there for any such purpose.

"We may, therefore, safely conclude, that the formation of an acetate of alumine, and its application as a mordant in calico-printing, was not an oriental discovery; and that it did not result from any knowledge of double elective attractions, or any other extensive chemical knowledge, either in ancient or modern times; since those who gradually stumbled upon and introduced the use of it, were totally ignorant of the decompositions and recompositions which took place in their mixtures, and always supposed, as all other calico-printers have till lately done, and as most of them do now, that the aluminous mordant really consisted of everything used in producing it."

We know that textiles are often made shower-proof by coating the fibers with some water-repellent hydrocarbon, wax or salt,<sup>1</sup> the aluminum salts being often used. We also know that the probability of electrostatic charges is greater the dryer the material we are studying. Both these facts were known empirically to Napier.<sup>2</sup> "Pieces [of cloth] mordanted with acetate of alumina and dried at a great heat, are highly charged with electricity. If the hand be suddenly drawn

---

<sup>1</sup> Weber: *Jour. Soc. Dyers and Colourists*, 17, 146 (1901).

<sup>2</sup> "A Manual of Dyeing," 125 (1875).

along the piece, a complete shower of fire is observed, with a sharp cracking noise, at the same time a prickling sensation is felt. Whether this has any effect upon the mordant, in its immediately combining with other substances we do not know but cloth in this state is very difficult to moisten—water runs off it as off a duck's wing; but we offer no explanation."

Liechti and Suida<sup>1</sup> have made some experiments on the amount of alumina fixed by cotton from various solutions; but it is rather hard to tell from the abstract exactly what they did. "A weighed quantity of cotton was evenly impregnated with say, an alum mordant until its weight was exactly doubled and then hung in a dry place on glass rods for thirty-six hours. A certain portion was then incinerated in order to determine the amount of alumina which the fibre had at its command. Another portion of the prepared fibre was then dried in a constant air current for six hours at a temperature of 40° C. The fibre was then washed for six hours with a definite amount of distilled water, and the amount of alumina in it was carefully estimated. From the number obtained it was possible to determine the percentage of alumina which had become fixed on the fibre." This sounds perfectly simple; but the catch is in the phrase "evenly impregnated." The cotton was apparently steeped in the bath and then dried with the mother liquor in it. Since all the solutions had the same amount of alumina in them, an amount equivalent to 200 g  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$  per litre, one would have supposed that the amount of alumina presented to the fiber would be approximately the same in each case. Actually it varies in a ratio of more than four to one. The data are given in Table II. In the first column is the hypothetical formula of the aluminum salt in solution. In the second column is the amount of alumina in grams presented to the fibers, an absolutely mysterious item. There is nothing to show to what weight of cotton it refers. In the third column is given the amount of alumina in grams fixed by the cotton and in the fourth the percentage fixed. The apparent accuracy is of course absolutely fictitious.

<sup>1</sup> Jour. Soc. Chem. Ind., 2, 538 (1883).

TABLE II  
Adsorption of Alumina by Cotton

Formula	Al <sub>2</sub> O <sub>3</sub> presented to the fiber	Al <sub>2</sub> O <sub>3</sub> fixed by the fiber	Percentage Al <sub>2</sub> O <sub>3</sub> fixed
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.6971	0.0901	12.92
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub>	0.4473	0.2283	51.04
Al <sub>4</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>6</sub>	0.1527	0.0897	58.74
Al <sub>2</sub> (SO <sub>4</sub> )(CH <sub>3</sub> CO <sub>2</sub> ) <sub>4</sub>	0.5750	0.5190	90.26
Al <sub>2</sub> (SO <sub>4</sub> )(CH <sub>3</sub> CO <sub>2</sub> ) <sub>3</sub> (OH)	0.5012	0.5012	98.90
Al <sub>2</sub> (SO <sub>4</sub> )(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> (OH) <sub>2</sub>	0.1851	0.1851	91.19
Al <sub>2</sub> (SO <sub>4</sub> )(CH <sub>3</sub> CO <sub>2</sub> )(OH) <sub>3</sub>	0.1987	0.1987	96.33
Al <sub>2</sub> (CH <sub>3</sub> CO <sub>2</sub> ) <sub>6</sub>	0.2631	0.2631	51.27
Al <sub>2</sub> (CH <sub>3</sub> CO <sub>2</sub> ) <sub>4</sub> (OH) <sub>2</sub>	0.2213	0.2213	99.46

From these data it is not permissible to draw the conclusion, which Liechti and Suida draw, that with aluminum sulphate the percentage of alumina fixed is greater the more basic the mordant. The percentage fixed varies with increasing basicity from 13 through 51 to 59; which is all that Liechti and Suida are considering. From what we know of adsorption, however, it is safe to say that the percentage adsorption would have been much greater than 51 if 0.15 g Al<sub>2</sub>O<sub>3</sub> had been presented to the cotton instead of 0.45 g. The percentage adsorption for the hypothetical Al<sub>4</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>6</sub> would have been less than 58 if 0.45 g Al<sub>2</sub>O<sub>3</sub> had been presented to the fibre instead of 0.15 g. It is quite possible, therefore, that under comparable conditions the percentage of alumina fixed by the fiber would have passed through a maximum with increasing basicity just as it appears to do with the so-called sulpho-acetates. On the other hand we do not know whether such a maximum, if found, would be real or would be due to the increased amount of sodium sulphate in the solution. In other words, although these experiments were made carefully, they are utterly worthless except as showing the errors which the next experimenter must avoid. Considering the time at which they were made, it is not surprising that the experiments are no better; but it is surprising that for nearly forty years they should have been considered as good work.



Kutschera and Utz<sup>1</sup> made some similar experiments except that they hung the cloth, after drying, in the moist air at about 34° for forty-eight hours. They got a much more uniform mordanting of the cotton than Liechti and Suida did. One square decimeter of their cloth averaged seven grams in weight, and it seems probable, though not explicitly so stated, that this is the amount of cloth to which the figures in Table III refer.

TABLE III  
Adsorption of Alumina by Cotton  
100 cm<sup>2</sup> of cotton averaged 7 grams

Formula	Al <sub>2</sub> O <sub>3</sub> presented to the fiber	Al <sub>2</sub> O <sub>3</sub> fixed by the fiber	Percentage Al <sub>2</sub> O <sub>3</sub> fixed
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> 18H <sub>2</sub> O	0.1566	0.0186	11.88
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> (CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub>	0.1456	0.1462	100.43
Al <sub>2</sub> (SO <sub>4</sub> )(CH <sub>3</sub> CO <sub>2</sub> ) <sub>4</sub>	0.1660	0.1324	79.76
Al <sub>2</sub> (CH <sub>3</sub> CO <sub>2</sub> ) <sub>6</sub>	0.1446	0.1479	102.29
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub>	0.1350	0.0688	51.79
Al <sub>2</sub> (SO <sub>4</sub> )(CH <sub>3</sub> CO <sub>2</sub> ) <sub>3</sub> (OH)	0.1495	0.1304	87.19

They confirm Liechti and Suida on the aluminum sulphate, and the basic aluminum sulphate. They are low (80 to 99) on the Al<sub>2</sub>(SO<sub>4</sub>)(CH<sub>3</sub>CO<sub>2</sub>)<sub>4</sub> and also (87 to 99) on Al<sub>2</sub>(SO<sub>4</sub>)(CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>OH. The great apparent difference is with aluminum acetate where Kutschera and Utz get all the alumina fixed, while Liechti and Suida get only 51 percent fixed. The difference may not be a real one because Liechti and Suida get more alumina fixed by weight than do Kutschera and Utz; but they present to the fiber 263 mg as against 145 mg. It is quite possible that all the loss in efficiency comes in at the higher concentrations. This argument cannot be used to cover the cases of Al<sub>2</sub>(SO<sub>4</sub>)(CH<sub>3</sub>CO<sub>2</sub>)<sub>4</sub> and Al<sub>2</sub>(SO<sub>4</sub>)(CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>(OH) because in both these experiments Liechti and Suida were getting higher percentages of alumina fixed with higher absolute amounts of alumina presented to the fiber.

<sup>1</sup> Mitt. techn. Gewerbe-Museums in Wien, Sektion für Färberei, 3, 110 (1886).



Sodium aluminate is not used as a mordant in dyeing cotton; but it is padded on for calico printing.<sup>1</sup> There is no direct mordanting and it is necessary to add ammonium chloride in order to precipitate the alumina. The use of aluminum formate<sup>2</sup> and of aluminum lactate<sup>3</sup> has been advocated. Whether one uses an acetate, formate, or lactate does not affect the general theory of the process.

Matthews,<sup>4</sup> who usually follows Ganswindt implicitly, breaks away from him on the question of mordanting cotton and comes out fairly boldly for the formation of a metallo-organic compound. "In mordanting cotton the case is somewhat different, for the metals employed as mordants are usually in the form of basic salts, and the solutions of these, by great dilution, by long exposure to the air, or by warming, may become dissociated and there may be precipitated either the hydroxide of the metal or a strongly basic salt; for example, in mordanting cotton with acetate of aluminum a hydrate or basic acetate is formed. This, however, cannot be considered as 'precipitation' in the chemical sense of the term. Although it may be shown that when cotton is steeped in a readily dissociated solution of aluminum acetate, a portion of the aluminum is withdrawn from the bath, it cannot be shown however, that aluminum hydrate as such has been precipitated in the fibre. If such were the case, washing with lukewarm acetic or hydrochloric acid would remove all the hydroxide from the fibre again; but this does not happen, which is an indication that the aluminum must be fixed in some other form. A properly mordanted fibre requires that the metallic compound with which the fibre is mordanted must be held by this in such a form and with sufficient energy that the mordant cannot be removed by water or even by dilute acids or alkalies."

After two paragraphs on the mordanting of wool with

---

<sup>1</sup> Ganswindt: "Theorie und Praxis der modernen Färberei," II, 224 (1903).

<sup>2</sup> Schwalbe: Zeit. Kolloidchemie, 5, 129 (1907).

<sup>3</sup> Boehringer and Sons: Zeit. Farben-Ind., 9, 237, 253 (1910).

<sup>4</sup> "Application of Dyestuffs," 602 (1920).

copper, aluminum, chromium and iron, Matthews concludes that "all these facts appear to show that in mordanting with metallic salts the metal is combined with the fibre in the form of a metallo-organic compound, and the fibre, thus chemically changed, then possesses the proper affinity for dyeing with the mordant dyes." The fallacy lies in the assumption that an adsorbed substance will necessarily have the same properties as the same substance in mass. If that were really the case charcoal could not take soluble substances out of solution practically completely and yet we know it does. If cotton takes alumina out of aluminum acetate, there is no reason why dilute acetic acid should take any appreciable amount of alumina out of cotton and still less out of wool which holds the alumina much more strongly.

Ganswindt<sup>1</sup> believes in distinguishing sharply between the mordanting of wool and of cotton. "The mordanting of cotton is quite different from the mordanting of wool and silk; it has also quite a different intention and significance. The cause of the difference is the inactivity or indifference of cotton towards solutions of salts of the metals. While silk and wool take up the metals in any form on heating, often quantitatively, and fix them chemically, that is not the case with cotton. Cotton has no affinity for metal salts and no tendency to form metallo-organic compounds; even boiling for hours has no effect. It is therefore necessary to have recourse to solutions of strongly basic salts, solutions which are so labile that a mere diluting with water, gentle heating, or just the presence of a textile fiber will cause the solution to dissociate into a normal solution and into a precipitate which latter, at the moment of precipitation, is taken up on or in the fiber. It is not necessary to decide whether the hydroxide is taken up or a more basic salt than that in the original solution, for that point has no bearing on what is to follow. It is a fact, however, that no chemical compound is formed and that the cotton fiber is not changed chemically in any way by the mor-

---

<sup>1</sup> "Theorie and Praxis der modernen Färberei," II, 214 (1903).

danting or, more properly speaking, by the steeping in the salt solution. Strictly speaking the cotton is not mordanted at all. When cotton is mordanted, the phenomenon is different from that with wool and silk, in that actually the metal hydroxide or possibly a very strongly basic salt, is precipitated mechanically on the cotton fiber and can be removed to some extent by vigorous rinsing. The hydroxide that is left is also held mechanically but in the intercellular spaces.

"The mordanting with tannin and tartar emetic must also be considered as a mechanical process, for there is only a very slight affinity between tannin and cellulose. If one mordants cotton with tannin, it is possible to wash the tannin out quantitatively by repeated treatments with hot water. That is why it is necessary to fix tannin with tartar emetic. Cotton mordanted with tannin and tartar emetic is nothing more than cotton impregnated mechanically with antimony tannate. It is exactly similar when cotton is mordanted with Turkey red oil and aluminum acetate. In all cases the cotton itself remains entirely unchanged. It is not altered or affected chemically in any way and therefore one really ought not to call the process mordanting at all. The only case where there is actually a chemical change in cotton by the action of reagents is curiously enough not called mordanting but—mercerization.

"From all this it is clear that the mordanting of cotton is not at all the same thing as the mordanting of wool. The mordanting of wool is pre-eminently a chemical process, while the mordanting of cotton is a mechanical impregnation of insoluble metallic compounds in the cell spaces and pores of the cotton fibre. For this reason the mordanting of cotton with metallic salts is nothing like as important or interesting as the mordanting of wool. The organic mordants, tannin and oil, are much more important."

This is quite an unreasonable attitude to take. The difference between wool and cotton is purely one of degree, so far as we now know. Wool adsorbs alumina more strongly than cotton does and is therefore able to take up alumina from less basic solutions than cotton can. Since it adsorbs

alumina more strongly than cotton does, it also holds it more firmly, thus makes a fixing of the mordant unnecessary. That point will be discussed in detail in a later paper. There is no satisfactory experimental evidence as yet of the formation of any definite chemical compound between alumina and either wool or cotton. Specific adsorption will account satisfactorily for all the phenomena which have been observed as yet.

It is interesting to note that the one case where Ganswindt is willing to admit a chemical change and a consequent mordanting is that of mercerized cotton; and Leighton<sup>1</sup> has since shown that all the earlier work on the theory of the process was wrong and that there is no definite chemical compound formed when cotton is mercerized. It is true, of course, that mercerized cotton does adsorb basic and substantive dyes more strongly than ordinary cotton does<sup>2</sup> and it is apparently true that mercerized cotton takes up basic mordants<sup>3</sup> rather more completely from concentrated solutions than ordinary cotton does; but there is no reason to suppose that this is anything more than an increased adsorption due to a change in structure.

The general results of this paper are:

1. All aluminum salts hydrolyze more or less in aqueous solution and the amount of the hydrolysis increases with rising temperature.

2. The actual hydrolysis is greater with weaker acids; but the apparent hydrolysis may be abnormally large in sulphate solutions owing to the coagulating effect of the sulphate ions on the colloidal alumina.

3. The different fibers adsorb alumina to different degrees, wool having a much greater adsorbing power than cotton, and silk being probably slightly inferior to wool.

4. Owing to this difference in specific adsorption, wool decomposes aluminum salt solutions which are distinctly acid while cotton is effective only in more basic solutions.

<sup>1</sup> Jour. Phys. Chem., 20, 188 (1916).

<sup>2</sup> Matthews: "Application of Dyestuffs," 165, 278 (1920).

<sup>3</sup> Schaposchnikoff and Minajeff: Zeit, Farben-Ind., 3, 165 (1904); 4, 81 (1905).

5. What is taken up and held firmly is the colloidal alumina. While coagulated alumina may be adsorbed to some extent, it rubs off easily.

6. It is probable that in all cases alumina is adsorbed and not a basic salt. The phenomena may be complicated by the fact that the alumina itself will adsorb some sulphuric acid, for instance, and that the wool may, and probably does, adsorb some sulphuric acid also.

7. Since alumina is adsorbed less strongly by cotton than by wool, it is also held less strongly by cotton than by wool.

8. If we add to cotton some substance like tannin which adsorbs alumina strongly, the cotton mordanted with tannin will be able to take alumina out of aluminum salt solutions which are not decomposed by cotton alone. A corollary from this is that alumina will be held more strongly by cotton mordanted with tannin than by cotton alone.

9. The increase in adsorbing power shown by mercerized cotton is undoubtedly due to structural difference in the cotton fibre; but we are not yet able to predict this change.

10. There is no evidence of the formation of any definite chemical compound between alumina and either wool, silk, or cotton.

*Cornell University*

## ON THE COAGULATION OF COLLOIDS

BY ARNE WESTGREN AND JOSEF REITSTÖTTER

One of the chief objects of colloid chemistry is certainly to find out the conditions of the stability of colloids. To attain this aim it must evidently be of great importance to know what happens, when a colloid for some reason suddenly loses its stability. The process of coagulation has therefore been subject to a great number of investigations and as a multitude of more or less well-founded hypotheses has been proposed in order to explain this phenomenon, it is certainly no easy task to give a well-posed and objective survey of this field of research.

It is not our intention to make any attempt in this direction, since M. Smoluchowski (1, 2, 3) a few years ago has given an excellent summary of the coagulation theories and R. Zsigmondy (4) has published a critical estimate of the measurements and speculations on the coagulation of colloids produced by electrolytic admixtures. The purpose of this paper is only to give a summary sketch of Smoluchowski's kinetic theory of coagulation which has made an exact treatment and experimental examination of the entire coagulation problem possible and also to give a short survey of the experimental work performed in order to try the new theory. Smoluchowski, the ingenious pioneer, who lived to see the first experimental confirmation of his work, was carried off by an epidemic war-disease at Cracow on September 5, 1917.

If a deep-red colloidal gold-solution is mixed with a diluted solution of sodium chloride, its colour turns more or less quickly into violet or blue. This conspicuous change of colour is a macroscopic characteristic of the coagulation of the colloidal gold-solution, the particles of which unite to larger complexes, and after a certain time sink to the bottom, while the liquid becomes almost colourless.

All attempts made hitherto to explain the respective laws

of this process in an empirico-inductive way, have been rather unsuccessful (S. Miyazawa, N. Ishizaka, H. Freundlich, I. A. Gann, etc.), and even certain formulae and laws framed in the beginning had to be withdrawn after more accurate researches (Freundlich and Gann), wherefore Smoluchowski, having recourse to a deduction method, stated some new principles for studies in this branch of colloid physics.

According to Smoluchowski, the reason why the empirical methods have proved a failure, is, that in all previous works certain factors (viscosity, the relative quantity of the substance dissolving under determinate conditions, transparency, etc.) were considered as measures of coagulation, whereas in reality there is no exact measure for it, as coagulation cannot be expressed by one variable quantity alone.

In spite of all pains bestowed on these researches, a precise cognition of the acting causes on which stability or coagulation are depending, was still wanting. Smoluchowski arrived at the assumption that, when sufficiently near together, the particles attract one another in consequence of the capillary effect, but that a combination does not take place under normal circumstances, which is to be attributed to a protective effect of the electric double-layer of the particles. An electrolyte being added, a partial or complete discharge of this double-layer takes place, owing to the adsorption of the ions demonstrated by Freundlich; thus the protective effect is diminished, and, from a certain concentration it does not suffice to prevent the particles from joining together. Still another influence must be taken into consideration: it causes a collision of the particles, but, at the same time, checks their permanent combination, viz., the molecular forces which, among other things, manifest themselves in the Brownian movement.

Before entering on the calculations made by Smoluchowski, we must still premise some general reflections on coagulation.

In order that coagulation may take place, a certain electrolytic concentration must be attained, "Bodländer's

limit" (*Schwellenwert*), below which there is no coagulation at all. This limit, however, is not sharply defined. Zsigmondy has proved by experiments, that small electrolytic admixtures exert no influence on a fine-grained colloidal gold-solution. A gradual increase of the electrolytic concentration leads into a domain of *slow* coagulation, through a zone rather limited with respect to the electrolytic concentration. In this zone small changes of the electrolytic concentration produce very great changes in the velocity of coagulation.

It has thus been proved, that the velocity of coagulation is a continuous function of the electrolytic concentration, i. e., coagulation does not suddenly occur at a certain degree of the latter; but when it begins after a gradually increased electrolytic admixture its velocity augments, and finally attains a maximum which is not exceeded even if the concentration is very considerable.

Hence it follows, that the notion of "coagulation-limit" so current in the literature of colloids, in reality has no explicit counterpart. It is therefore more proper to speak with Zsigmondy of a "limit-zone" within which the velocity of coagulation varies with the electrolytic concentration. This zone passes continuously into the adjoining concentration-regions, into the region where no coagulation takes place, in the one direction and into the region where the velocity of coagulation becomes a maximum in the other. If we use the term "coagulation-limit," we must do as Zsigmondy and Reitstötter have done, i. e., connect it with a certain velocity of coagulation within the limit-zone.

That the particles of a colloid do not agglutinate is evidently due to powers of repulsion manifesting themselves at their mutual immediate approach. These powers must be connected with a protective effect of an electrically charged double-layer. The presence of these repelling powers has been shown by J. Perrin and R. Costantin.<sup>1</sup>

If we mix the colloid with increasing quantities of an

---

<sup>1</sup> Comptes rendus, 158, 1171 (1914).



electrolyte, the potential of the double-layer decreases, as we have already shown. At a certain standard (Bodländer's limit), the limit of stability is exceeded, and then there is a tendency towards coagulation which rapidly increases with the increase of the electrolytic admixture; in other words, the protective effect of the charge of the double-layer is in part neutralized by a rising effect of attraction.

These considerations form the foundation of Zsigmondy's doctrine, according to which the maximum of the coagulation-velocity, designated as "quick" coagulation in the following lines, corresponds to a discharge of the double-layer down to a certain potential. In this state the attraction forces of the particles are fully developed.

According to Smoluchowski, each particle of the colloid is, from the moment of the admixture of the electrolyte, surrounded by a sphere of attraction of the radius  $R$ , within which there is so intense an attraction, that any other particle is retained in it, forming an indissoluble combination with the first, as soon as its centre gets into that sphere.

This view of the coagulation-process has the advantage of not meddling with the question of the structure of the double-layer, its connection with the nature and number of the ions, etc. Besides, it enables us mathematically to formulate the kinetics of coagulation.

Smoluchowski considers, that the main object for a mathematical treatment of the problem must be to calculate the numbers  $\nu_1, \nu_2, \nu_3, \dots$  of the simple, double, treble . . . particles from the factors characterizing the whole system, viz., the original number of particles  $\nu_0$ , the dimension of the radius of action  $R$ , and the constant of velocity  $D$  of the Brownian movement. The problem therefore, is: If  $n_0$  particles exist in the unit of space at the time  $=0$ , how great is, at the time  $t$ , the average number  $n$  of those particles, whose centres until then have not passed into the sphere of action  $R$ ? Instead of considering all the particles in the unit of space, we select a single one. The probability  $P_1(t)$  of its not having been touched by another until the time  $t$ ,

is expressed by the percentage of the single particles still remaining free:

$$\frac{n_1}{n_0} = P_1(t)$$

To make the remaining calculation easier we assume, that this special particle is at rest, that it is retained and that only this one possesses a sphere of attraction. Therefore all the other particles can join only with it, but not with each other. We thus assume, that the spherical surface of the radius  $R$  retains each arriving particle, and that it acts absolutely adsorbing; in other words, that the concentration on the spherical surface always is 0.

In order to calculate the amount of the substance diffused on to the sphere, we have only to determine the distribution of a substance that at first has uniformly filled space (initial concentration =  $c$ ) but, from the moment  $t = 0$ , is diffusing towards the sphere of the radius  $R$ , to whose surface it fully adheres, thus making the concentration immediately outside the sphere constantly  $u = 0$ .

From the general equation of diffusion<sup>1</sup> it results, that, on

$$\frac{\partial(ru)}{\partial t} = D \frac{\partial^2(ru)}{\partial r^2}$$

$D = \frac{H\theta}{N} \frac{1}{6\pi\eta\alpha}$ ;  $H$  is the gas-constant  $83.19 \times 10^6$ ;  $\theta$  the absolute temperature;  $N$  the constant of Avogadro  $60,6 \cdot 10^{23}$ ;  $\eta$  the viscosity of the system, and  $\alpha$  the radius of the particle.

$$\begin{aligned} u &= c \text{ when } t = 0, r > R \text{ and} \\ u &= 0 \text{ when } r = R, t > 0 \end{aligned}$$

$$u = c \left[ 1 - \frac{R}{r} + \frac{2R}{r\sqrt{\pi}} \int_0^{\frac{r-R}{2\sqrt{Dt}}} e^{-z^2} dz \right]$$

Hence it follows that the amount diffused on to the sphere  $R$  in the time  $t \dots t + dt$  is

$$Tdt = 4\pi DR^2 \frac{\partial u}{\partial r} \Big|_R dt = 4\pi DRc \left[ 1 + \frac{R}{\sqrt{\pi Dt}} \right] dt.$$

the stipulated conditions, the amount diffused on to the sphere  $R$  in the space of time  $t \dots t + dt$  is

$$4\pi DR c \left[ 1 + \frac{R}{\sqrt{\pi Dt}} \right] dt,$$

and the total quantity disengaged from the beginning is

$$M = 4\pi DR c \left[ t + \frac{2R\sqrt{t}}{\sqrt{\pi D}} \right]$$

To simplify the calculation we neglect the root quantity, that is to say, we consider the process of coagulation at a stage, in which  $t$  is great compared to  $R^2/D$ .

The probability, that a certain particle existing at first anywhere in the space  $V$  joins the sphere  $R$  in the time  $t \dots t + dt$  (when  $c = \frac{1}{v}$ ) is:

$$P_t = \frac{4\pi DR}{V} dt$$

The coagulation-time in which, on an average, a particle sticks to the one selected, is

$$T = \frac{1}{4\pi RD\nu_0} = \frac{1}{\beta'}$$

the concentration  $c$  having been substituted by the number of the particles  $\nu_0$  in the unit of space; the number of the particles during the unit of time sticking to the selected adsorption-nucleus is  $4\pi RD\nu_0$ .

But now we must take into consideration, that the selected particle  $R$  is not at rest, but subjected to the Brownian movement; its relative motion, therefore, comes into consideration for coagulation. But as the relative motion of two particles which, independently of each other, are subjected to Brownian molecular movement characterized by the diffusion-constants  $D_1, D_2$ , is likewise a Brownian molecular movement, viz., such a one as is characterized by a diffusion-con-

stant  $D_{1,2} = D_1 + D_2$ , we need only double the coefficient  $D$  in the present case.<sup>1</sup>

The decrease of the number of the simple primary particles is given by

$$v_1 = \frac{v_0}{1 + 8\pi DRv_0 t} = \frac{v_0}{1 + \frac{2t}{T}}$$

But here we have taken into account only the uniting of simple particles into double particles; whereas, in reality, also the formation of multiple particles is to be considered. The double and treble particles already formed act in their turn as nuclei of coagulation, unfortunately in such a manner as cannot be exactly calculated, the form of the multiple particles being in all probability not spherical. Also here exist similar relations as before in the simple case, and the total decrease of the primary particles may be represented by the equation

$$\frac{1}{8\pi DR} \cdot \frac{1}{v_1} \cdot \frac{dv_1}{dt} = -v_1 - v_2 - v_3 - \dots$$

In an analogous manner we get the reaction-equations for the different categories of multiple particles. By integration we get the total number of particles

$$\sum v = v_1 + v_2 + v_3 + \dots = \frac{v_0}{1 + \beta t}$$

$$\text{As } P(x) dx = \frac{1}{2\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} dx,$$

the probability that a particle at the end of the time  $t$  has been displaced  $\xi$ . . . .  $\xi + d\xi$  out of its original position is evidently the product of the two probabilities, independent of each other, that one particle has been dislocated  $x$  and another particle  $\xi + x$ :

$$P(\xi) d\xi = \int_{-\infty}^{+\infty} P(x) dx P(\xi + x) d\xi = \frac{d\xi}{2\pi t \sqrt{D_1 D_2}} \int_{-\infty}^{+\infty} e^{-\frac{x^2}{4D_1 t} - \frac{(\xi+x)^2}{4D_2 t}} dx = \frac{e^{-\frac{\xi^2}{4(D_1 + D_2)t}}}{2\sqrt{\pi(D_1 + D_2)}} d\xi.$$

where  $\beta = 4 DR \nu_1$ . The number of the primary particles then is:

$$\nu_1 = \frac{\nu_0}{[1 + \beta]^2}$$

that of the double particles

$$\nu_2 = \nu_0 \frac{\beta t}{[1 + \beta]^3}$$

and that of the  $n$ -fold particles:

$$\nu_n = \nu_0 \frac{(\beta t)^{n-1}}{[1 + \beta]^{n+1}}$$

Introducing the diffusion-constant into the formula of coagulation-time, we get from

$$T = \frac{1}{4\pi DR \nu_0}$$

and

$$D = \frac{H\theta}{N} \frac{1}{6\pi\eta\alpha}$$

the coagulation-time

$$T = \frac{3 N \eta}{2 H \theta \nu_0} \cdot \frac{\alpha}{R}$$

This formula, however, applies only to quick coagulation, discussed in the beginning of this paper, when the electrolytic admixture is considerable, the sphere of attraction being already independent of the electrolytic concentration. If the electrolytic admixture is small, we may imagine, that, of the immediate collisions of the particles, only a fraction, dependent on the electrolytic concentration, leads to the joining of particles. It is evident, that this causes only a retardation of the process, the inner progress of the same remaining unchanged.

Smoluchowski is of opinion, that in the case of an incomplete discharge of the double-layer, the attractive powers of the sphere of action are not fully developed and, because of that, only a certain fraction of the immediate collisions of the particles causes their instantaneous combination. In the formula, already given,  $\epsilon \beta t$  must then be put in the place of  $\beta t$ .

$$\text{Is } \alpha = 4\pi RD,$$

it follows that

$$\alpha = 8\pi r D \epsilon = \frac{4}{3} \frac{H\theta}{N} \cdot \frac{\epsilon}{\eta}$$

where  $\epsilon$  represents a coefficient corresponding to that fraction.

The coagulation-curves obtained from the different concentration series of the colloid and the electrolyte must therefore be similar. By a corresponding change of the measure of time, they can be brought to coincide.

The above theory of coagulation-kinetics was worked out, in a more deductive manner, by Smoluchowski at the instigation of R. Zsigmondy, and was brought before the public in a course of lectures delivered at Göttingen on the 20th, 21st and 22nd of June, 1916.

Smoluchowski's calculations were first confirmed by R. Zsigmondy's experiments (4, 5, 6) on colloidal gold-solutions, which were brought to quick coagulation by a considerable electrolytic admixture. By adding a strong protective colloid (solution of gum arabic) Zsigmondy and Reitstötter, after a certain time interrupted the process of coagulation, and counted the remaining primary particles by means of the ultramicroscope. Equally satisfactory and corroborative for the theory are the results obtained by Westgren and Reitstötter (7), who, instead of the primary particles ( $\nu_1$ ) determined the total number ( $\epsilon_1$ ) of the particles. A few years ago, by investigating coarse-grained gold hydrosols, Westgren (8), has also found, that Smoluchowski's view concerning slow coagulation is likewise correct, that the radius of action, when fully developed is in all probability exactly twice as great as that of the particle, and that the particles thus exercise no effect on each other before colliding or at least not until they come very near each other.

In a theoretical work H. Freundlich (9) has made a very interesting attempt to explain the mechanism of the slow coagulation. He assumes, that the partially discharged particles in a slowly coagulating colloid do not join together, unless their power of collision exceeds a minimum value. It

would be of a certain interest mathematically to investigate whether this hypothesis is compatible with the experimental results, gained by Westgren (8), that uniform gold-sols of different particle-size, that are coagulated with the same electrolyte show identical curves of coagulation. It seems, at least at a superficial estimation, that this can hardly be the case. If the violence of collision is of decisive importance for the aggregation, not only the relative velocity of the particles, but also their mass should have some influence on the progress of coagulation.

The change in colour of Congo ruby hydrosols, mixed with an electrolyte, has been studied by H. Lüers (10), who found Smoluchowski's formula applicable to this phenomenon. In connection with this, he has also gained some interesting results concerning the influence of protective colloids on the said change in colour.

Quite recently H. R. Kruyt and A. E. van Arkel (11, 12, 13) have experimentally contributed to the question whether Zsigmondy's and Smoluchowski's opinion on the mechanism of coagulation holds good. These scientists have carried out a series of investigations on the coagulation of selenium hydrosols. Their results differ to a certain degree from those obtained formerly by the examination of coagulating gold-sols. In several experiments the total number of particles ( $\Sigma v$ ) was found to decrease during the coagulation in a way not at all consistent with Smoluchowski's formula, and in the cases, where agreement was established, the values obtained for the ratio of the attraction-radius to the particle-radius,  $R/a$ , were varying from 0.5 to 1.0. Thus only part of the particle-collisions should lead to aggregation. Kruyt and van Arkel have tried different ways of explaining these divergences from Smoluchowski's theory. A source of error, however, to which they seem to have paid no attention, is the possibility, that their selenium sols have contained not only a main quantity of almost equally big submicroscopic grains, but also a considerable fraction of a microscopic selenium-particles. If the colloids have had such a composition the total number of par-

ticles visible in the ultramicroscope must evidently change in a complicated manner during coagulation. Selenium sols, which have not by centrifuging been freed from eventual amicroscopic particles and electrolytes cannot be said to be as well defined and suitable material for investigations of this art, as coarse-grained gold sols, that have been prepared by repeated sedimentation of the particles and pouring off of the supernatant liquid.

From the above short survey of the experimental examination of Smoluchowski's valuable theory it may be evident, that there still remains very much to do before colloid chemistry has made the most of it as a leading principle on this sphere of research. If this short review can cause any scientist of colloids to perform a new investigation of the coagulation process based on the said theory, the present writers consider the purpose of their paper fulfilled.

#### List of works quoted

1. M. Smoluchowski: "Drei Vorträge über Diffusion, Brownsche Molekularbewegung und Koagulation von Kolloidteilchen." *Physikalische Zeitschrift*, 17, 557, 585 (1917).
2. M. Smoluchowski: "Versuch einer mathematischen Theorie der Koagulationskinetik kolloider Lösungen." *Zeitschrift für physikalische Chemie*, 92, 129 (1917).
3. M. Smoluchowski: "Grundriss der Koagulationskinetik kolloider Lösungen." *Kolloid-Zeitschrift*, 21, 98 (1917).
4. R. Zsigmondy: "Über Koagulation und Teilchenattraktion." *Nachr. der Akademie der Wissensch. Göttingen* 1917, Heft 1, p. 1.
5. R. Zsigmondy: "Über Koagulation und Teilchenattraktion." *Zeitschrift für physikalische Chemie*, 92, 600 (1917).
6. R. Zsigmondy: "Über Koagulation." *Zeitschrift für Elektrochemie*, 23, 148 (1917).
7. A. Westgren and J. Reitstötter: "Zur Koagulation grobdispenser Goldhydrosole." *Zeitschrift für physikalische Chemie*, 92, 750 (1917).
8. A. Westgren: "Zur Kenntnis der Koagulation." *Arkiv för kemi, mineralogi och geologi*, utg. av K. Svenska Vetenskapsakad., Stockholm, 1918, Bd 7, Nr 6, p. 1.
9. H. Freundlich: "Zur Theorie der Koagulationsgeschwindigkeit." *Kolloid-Zeitschrift*, 23, 163 (1918).
10. H. Lüers: "Der zeitliche Verlauf des Kongorubin-Farbenumschlags unter dem Einfluss von Elektrolyten und Schutzkolloiden." *Kolloid-Zeitschrift*, 27, 123 (1920).



11. H. R. Kruyt and A. E. van Arkel: "La vitesse de floculation du sol de sélénium, 1ère communication: Floculation à l'aide de chlorure de potassium." *Recueil des travaux chimiques des Pays-Bas*, (4) 39, 656 (1920).
12. A. E. van Arkel: "Uitvlokkingsnelheid van het seleensol." Diss. Utrecht 1920.
13. H. R. Kruyt and A. E. van Arkel: "La vitesse de floculation du sol de sélénium. II: Floculation au moyen de chlorure de baryum." *Recueil des travaux chimiques des Pays-Bas*, (4) 40, 916 (1920).

J. B. L. 1111 1111 1111 1111

THE MELTING INTERVAL OF CERTAIN UNDER-  
COOLED LIQUIDS WITH A NOTE ON THE  
USE OF LIQUID AIR AS A  
REFRIGERANT<sup>1</sup>

BY JOHN BRIGHT FERGUSON

Bancroft<sup>2</sup> has drawn attention to the unusual type of melting curve, obtained with solids formed by the sudden chilling of aqueous salt and acid solutions, which was first observed by McIntosh and Edson.<sup>3</sup> The latter noted that such material did not show a melting interval extending from the eutectic temperature to the temperature at which such a liquid solution would be in equilibrium with a trace of pure ice, but rather melted exactly at this latter temperature. In other words, the melting temperature corresponded to the point on the liquidus curve of an equilibrium temperature-concentration diagram representing the proper composition.

These workers ingeniously prepared constant temperature baths, using such chilled materials. They also suggested that this procedure might have a wide application including the possible use of molten salts. Their results led them to believe, apparently, that the relation between the liquidus temperature and the melting temperature was an exact one and of rather wide application. The present investigation was undertaken with a view of testing these deductions.

When a liquid is suddenly cooled so that an amorphous solid is formed, the resultant material is usually called a glass. There seems therefore to be no good reason why the chilled materials under discussion should not be so designated.

The melting temperatures of most glasses such as the silicate glasses lie considerably below the liquidus temperatures,

---

<sup>1</sup> Contribution from the Chemical Department of the University of Toronto.

<sup>2</sup> Bancroft: *Jour. Ind. Eng. Chem.*, **13**, 88 (1921).

<sup>3</sup> McIntosh and Edson: *Jour. Am. Chem. Soc.*, **38**, 613 (1916).

and these temperatures are not sharp but extend over various intervals, depending on the nature of the glass. When a borax glass melts, a slight absorption of heat occurs,<sup>1</sup> and Tool and Valasek<sup>2</sup> have observed that a silicate glass which crystallized on melting, first absorbed a small quantity of heat on melting, and later set free a relatively very great quantity of heat upon crystallization. These facts seem to indicate, that the constant temperatures found with the salt solution, and acid solution glasses must be the result of a peculiar balancing of such heat effects. One might therefore expect that different experimental conditions might give rise to different constant temperatures using the same initial solution and that different solutions would not behave alike.

Glasses were prepared by the method out-lined by McIntosh and Edson, using liquid air as a refrigerant. The solid cores of glass were either ground up in a chilled mortar as each was obtained, or the cores were kept in a vacuum bottle until enough were prepared and all ground up at the same time. The ground material was quickly transferred to a small-size vacuum bottle ( $\frac{1}{2}$  pint). Solutions of sodium chloride and of hydrochloric acid<sup>3</sup> in distilled water were used. An alcohol thermometer was inserted into the ground mass<sup>4</sup> in the bottle and the temperatures read from time to time.

The salt solutions were analyzed by evaporating off the water and weighing the salt; the hydrochloric acid solutions were titered with barium hydroxide solution. In several cases an attempt was made to obtain the composition of the solid material present during the latter stages of the melting. The procedure was as follows: the slush as free from liquid as possible was placed in a small evaporating dish; melting was permitted to take place for a moment and the liquid poured

---

<sup>1</sup> Day and Allen: Carnegie Institution of Washington, Pub., 31, 34 (1905).

<sup>2</sup> Tool and Valasek: Bur. Standards, Sci. Papers, 358 (1920).

<sup>3</sup> Our hydrochloric acid glasses could not be ground up as they formed a thick slush even in the vacuum bottle.

<sup>4</sup> 70 grams approximately.

off; the latter operation was repeated several times and the residual slush used for the analysis.

The results of a number of experiments are given in Table I.

TABLE I  
The results of the Melting Point Experiments

	I	II	III	IV	V	Remarks
NaCl	15	14.8	-11.5	-11.7	-13.7	Slush still present at -10.6. Cores ground up separately.
NaCl	14.67	14.3	-10.5	-11.3	-12.1	Melting practically complete at -8.7. Sticks ground up at one time.
NaCl	14.5	—	—	-11.1	-11.4	Sticks ground up at one time.
HCl	12.1	—	—	-20.25	-32.4	Slush practically gone at the liquidus temperature.
HCl	6.9	—	—	-9.75	-14.9	
HCl	6.9	—	—	-9.75	-16.5	
Ice	—	—	—	0.	0.	There was a trace of ice left at 0.1.

- I. The composition of the solutions in Wt. percent.  
 II. The composition of the slush in Wt. percent.  
 III. Temperature of slush removal.  
 IV. Liquidus temperatures.  
 V. Constant temperatures found.

The liquidus temperatures were obtained by plotting the data given in Landolt-Börnstein Tabellen, pages 485 and 470. The following eutectic temperatures are given in the same tables:

- ice + sodium chloride. 2 aq.  $-21.2^{\circ}\text{C}$   
 ice + sodium chloride  $-22.4^{\circ}\text{C}$  (labile)  
 ice + hydrogen chloride. 3 aq.  $-86^{\circ}\text{C}$

From these results we may conclude:

1. The constant temperatures obtained on melting such glasses are dependent upon the particular experimental procedures used.
2. With the salt solution glasses, these temperatures approximate the liquidus temperatures but lie below them.

3. The analyses of the residual slushes indicate that the salt solution glasses may persist for some time at temperatures above the liquidus temperatures. The evidence cannot be considered as conclusive, however, owing to the nature of the material used in the analyses.

4. Since there does not appear to be an exact relation between the melting temperatures and the liquidus temperatures, the use of such glasses for constant temperature baths cannot be regarded as of general application.

One explanation of the constant temperature obtained with these glasses would be that this temperature is the temperature at which the heat absorbed by the melting glass just equals the heat of partial crystallization of the excess component plus the heat lost through the walls of the vacuum bottle. The heat given out when a unit weight of the excess component crystallizes is probably very great as compared with the heat absorbed when a unit weight of the glass melts. If the glass melts slowly, a constant temperature would result which would be near the liquidus temperature. On the other hand, if the glass melts quickly the constant temperature would be considerably below the liquidus temperature.

#### **Note on the Use of Liquid Air as a Refrigerant**

Most liquids under-cool readily below their freezing points while most solids cannot be super-heated above their melting points. One might therefore expect less trouble in the determination of the melting curve than in the determination of the freezing curve for a given solution. The work of McIntosh and Edson, and ourselves, would indicate that if liquid air were used to "freeze" the solution the true melting curve might be obscured by the presence of glass in the melting mass.

Attention is called to this possible source of error since it is not one that might appear at first sight to be of importance with aqueous solutions. In addition, liquid air when available is used freely as a refrigerant.

*Toronto, Canada*

## THE SOLUBILITY OF GASES IN LIQUIDS<sup>1</sup>

B. S. NEUHAUSEN

In an article by the writer<sup>2</sup> and Prof. W. A. Patrick, it was shown that the solubilities of NH<sub>3</sub>, HCl, CO<sub>2</sub> and SO<sub>2</sub> in water could be expressed by the equation

$$V = K \left( \frac{P\sigma}{P_0} \right)^{1/n}$$

In this formula  $V$  is the volume of liquefied gas dissolved per gram of water (i. e., the weight of gas dissolved per gram divided by the density of the liquefied gas at that temperature);  $P_0$  is the vapor tension and  $\sigma$  the surface tension of the liquefied gas at the temperature of measurement while  $P$  is the equilibrium gas pressure.  $K$  and  $1/n$  are specific constants. The fact that this formula fitted likewise the adsorption data for various gases by solid adsorbents, was considered as a support for the theory first advanced by Graham<sup>3</sup> that solutions of gases in liquids are cases of condensations of the gases in liquids.

In that paper solubility data in water only were presented. To show the extent of the validity of this generalization in solvents other than water, the following data on the solubilities of NH<sub>3</sub>, HCl, SO<sub>2</sub>, and CO<sub>2</sub> in methyl and ethyl alcohols are plotted according to this formula in Fig. 1.

In curves IM and IE there have been plotted the solubility data of de Bruyn<sup>4</sup> for SO<sub>2</sub> in methyl and ethyl alcohol, respectively, at atmospheric pressure and at temperatures of

---

<sup>1</sup> Contribution from the Laboratory of the Department of Physiology of the Johns Hopkins University.

<sup>2</sup> Jour. Phys. Chem., 25, 693 (1921).

<sup>3</sup> Annals of Philosophy, 12, 69 (1826).

<sup>4</sup> Rec. Trav. chim. Pays-Bas, 11, 112 (1892).

0° C to 26° C. The values of the surface tension of liquid SO<sub>2</sub> were calculated from values given by Landolt-Börnstein to be

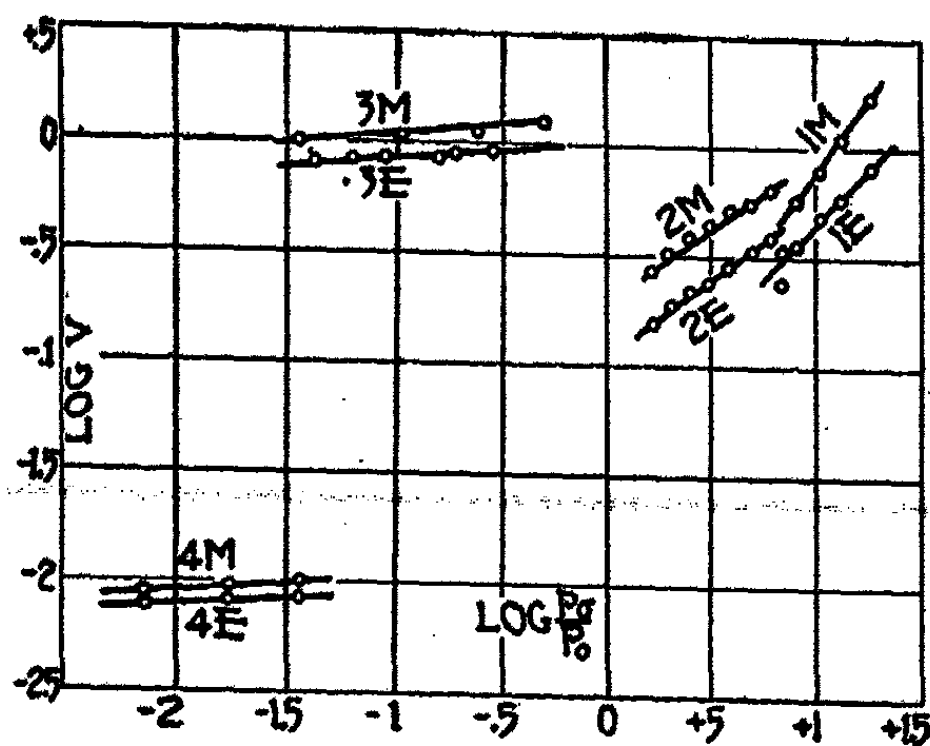


Fig. 1

Temperature °C	0	7	12.3	18.2	26
Surface Tension	28.4	27.2	26.13	25.0	23.52

The density of liquid SO<sub>2</sub> at the different temperatures was obtained by interpolation from the data of Cailletet and Mathias.<sup>1</sup> Regnault's values for the vapor tensions as given by Landolt-Börnstein were used.

On curves 2M and 2E have been plotted de Bruyn's<sup>4</sup> solubility data for NH<sub>3</sub> in methyl and ethyl alcohol at from 0° C to 30° C. The values of the surface tension of liquid NH<sub>3</sub> were obtained from the data of Berthoud;<sup>2</sup> the liquid densities from Cragoe and Harper;<sup>3</sup> the vapor tensions from Cragoe et al.<sup>4</sup>

On curves 3M and 3E are found de Bruyn's<sup>4</sup> data on solubility of HCl at temperatures from -10° C to 32° C. The

<sup>1</sup> Comptes rendus, 104, 1565 (1887).

<sup>2</sup> Hel. Chim. Acta I, 84-7 (1918); Jour. Chim. phys., 16, 429 (1918).

<sup>3</sup> Bureau of Standards, Sci. Paper, 420.

<sup>4</sup> Ibid., 369.

values of the surface tension were calculated from the work of McIntosh & Steele<sup>1</sup> to be

Temperature	-10	0	6.5	11.5	18	20	23.5	32
Surface Tension	9.4	7.6	6.48	5.64	4.5	4	3.37	2

The liquid densities were interpolated from values of Ansdell;<sup>2</sup> the vapor tensions up to 0° C from Faraday<sup>3</sup> and over 0° C from Ansdell.<sup>4</sup>

On curve 4E and 4M are plotted Just's<sup>5</sup> data on the solubility of CO<sub>2</sub> the values given in terms of the Ostwald solubility coefficient being recalculated into weights per gram of water. The values of the surface tension were interpolated from data given by Landolt-Börnstein, 1.82, 1.00, and 0.50 dynes being used for 15, 20, and 25° C respectively. Liquid densities were obtained from data of Warburg and v. Babo;<sup>6</sup> the vapor tensions from the data of Tate.<sup>7</sup>

From these curves it is evident that the formula

$$V = K \left( \frac{P_{\sigma}}{P_0} \right)^{1/n}$$

holds very well for each individual gas. It may be noted that, with the exception of SO<sub>2</sub>, the curves of each gas in the two solvents are parallel, but as was already found in the case of water as a solvent, these curves do not coincide.

When the above formula is written in logarithmic form the following equation is obtained:

$$\log V = \log K + 1/n \log \frac{P_{\sigma}}{P_0}$$

<sup>1</sup> Zeit. phys. Chem., 55, 141 (1906).

<sup>2</sup> Proc. Roy. Soc., 30, 117.

<sup>3</sup> Phil. Trans., 135, I, 155 (1845).

<sup>4</sup> Chem. News, 41, 75 (1880).

<sup>5</sup> Zeit. phys. Chem., 37, 343 (1901).

<sup>6</sup> Ber. Berl Akad., 1882, 509.

<sup>7</sup> Phil. Mag., (4) 26, 592.



In this equation there are two constants  $K$  which becomes equal to  $V$  when  $\frac{P_{\sigma}}{P_0}$  is set equal to 1, and  $1/n$  which obviously is the slope of the line. As Chwolson<sup>1</sup> has so painstakingly pointed out, it is incorrect to attribute any physical significance to a proportionality constant, and if its value is other than 1, the law has been incompletely expressed or a factor omitted. As may be seen from the table below of the value  $K$  of the four gases in water ethyl, and methyl alcohol as solvents, it is not a proportionality constant but is a variable depending on some physical quantity.

TABLE I  
Value of  $K$  of gases in different solvents

	Water	Methyl alcohol	Ethyl alcohol
NH <sub>3</sub>	0.49	0.205	0.108
HCl	1.05	1.23	0.979
SO <sub>2</sub>	0.012	0.04	0.04
CO <sub>2</sub>	0.006	0.0126	0.0103

If solutions of gases in liquids are considered as binary liquid mixtures it is evident that the greater the degree of miscibility of the gas in the liquefied form with the liquid solvent the greater the solubility, for miscibility may well be taken as an indication of the degree that molecules of the solute fit into the interstices of the solvent and vice versa. Upon examining Table I it is seen that HCl which is miscible with water and methyl and ethyl alcohols in all proportions gives a high value for  $K$  in all three cases. NH<sub>3</sub> likewise gives a high value for  $K$  in water though the values are lower for the alcohols. SO<sub>2</sub> which in the liquefied form is miscible with water only in a limited extent gives a much lower value for  $K$ ; while in the alcohols with which it is miscible to a greater extent,  $K$  has a greater value. CO<sub>2</sub> likewise gives a very small value for  $K$  in water, with which CO<sub>2</sub> in the liquefied form is only slightly miscible, while with the alcohols with which liquefied gas is

<sup>1</sup> Section on Physikalische Gesetze. Lehrbuch, d. Physik, I, 1, 25, 2nd edition.

much more miscible the values of  $K$  are twice as great. That the values of  $K$  for  $\text{CO}_2$  in the alcohols are so much lower than those for  $\text{HCl}$  is not surprising for  $\text{CO}_2$  and the alcohols though they possess a great range of miscibility are not miscible in all proportions as has been shown by Buchner.<sup>1</sup> The value of  $K$  may therefore be taken as a function of the degree of miscibility of the liquefied gas and solvent.

The other constant occurring in the equation is  $1/n$ . The values of  $1/n$  for the 3 gases are given in the following table:

TABLE II  
Values of  $1/n$  for the gases

	Water	Methyl alcohol	Ethyl alcohol
$\text{NH}_3$	0.69	0.69	0.71
$\text{HCl}$	0.12	0.062	0.065
$\text{SO}_2$	0.91	1.20	1.00
$\text{CO}_2$	0.33	0.07	0.055

It will be noted that the constant is practically the same for ammonia in the three solvents. For  $\text{HCl}$  the constant is practically the same in the two alcohols but the value is lower than that for water. In  $\text{CO}_2$  and  $\text{SO}_2$  for which the degree of miscibility with alcohols is different from that of water, the values for the alcohols are different from those in water, but the difference is in opposite directions. Attempts to correlate this value in  $1/n$  with various physical properties of the gases and liquids have been without result. Very probably it is a complex function of the properties of both the solvent and solute.

#### Summary

It is shown that the formula

$$V = K \left( \frac{P_\sigma}{P_0} \right)^{1/n}$$

is applicable to the solubility data of  $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{SO}_2$  and  $\text{CO}_2$  in ethyl and methyl alcohols, as was previously shown for water.

The values of  $K$  and  $1/n$  are given for these gases in the three solvents.

*Baltimore, Md.*

<sup>1</sup> Zeit. phys. Chem., 54, 665 (1906).

## NOTE ON THE MEASUREMENT OF SURFACE TENSIONS

BY ROBERT B. ELDER

By the use of Jaeger's Method, Ferguson<sup>1</sup> has obtained some results bearing on the question of the effect of adsorbed gases on the surface tension of water, recently discussed by Mr. S. S. Bhatnagar.<sup>2</sup> Ferguson measured the surface tension of water in contact with air and with CO<sub>2</sub> at 15° C and obtained 73.88 and 73.04 dynes/cm respectively as the tension of these interfaces. Bhatnagar's results are 73.1 and 73.00 for the same interfaces at the same temperatures. Bhatnagar also gives results on other gases besides air and CO<sub>2</sub> in contact with water, and Ferguson gives results on other liquids besides water in contact with air and with CO<sub>2</sub>.

There is reason to question the accuracy of Bhatnagar's results, however, as his method involves certain errors, which are partially compensating and evidently for this reason yield results in close agreement with those obtained by other methods.

Bhatnagar's method, briefly, is as follows:

A segment of a sphere of known radius is suspended from a Jolly balance spring. A dish containing the liquid whose surface tension is to be measured is slowly raised till contact is made between the liquid surface and the sphere. The dish is then lowered till this contact is broken, the segment of the sphere being pulled from the liquid surface by the spring, and the distance the dish is moved vertically from the making to the breaking of this contact is taken as the amount the balance spring is extended. Knowing the constant of the spring the downward force exerted on the sphere by the liquid can then be found. The mistake in this lies in the assumption that the sphere and dish are in the same relative positions at the making and at the breaking of the contact. This might be

<sup>1</sup> Phil. Mag., (6) 28, 403 (1914).

<sup>2</sup> Jour. Phys. Chem., 24, 716 (1920).

true in a very special case, but in general is not true as will be shown.

Ferguson's formula,<sup>1</sup> which Bhatnagar uses in interpreting the experimental results described is,

$$M = 4\pi\rho a^2 \left\{ R - \frac{\sqrt{aR}}{3} - \frac{a}{3} \right\} \quad (1)$$

and Bhatnagar explains that, in this formula "M = weight required to detach the circular disk from the surface of water." This is a mistake, as this equation represents the condition of equilibrium when the sphere is in contact with the liquid, and its lowest point is in a line with the level portion of the liquid surface—(it being assumed that the angle of contact between the sphere and liquid is zero). A careful analysis of Ferguson's derivation and use of this formula will show that it applies only when relative positions of the sphere and the liquid surface are as stated.

The following quotation<sup>2</sup> describes his application of this formula:

"In order to apply equation (1) to determine surface tensions, a large hollow sphere of glass was taken and its external radius measured by means of a spherometer. No appreciable variation in the radius could be detected over the portion which was subsequently in contact with the liquid under examination. The sphere, after having been cleansed by alternate washings with caustic soda solution and distilled water, was dried and fastened by a thread about 20 cm in length to the underside of the pan of a balance standing on a high shelf, the thread passing through holes in the baseboard of the balance of the shelf. On a lower shelf, underneath the sphere, stood a small table whose height could be adjusted by

<sup>1</sup> Ferguson: *Phil. Mag.*, (6) 26, 925 (1913)

R = Radius of sphere,

$\rho$  = Density of the liquid

$\alpha^2 = \frac{T}{\rho g}$ , in which T = surface tension in dynes/cm and g is the gravity constant.

<sup>2</sup> *L. c.*, page 931.

means of a screw which table carried a carefully cleaned porcelain basin containing the liquid under examination.

"The sphere having been first counterpoised, the balance was left perfectly free and the height of the table adjusted until the liquid just touched the vertex of the sphere. This point was sharply defined by the sudden swing of the balance-pointer as the sphere touched the liquid and was pulled down. (In order to obtain consistent results, great care must be taken that the balance is quite at rest and the pointer exactly over the zero at the instant when the sphere and liquid make contact.) Weights were then added till the pointer was brought back to the zero, the mass of these weights being the  $M$  of equation (1)."

In a later paper Ferguson<sup>1</sup> deals with the general case of the sphere in contact with liquid, and shows that the maximum downward force exerted on the sphere is developed when the lowest point of the sphere is at a distance,  $d_1 = a^2 \left( \frac{1}{6\sqrt{aR}} - \frac{1}{R} \right)$ , from the horizontal surface of the liquid.

Ferguson<sup>2</sup> further states that the "pull is therefore a maximum when the vertex of the sphere is slightly *below* the level of the free horizontal surface of the liquid." (The italics are the present writer's.) This is an inaccurate statement of the case, as it will be seen that  $d_1$  will be positive or negative depending on the relative values of  $R$  and  $a$ . If  $R$  is less than  $36a$  the expression  $\left( \frac{1}{6\sqrt{aR}} - \frac{1}{R} \right)$  is negative, and hence  $d_1$  is negative i. e., the lowest point of the sphere is *above* the "free" horizontal surface of the liquid. For water at 20° C,  $T = 72.8$ ,  $\rho = 1.0$ ,  $g = 981$ , and  $a^2 = \frac{T}{\rho g} = \frac{72.8}{981} = 0.0742$ . Then  $a = \sqrt{0.0742} = 0.2724$ , and  $36a = 9.8$  approximately, so that with water and any sphere smaller than about 9.8 cm radius, the

<sup>1</sup> Phil. Mag., (6) 28, 149 (1914).

<sup>2</sup> L. c., page 153.

maximum force is developed with the lowest point of the sphere *above* the level surface of the liquid, and not below, as Ferguson states. The sphere Ferguson used in this test was 7.321 cm radius, and that used by Bhatnagar was 5.007 cm radius.

Substituting 5.007 for R in the above formula we find that the maximum forces would be developed on Bhatnagar's sphere with the lowest point of the sphere at a distance (approximately) 0.0042 cm vertically *above* the horizontal portion of the liquid surface.

It is obvious that Ferguson's experiment with the sphere suspended from the balance arm would have been impossible if the maximum development of forces occurred when the lowest point of the sphere was below the level portion of the liquid surface. It would, in fact, be impossible under otherwise similar conditions, and using a sphere larger than 9.8 cm radius.

Considering the case of a segment of a sphere suspended from the spring of a Jolly balance, as is the case in Bhatnagar's experiment, it is evident that the rupture between the sphere and the liquid in the dish will not take place *before* the forces acting on the sphere are at their maximum. This maximum occurs when the first derivative of the forces pulling down becomes zero, but, since the force pulling the sphere up also varies differentially with the vertical motion of the sphere, rupture does not occur at the point of maximum development of the forces, because at this point a slight upward movement of the sphere will decrease the force pulling up more than it decreases the force pulling down.

In general, for a solid of any shape being pulled from a liquid surface, the position in which rupture occurs is fixed by the equality between the first derivative of the force pulling the solid up and that of the forces pulling it down, rather than by the maximum development of these forces. In the case of the gravity balance, the derivative of the force pulling up is zero, and the rupture occurs when the forces pulling down reach a maximum, that is, when their derivative becomes equal to zero. If the force pulling up varies with the differential vertical motion of the solid, the

position of rupture is that position after the maximum development of forces is obtained in which the derivative of the forces pulling down equals that of the forces pulling up.<sup>1</sup>

In Bhatnagar's experiment the rupture between the liquid and the sphere comes after the maximum development of forces and when the lowest point of the sphere is above the level or "free" portion of the liquid surface. The level liquid surface is lower in the dish at the time of breaking the contact than at the time of making it, since some of the liquid is lifted up with the sphere. The amount of this lowering of the liquid surface in the dish would depend, among other things upon the size of the dish. These two errors, i. e., the lowering of the liquid surface in the dish and the lifting of the lowest point of the sphere above the level liquid surface at the time rupture occurs, tend to compensate each other under the conditions of Bhatnagar's experiment. In addition to these errors there is the misinterpretation of Ferguson's formula, so that Bhatnagar's results are of little value as to their absolute accuracy. Their relative values as compared with one another are doubtless correct.

The lowering of the level liquid surface in the dish due to some of the liquid being lifted by its contact with the sphere would also be a factor for consideration in Ferguson's experiment with the segment of the sphere suspended from the pan of the gravity balance, and Ferguson has apparently overlooked this. In this case, however, the area of the dish might have been so large that the error introduced by neglecting this factor would have been negligible, which is not likely to have been the case in Bhatnagar's experiment.

*Idaho School of Mines  
Moscow, Idaho*

---

<sup>1</sup> For a mathematical discussion of the forces involved in the case of a wedge-shaped solid suspended from a Jolly balance spring, and a method of measuring surface tensions thereby, see Pamphlet No. 1, of the Idaho Bureau of Mines and Geology—"Interfacial Tension Measurements and Some Applications to Flotation" by R. B. Elder, and for further discussion of the subject and description of an apparatus for accurately and rapidly measuring surface tension by this method, see "Surface-Energy and Adsorption in Flotation" by A. W. Fahrenwald: Min. and Sci. Press, 123, 127 (1921).

## REACTIONS IN FUSED SALT MEDIA. II STUDIES IN SOLVOLYSIS

BY J. F. G. HICKS WITH WALLACE A. CRAIG

In a previous paper<sup>1</sup> it was pointed out that the mechanism of the interactions between certain fused salts and certain solutes dissolved by them probably resembled hydrolysis quite closely. A study of the interactions of both lead oxide and lead chromate with fused sodium chloride furnished evidence for such a conclusion, as did also a study of the behavior of lead chromate in the presence of a fused mixture of sodium and potassium nitrates (*q. v.*). For such reactions the name "solvolysis" was suggested. It was the purpose of this investigation to ascertain whether these "solvolyses" were or were not true equilibria, thereby defining their relation to hydrolysis.

### I. Hydrolysis Experiments

These were carried out for a twofold purpose: (1) to furnish a means of comparison when studying the solvolytic (fusion) reactions from the standpoint of the mass law, and (2) to further establish the analogy between hydrolysis and solvolysis through the formation of analogous "basic lead chromates" by the two methods.

*A. Hydrolysis Under Ordinary Pressure: (a) Lead Chromate.*—Increasing quantities of lead chromate were boiled with 100 grams of water, loss from evaporation being made up from time to time. The resulting "basic lead chromates" varied in color from dark yellow to very deep orange; no red ones were observed, nor did the hand-lens (Hastings triplet) reveal any red particles. At the end of each experiment a known quantity of ferrous ammonium sulphate was added to the filtrate from the insoluble "basic chromate" and the excess  $\text{Fe}^{++}$  titrated with potassium permanganate in the usual manner.

<sup>1</sup> Jour. Phys., Chem., 25, 545 (1921).



The continuous increase in weight of initial samples has no particular significance. The samples were weighed out, arranged in order of increasing weight and then treated. This order of treatment was selected in order that the largest sample should be exposed to the action of a particular reagent for the longest time. The above arrangement holds true for all similar succeeding series of experiments.

Results of hydrolysis experiments are tabulated below:

TABLE I\*  
Hydrolysis of Lead Chromate at 100°. Concentration of H<sub>2</sub>O Constant; of PbCrO<sub>4</sub> increasing

Time (minutes)	Init. CrO <sub>3</sub> (mols) (weighed as PbCrO <sub>4</sub> ) (M)	CrO <sub>3</sub> in filtrate (mols) (m)	% init. CrO <sub>3</sub> removed by hydrolysis	K hydrolysis = $\frac{m}{M-m}$
10	0.0018	0.053	0.17	0.0017
20	0.0029	0.055	0.17	0.0017
30	0.0039	0.058	0.21	0.0021
40	0.0056	0.0418	0.33	0.0032
50	0.0076	0.0444	0.58	0.0058
60	0.0090	0.0465	0.72	0.0073
70	0.0105	0.0491	0.87	0.0087
80	0.0122	0.03177	0.96	0.0097
90	0.0130	0.03133	1.02	0.0103
100	0.0148	0.03160	1.08	0.0109
110	0.0159	0.03184	1.16	0.0111
120	0.0182	0.03218	1.19	0.0121
130	0.0196	0.03245	1.25	0.0127
140	0.0213	0.03277	1.30	0.0132
150	0.0224	0.03284	1.27	0.0128
160	0.0251	0.03331	1.32	0.0125
170	0.0274	0.03353	1.29	0.0131
180	0.0287	0.03373	1.30	0.0132
190	0.0313	0.03391	1.25	0.0127
200	0.0322	0.03409	1.27	0.0129

(b) *Lead Oxid.*—Boiling with water for 6–8 hours did not dissolve sufficient PbO for the estimation of Pb<sup>++</sup>. The acidified filtrate darkened when saturated with H<sub>2</sub>S.

\*The writer gratefully acknowledges his indebtedness to Mrs. Mary B. Hicks for assistance in checking this and subsequent tables.

(c) *Lead Chromate-Lead Oxid (50-50 molar % mixture).*—This mixture was hydrolyzed by boiling for seven hours as for the other hydrolyses. The reddish orange "basic lead chromate" contained 81.78% PbO and 18.06% CrO<sub>2</sub>.

*B. Hydrolysis Under Increased Pressure:*\* (a) *Lead Chromate.*—Lead chromate and an excess of water were heated in sealed bomb-tubes in the usual manner.

Analytical procedure was the same as for the hydrolyses under ordinary pressures. Results are tabulated below:

TABLE II  
Hydrolysis of Lead Chromate under Increased Pressure

No.	Temp. (°C)	Time (hrs.)	Init. mols CrO <sub>2</sub> (weighed as PbCrO <sub>4</sub> ) (M)	CrO <sub>2</sub> in filtrate (mols) (m)	% of M removed by hydrolysis	K hydrolysis = $\frac{m}{M-m}$
1	150-155	1	0.19	0.009	4.7	0.049
2	150-155	2	0.27	0.013	4.8	0.054

Both "basic lead chromates" were deep orange in color, the second being slightly darker than the first.

(b) *Lead Oxid.*—Lead oxid (PbO) was treated in the same manner as above. The acidified filtrate turned yellowish brown when saturated with H<sub>2</sub>S, but the resulting PbS could not be filtered out. It is probable that a larger quantity of PbO than indicated was in solution while the pressure was above normal, but precipitated when normal pressure was re-attained.

(c) *Lead Chromate-Lead Oxid (50-50 molar % mixture).*—This mixture was treated as above, with excess water, in bomb-tubes. Results follow:

\* Acknowledgment is hereby made to Mr. E. L. Gustus for the preparation of the bomb-tubes and the treatment of the samples hydrolyzed under increased pressure.

TABLE III  
Hydrolysis of 50-50 Molar % PbCrO<sub>4</sub>-PbO under Increased Pressure

No.	Temp. (° C)	Time (hrs.)	PbO (%)	CrO <sub>3</sub> (%)	Color of residue
1	150-155	1	82.28	17.58	Deep orange-red
2	150-155	2	83.64	10.22	Deep orange-red

## II. Solvolysis Experiments

A. Lead Chromate in "Nitrate Flux."—Increasing quantities of lead chromate were "solvolysed" in increasing quantities of a fused mixture of sodium and potassium nitrates (50-50

TABLE IV  
Solvolysis of PbCrO<sub>4</sub> in Nitrate Flux at 225°-230°. Concentration of both PbCrO<sub>4</sub> and Flux increasing

Time (minutes)	Init. CrO <sub>3</sub> (mols) (weighed as PbCrO <sub>4</sub> ) (M)	CrO <sub>3</sub> in filtrate (mols) (weighed as PbCrO <sub>3</sub> ) (m)	% init. CrO <sub>3</sub> removed by solvolysis	K solvolysis = $\frac{m}{M-m}$
10	0.0015	0.0413	0.86	0.01
20	0.0016	0.0423	1.44	0.01
30	0.0017	0.0446	2.70	0.03
40	0.0019	0.03103	5.42	0.06
50	0.0020	0.03159	7.95	0.11
60	0.0022	0.03245	11.10	0.10
79	0.0023	0.03372	16.19	0.21
80	0.0026	0.03543	20.89	0.24
90	0.0027	0.03699	25.13	0.35
100	0.0028	0.03788	28.14	0.40
110	0.0029	0.03915	31.55	0.45
120	0.0032	0.021129	35.29	0.52
130	0.0033	0.021187	35.99	0.57
140	0.0037	0.021372	37.08	0.61
150	0.0043	0.021608	37.39	0.59
160	0.0045	0.021675	37.22	0.67
179	0.0052	0.021974	37.14	0.63
180	0.0054	0.022038	37.74	0.59
190	0.0069	0.022597	37.66	0.60
200	0.0076	0.022862	37.66	0.62

molar %, eutectic at 218°)<sup>1</sup> after the manner of the previous work in preparing "basic lead chromates" by fusion methods.<sup>2</sup> The solvolyses were performed simultaneously in porcelain crucibles in an oven at 225°-230°. The insoluble residues were bright red. The cooled fusions were extracted with water at room temperature (to avoid hydrolysis, which would increase the concentration of  $(\text{CrO}_4)^{2-}$  in the filtrates), and the  $\text{CrO}_3$  determined as  $\text{PbCrO}_4$  in the usual manner. Results are tabulated in Table IV.

In order to make sure that this "solvolysis" represented a true state of equilibrium, increasing quantities of lead chromate were fused with a nearly constant quantity of nitrate flux (37 g  $\pm$  0.05 g = 2 mols, approximately) for two hours at 225°-230°, using the same procedure as before. The difference in weight between successive initial samples of  $\text{PbCrO}_4$  were purposely made much larger than in the preceding series of experiments. Table IV would indicate that equilibrium is attained in about 100 minutes, hence a two-hour run should be sufficient. Should a true state of equilibrium

TABLE V

Check-runs for Equilibrium. Solvolysis of  $\text{PbCrO}_4$  in Nitrate Flux at 225°-230°. Concentration of Flux Constant; of  $\text{PbCrO}_4$  increasing

No.	Init. $\text{CrO}_3$ (mols) (weighed as $\text{PbCrO}_4$ ) (M)	$\text{CrO}_3$ in filtrate (mols) (weighed as $\text{PbCrO}_4$ ) (m)	% of init. $\text{CrO}_3$ removed by solvolysis	K solvolysis $= \frac{m}{M-m}$
1	0.0026	0.0009	34.62	0.53
2	0.0042	0.0014	33.33	0.50
3	0.0086	0.0024	27.91	0.388
4	0.0162	0.0040	24.69	0.328
5	0.0240	0.0049	20.42	0.256
6	0.0306	0.0054	17.68	0.214
7	0.0355	0.0058	16.34	0.195
8	0.0459	0.0065	14.09	0.165
9	0.0588	0.0069	11.73	0.133
10	0.0621	0.0072	11.58	0.131

<sup>1</sup>Landolt-Börnstein-Roth: "Physicalische-chemische Tabellen," 4 Auflage, pp. 611-635.

<sup>2</sup>Jour. Phys. Chem., 25, 545 (1921).

obtain, the  $\text{CrO}_3$  removed by solvolysis should increase with the time, but the percent of a mol of  $\text{CrO}_3$  so removed should decrease. Results are shown in Table V.

These results indicate a true state of equilibrium between lead chromate and the fused nitrate flux.

*B. Lead Chromate in Fused Sodium Chlorid.*—Since a temperature of  $850^\circ$ – $870^\circ$  could not be obtained in an ordinary oven, these solvolyses could not be run simultaneously. The porcelain crucibles containing the several fusion-mixtures were heated in a resistance-furnace which accommodated but one crucible at a time. The insoluble residue was orange to light brown in color. The temperature was controlled by means of a Pt/Pt–Rh thermo-couple. In other respects the procedures were the same as before. Results of this series of solvolyses are tabulated below:

TABLE VI  
Solvolysis of  $\text{PbCrO}_4$  in Fused Sodium Chlorid at  $850^\circ$ – $870^\circ$ . Relative Concentration of Both  $\text{PbCrO}_4$  and  $\text{NaCl}$  increasing

Time (minutes)	Init. $\text{CrO}_3$ (mols) (weighed as $\text{PbCrO}_4$ ) (M)	$\text{CrO}_3$ in filtrate (mols) (weighed as $\text{PbCrO}_4$ ) (m)	% init. $\text{CrO}_3$ removed by solvolysis	K solvolysis = $\frac{m}{M-m}$
10	0.0389	0.056	0.67	0.007
20	0.0397	0.0411	1.13	0.01
30	0.02109	0.0417	1.43	0.02
40	0.02114	0.0427	2.18	0.03
50	0.02127	0.0435	2.76	0.03
60	0.02132	0.0441	3.11	0.03
70	0.02136	0.0450	3.68	0.04
80	0.02139	0.0458	4.17	0.05
90	0.02152	0.0473	4.80	0.05
100	0.02155	0.0486	5.61	0.06
110	0.02161	0.03102	6.33	0.07
120	0.02176	0.03121	6.87	0.06
130	0.02182	0.03133	7.31	0.06
140	0.02189	0.03144	7.60	0.06
150	0.02197	0.03154	7.82	0.06
160	0.02203	0.03165	8.13	0.06
170	0.02211	0.03175	8.29	0.06
180	0.02217	0.03180	8.30	0.05
190	0.02223	0.03187	8.38	0.05
200	0.02229	0.03191	8.34	0.05

In order to make sure that a true state of equilibrium existed in the system  $\text{PbCrO}_4\text{-NaCl}$  under the above conditions, a series of check-runs was made, using a nearly constant quantity of sodium chlorid ( $30\text{ g} \pm 0.05\text{ g} = 0.5\text{ mol}+$ ), exactly as for the preceding series of check-runs with nitrate flux. Wider differences in weight between successive initial samples of lead chromate were purposely made, as before. Results follow:

TABLE VII  
Check-runs for Equilibrium. Solvolysis of  $\text{PbCrO}_4$  in fused  $\text{NaCl}$  at  $850^\circ\text{-}870^\circ$ . Concentration of  $\text{NaCl}$  Constant; of  $\text{PbCrO}_4$  increasing

No.	Init. $\text{CrO}_3$ (mols) (weighed as $\text{PbCrO}_4$ ) ( $M$ )	$\text{CrO}_3$ in filtrate (mols) (weighed as $\text{PbCrO}_4$ ) ( $m$ )	% init. $\text{CrO}_3$ removed by solvolysis	$K$ solvolysis $= \frac{m}{M-m}$
1	0.00178	0.00012	6.74	0.0724
2	0.00377	0.00016	4.24	0.0444
3	0.00653	0.00018	2.76	0.0284
4	0.0117	0.00021	1.79	-0.0183
5	0.0149	0.00022	1.47	0.0150
6	0.0158	0.00022	1.39	0.0141
7	0.0213	0.00028	1.31	0.0133
8	0.0227	0.00029	1.28	0.0130
9	0.0248	0.00031	1.25	0.0126
10	0.0294	0.00035	1.19	0.0120

These results indicate a true state of equilibrium for the system  $\text{PbCrO}_4\text{-NaCl}$  under the recorded conditions.

*C: Lead Oxid in Fused Sodium Chlorid.*—It has been shown<sup>1</sup> that one mole of lead oxid ( $\text{PbO}$ ) completely dissolves in five mols of fused sodium chlorid at  $880^\circ$  and that conversion to lead chlorid is practically complete in two hours. Hence one should expect a very nearly complete reaction at a temperature slightly above the melting-point of sodium chlorid; the solvolyses were carried out at  $850^\circ\text{-}870^\circ$  as in the case of lead chromate. In view of this, one should also expect that the calculation of a constant of

<sup>1</sup> Jour. Phys. Chem., 25, 545 (1921).

solvolysis would be of no value, and that a series of check-runs, made in the previous series, should be omitted. The appended results would seem to justify this assumption and procedure:

TABLE VIII  
Solvolysis of PbO in Fused NaCl at 850°-870°. Relative Concentration of PbO and NaCl both increasing

Time (minutes)	Init. PbO (mols)	PbO (mols) solvolyzed to PbCl <sub>2</sub> (weighed as PbCrO <sub>4</sub> )	% init. PbO solvolyzed to PbCl <sub>2</sub>
10	0.0008	0.0001	12.50
20	0.0009	0.0004	44.44
30	0.0010	0.0006	60.00
40	0.0011	0.0009	81.82
50	0.0012	0.0010	83.33
60	0.0013	0.0012	92.31
70	0.0014	0.0013	92.86
80	0.0015	0.0014	93.33
90	0.0016	0.0015	93.75
100	0.0017	0.0016	94.12
110	0.0018	0.0017	94.44
120	0.0019	0.0018	94.74
130	0.0020	0.0019	95.00
140	0.0021	0.0020	95.24
150	0.0022	0.0021	95.45
160	0.0023	0.0022	95.65
170	0.0024	0.0023	95.83
180	0.0026	0.0025	96.15
190	0.0027	0.0026	96.29
200	0.0028	0.0028	96.43

These results point to a completion of reaction, or at least to a set of conditions under which the reaction would soon be completed. The insoluble residue was white, containing a small quantity of admixed PbO (orange). From these and the previous observations it would seem practically certain that the reaction would be complete at a temperature not much higher than that of the experiments. An inspection of the table will also show that the calculation of a constant of solvolysis would be without significance.

TABLE IX  
 Solvolysis of Silver Chromate in Nitrate Flux at 230°-240°. Concentration of Flux Constant; Concentration of Silver Chromate increasing

Time (minutes)	Init. CrO <sub>3</sub> (mols) (weighed as Ag <sub>2</sub> CrO <sub>4</sub> ) (M)	CrO <sub>3</sub> in filtrate (mols) (weighed as Ag <sub>2</sub> CrO <sub>4</sub> ) (m)	% init. CrO <sub>3</sub> removed by solvolysis	K solvolysis = $\frac{m}{M-m}$
10	0.037536	0.04742	9.08	0.109
20	0.0215071	0.04567	3.77	0.039
30	0.0222607	0.04262	1.17	0.0175
40	0.0230142	0.04172	0.571	0.0057
50	0.0237678	0.04163	0.433	0.0044
60	0.0245214	0.04127	0.281	0.0028
70	0.0252750	0.04220	0.417	0.0042
80	0.0260284	0.0566	0.109	0.0011
90	0.0267820	0.0599	0.146	0.0015
100	0.0275355	0.04130	0.173	0.00173
110	0.0282891	0.04148	0.179	0.0018
120	0.0290426	0.0554	0.060	0.0006
130	0.0297962	0.0599	0.101	0.0010
140	0.0105497	0.04142	0.135	0.00135
150	0.0113033	0.04154	0.136	0.0014
160	0.0120568	0.04115	0.095	0.00095
170	0.0128104	0.04142	0.111	0.0011
180	0.0135639	0.04105	0.078	0.0008
190	0.0142175	0.04151	0.106	0.0011
200	0.0150710	0.0590	0.060	0.0006

TABLE X  
 Solvolysis of Silver Chromate in Fused Sodium Chloride at 850°-870°. Constant Concentration of Flux; increasing Concentration of Silver Chromate

Time (minutes)	Initial CrO <sub>3</sub> (mols) (weighed as Ag <sub>2</sub> CrO <sub>4</sub> )	CrO <sub>3</sub> equivalent to ppt. AgCl (mols)	% initial CrO <sub>3</sub> solvolyzed out
5	0.03392	0.03391	99.7
10	0.03754	0.03719	95.3
15	0.02115	0.02112	97.4
20	0.02151	0.02148	98.0
25	0.02187	0.02179	95.7
30	0.02226	0.02224	99.1
40	0.02301	0.02297	98.6



*D. Silver Chromate in Nitrate Flux.*—The procedure for this series of solvolyses was the same as for lead chromate except that the temperature of operation was 230°–240°. This would lead one to expect a state of equilibrium to be attained in a shorter time than in the previous solvolyses, which prediction was borne out experimentally. Equilibrium is attained at 80 minutes at 230°–240° as against 100 minutes at 225°–230°. The extent of the solvolysis-reaction could not, of course be predicted, it depending upon the nature of the substance solvolyzed and the solvolyzing medium.

TABLE XI  
Solvolysis of Barium Chromate in Nitrate Flux at 230°–240°. Concentration of Flux Constant; of Barium Chromate increasing

Time (minutes)	Initial CrO <sub>3</sub> (mols) (weighed as BaCrO <sub>4</sub> ) (M)	CrO <sub>3</sub> in filtrates (mols) (weighed as BaCrO <sub>4</sub> ) (m)	% init. CrO <sub>3</sub> removed by solvolysis	K solvolysis = $\frac{m}{M-m}$
10	0.000987	0.000184	18.75	0.229
20	0.00198	0.000187	9.48	0.104
30	0.00296	0.000257	8.69	0.096
40	0.00395	0.000201	5.11	0.054
50	0.00494	0.000232	4.70	0.049
60	0.00593	0.000238	4.01	0.042
70	0.00691	0.000221	3.21	0.033
80	0.00790	0.000218	2.76	0.029
90	0.00890	0.000263	2.96	0.030
100	0.00980	0.000340	3.44	0.036
110	0.01085	0.000286	2.64	0.027
120	0.01184	0.000338	2.85	0.030
130	0.01283	0.000321	2.50	0.026
140	0.01381	0.000356	2.57	0.027
150	0.01480	0.000338	2.28	0.024
160	0.01580	0.000296	1.87	0.019
170	0.01680	0.000334	1.99	0.020
180	0.01779	0.000327	1.84	0.019
190	0.01879	0.000334	1.78	0.018
200	0.01975	0.000411	2.08	0.021

In order to save time, a nearly constant quantity of flux was used in each solvolysis, that is, the procedure of the check-runs for lead chromate solvolysis (Table V) was followed rather

than that of the other runs (Table IV). Since a state of equilibrium was shown to exist in this and other similar experiments, it seemed safe to assume such a state in these solvolyses. In this way double work was saved.

Twenty samples of silver chromate varying in weight from 0.25 gram to 5.0 grams were solvolysed with 25 grams ( $\pm 0.05$  g) of the nitrate flux. The  $\text{CrO}_3$  removed by the solvolysis was determined as silver chromate in the usual manner. Results are shown in Table IX.

*E. Silver Chromate in Fused Sodium Chlorid.*—Seven samples of silver chromate were fused with a constant quantity (25 g  $\pm 0.05$  g) of sodium chloride at  $850^\circ$ – $870^\circ$ . Complete solvolysis is brought about almost immediately, as an in-

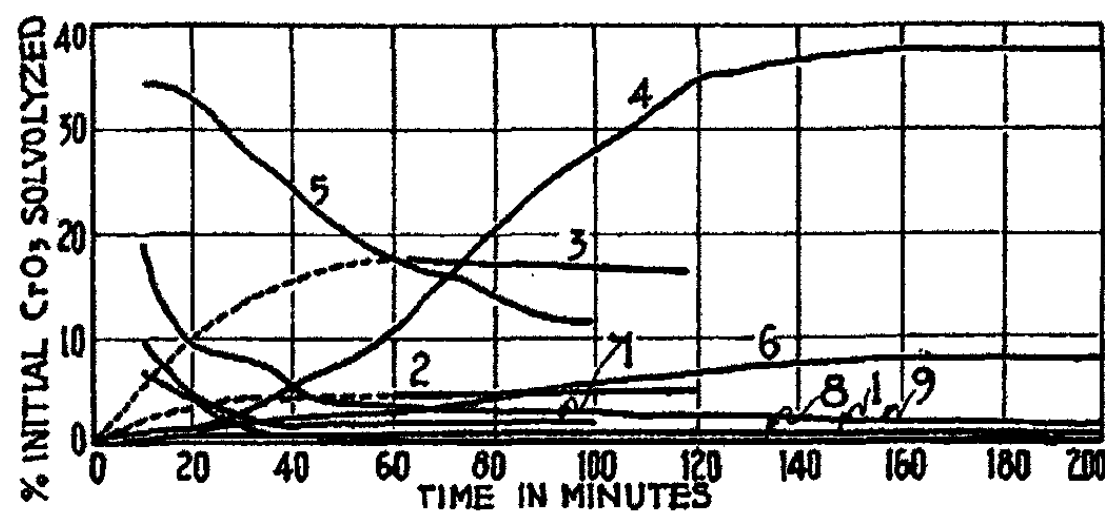


Fig. 1

- No. 1. Hydrolysis of lead chromate at  $100^\circ$ .  $\text{PbCrO}_4$  increasing;  $\text{H}_2\text{O}$  constant.
- No. 2. Hydrolysis of lead chromate under pressure at  $150^\circ$ – $155^\circ$ .
- No. 3. Hydrolysis of 50–50 molar percent  $\text{PbO}$ – $\text{PbCrO}_4$  under pressure.
- No. 4. Solvolysis of  $\text{PbCrO}_4$  in nitrate flux at  $225^\circ$ – $230^\circ$ . Concentration of flux and  $\text{PbCrO}_4$  increasing.
- No. 5. Solvolysis of  $\text{PbCrO}_4$  in nitrate flux at  $225^\circ$ – $230^\circ$ . Flux constant;  $\text{PbCrO}_4$  increasing.
- No. 6. Solvolysis of  $\text{PbCrO}_4$  in fused  $\text{NaCl}$  at  $850^\circ$ – $870^\circ$ .  $\text{NaCl}$  and  $\text{PbCrO}_4$  increasing.
- No. 7. Solvolysis of  $\text{PbCrO}_4$  in fused  $\text{NaCl}$  at  $850^\circ$ – $870^\circ$ .  $\text{NaCl}$  constant;  $\text{PbCrO}_4$  increasing.
- No. 8. Solvolysis of  $\text{AgCrO}_4$  in nitrate flux at  $230^\circ$ – $240^\circ$ . Flux constant;  $\text{AgCrO}_4$  increasing.
- No. 9. Solvolysis of  $\text{BaCrO}_4$  in nitrate flux at  $230^\circ$ – $240^\circ$ . Flux constant;  $\text{BaCrO}_4$  increasing.

spection of the results will show (Table X). Since the reaction proceeds to completion, a "constant of solvolysis" would

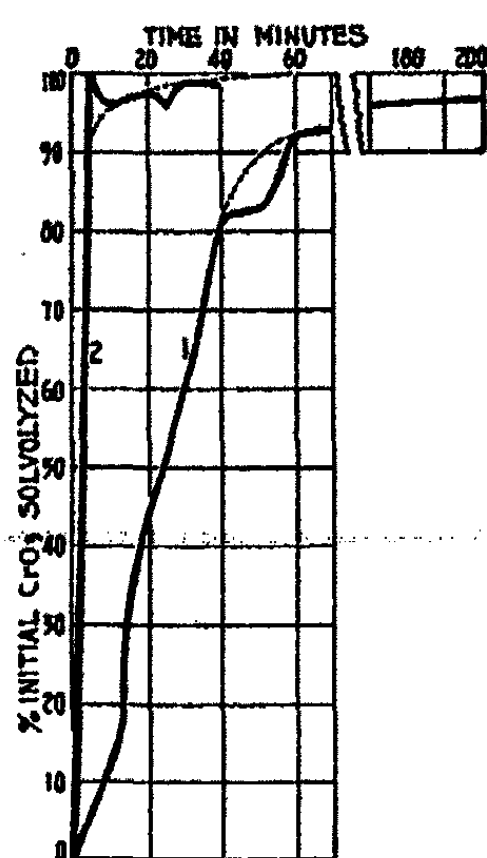


Fig. 2

No. 1. Solvolysis of PbO in fused NaCl at 850°-870°. NaCl and PbO increasing.

No. 2. Solvolysis of AgCrO<sub>4</sub> in fused NaCl at 850°-870°. NaCl constant. AgCrO<sub>4</sub> increasing.

of comparison a series of graphs have been prepared, in which the percentage of initial CrO<sub>3</sub> removed by solvolysis has been plotted against the time of solvolysis, Figs. 1 and 2.

### III. Summary: Conclusions

(1) Solvolysis of lead, silver and barium chromates by a fused mixture of sodium and potassium nitrates (50-50 molar %) represent states of equilibria analogous to hydrolysis. Of these reactions the solvolysis of lead chromate is the most complete, that of barium chromate next, and that of silver chromate the least complete. The regularity with which the constants of solvolysis vary between consecutive observations follows the same order. The marked irregularity in the case

have no signification, and was not calculated. Results are shown in Table X.

F. Solvolysis of Barium Chromate in Nitrate Flux.—Increasing quantities of barium chromate were solvolyzed with constant quantity (25 g ± 0.05 g) of "nitrate flux" at 230°-240°, from 10 to 200 minutes, at ten-minute intervals. The usual procedure was followed. The cold fusions were extracted with cold water, and CrO<sub>3</sub> determined in the filtrates in the usual manner. Results are shown in Table XI.

It had been planned to study the solvolysis of barium chromate in fused sodium chloride, but time did not permit.

For the sake of convenience

of silver chromate suggests the possibility of another factor entering into the reaction; this will be investigated later.

(2) Solvolysis of lead chromate by sodium chlorid (fused) also represents a true state of equilibrium. In the case of silver chromate the reaction proceeds to completion; it was not tried for barium chromate.

(3) In the solvolytic reactions studied, equilibrium is attained in about 100 minutes. Constants of solvolysis can be calculated with a fair degree of accuracy, considering the conditions of experimentation.

(4) Solvolysis of lead oxid by fused sodium chlorid proceeds practically to completion at  $850^{\circ}$ – $870^{\circ}$ . This was expected, and confirms previous observations. The complete solvolysis of silver chromate by fused sodium chlorid at  $850^{\circ}$ – $870^{\circ}$  is brought about in a shorter time.

(5) The present investigation would seem to show that lead chromate and lead oxid (PbO) combine by simple "molecular addition" *after* part of the former has undergone solvolysis in the nitrate flux. In other words, the red "basic lead chromates" are "higher order" compounds.

(6) The relatively small degree of solvolysis of lead chromate and the practically complete solvolysis of lead oxid (PbO) by the same reagent under the same conditions will account for:

(a) The failure to obtain red "basic lead chromates" when a fusion containing lead chromate, lead oxid (PbO) and sodium chlorid is *quickly* cooled.

(b) The appearance of the red "basic lead chromates" when such a fusion as the above (a) is *slowly* cooled.<sup>1</sup>

(7) A study of the solvolytic reactions apparently confirms the assumption of the dissociation  $\text{Pb}_2\text{CrO}_5 \rightleftharpoons \text{PbO} + \text{PbCrO}_4$ . This assumption was previously offered as an explanation of the failure to obtain red "basic lead chromates" when a fusion containing lead chromate, lead oxid (PbO) and sodium chlorid was poured into water, and agrees well

<sup>1</sup> Jour. Phys. Chem., 25, 545 (1921).

with the evidence offered by the thermal equilibrium diagram plotted for the system lead chromate-lead oxid.<sup>1</sup>

(8) Graphs showing the rates of solvolysis for the different reactions studied have been plotted.

*Stanford University*  
*California*

---

<sup>1</sup> Jour. Phys. Chem., 25, 545 (1921).

## ON THE CONDUCTIVITY OF THE LATENT IMAGE

BY A. G. RABINOVICH

The nature of the latent image, i. e., of the invisible image, which exists in the exposed, but undeveloped photographic plate, is not clear till now. There are many theories<sup>1</sup> which attempt to reduce it to chemical or physical changes of the sensitive layer, but no one of them could prevail over the others. The causes of this are: that the latent image can be produced not only by light, but also by other factors, that its character depends both on the sensitive silver halide and on the properties of the gelatine film, in which it is emulsified; but the principal cause is that the amount of silver bromide changed by light, forms such a small part of the whole that it could be detected by no analytical means.

The adherents to the "physical" theories describe the latent image as the alteration only of the physical properties of silver bromide, without chemical decomposition of its molecules: such are Chapman Jones, and Namias, who reduce it to polymerization; Hurter and Driffield on the contrary—to depolymerization; DeHeen<sup>2</sup>—to ionization (without separation of ions) etc.

The adepts of the "chemical" theories believe that the formation of the latent image consists in the reduction of AgBr, the particles of which are decomposed under the action of light. Abegg and Ostwald suppose that a part of the molecules of AgBr are reduced to metallic silver, forming each a "nucleus" or germ around which further quantities of silver are deposited during the developing process.

The upholders of the "subhalide" theory, which predominated at a certain time (Eder, Luther, Baur, Schaum, Trivelli and others) believe that silver bromide is reduced not to silver,

<sup>1</sup> For the bibliography see W. D. Bancroft: *Jour. Phys. Chem.*, 15, 313, 551 (1911); 16, 29, 89 (1912); 17, 93 (1913).

<sup>2</sup> De Heen: *Bull. Ac. roy. Belg. sc.*, 1910, 546.

but to a compound containing less halogen than AgBr, a "subhalide," as Ag<sub>2</sub>Br.

After Carey Lea's discovery of colloidal silver in many coloured modifications and of photohalides a new "adsorption" theory arose, taking the latent image for silver bromide which has adsorbed the subhalide. Later another theory (R. Lorenz, Lüppo-Cramer, W. Bancroft, Reinders and others) has been put forward, where the adsorbed substance is supposed to be colloidal silver.

The partisans of the old theories have not all been convinced by the arguments of the supporters of the new one, and polemics on the pages of photographic and general scientific journals continue till today.

The elucidation of the nature of the latent image may be advanced by the investigation of its physical properties. Many of them are known. Yet, there is no sufficient experimental material on the important question about the possible change of the electrical conductivity of the photographic plate after insolation, i. e., how the formation of the latent image does influence the conductivity of the plate. This question was investigated by H. Meyer,<sup>1</sup> but only in application to the chromated gelatine, where the process is of course different from that in the bromogelatine silver emulsion. The resistance of the last (in the wet state only) has been measured by Novák<sup>2</sup> by means of alternating current wire bridge and a sensitive dynamometer. He has found that when a wet plate is exposed to the light of an Auer burner its resistance decreases at once very little, then increases during an hour to 1%, then diminishes again, falling to a value lower than before the experiment. In this work the effect of the heating by the source of light has not been measured, the exposure was much longer than usual and gave not a normal image, but rather an effect of solarization. Therefore the work of Novák does not give

<sup>1</sup> H. Meyer: *Zeit. wiss. Photogr., Photoch.*, 8, 1 (1910); *Zeit. phys. Chem.*, 66, 48 (1909).

<sup>2</sup> V. Novák: *Sitzungsber. Rgl. Böhm. Ges. Wiss.*, 1902, 41 (with a brief English summary).

a clear reply to the question, how the conductivity of the layer changes when a latent image be formed in it.

On the other side, however, there are many papers stating the influence of light on the conductivity of individual (pure) substances. Such are first the numerous works describing the well-known properties of selenium. Later the same property (increase of the conductivity under the influence of light) in the less pronounced manner has been found in some other substances, especially of mineral origin, e. g., the compounds of sulfur, arsenic, etc., with heavy metals.<sup>1</sup> Arrhenius<sup>2</sup> has shown that the conductivity of thin films of halide silver salts increases in all parts of the visible spectrum approximately in proportion to the (photometric) intensity of the light. The maximum of the light action was observed on the boundary between the visible and the ultra-violet parts of the spectrum. When the salts have been impregnated with optical sensitizers, the maximum of the light action migrated to the maximum of light absorption of the given sensitizer. Rudert<sup>3</sup> also found a decrease of resistance of cuprous iodide under the influence of light. Scholl<sup>4</sup> exposed thin membranes of silver iodide to the light of an arc lamp, which made their conductivity 40-50 times larger than before. From the diffusion, he calculated the velocity of migration of the electricity bearers and found it to exceed many times all known ionic velocities. He concluded from this that the bearers of electricity, which appear in the Ag under the action of light, are free electrons. W. Wilson<sup>5</sup> has studied the photoelectric effect in AgI by another method: in front of the plate of silver iodide exposed to the influence of light he placed a copper plate which caught the electrons emitted by AgI, and the quantity of electricity brought away by them was measured by a special device.

<sup>1</sup> Pfund: *Phys. Rev.*, 7, 298 (1916); T. W. Case, *Phys. Rev.*, 9, 305 (1917); Martin: *Phys. Zeit.*, 12, 41 (1911).

<sup>2</sup> Arrhenius: *Sitzungsber. Akad. Wiss., Wien*, 96, 831 (1887).

<sup>3</sup> Rudert: *Ann. Phys.*, (4) 31, 559 (1910).

<sup>4</sup> Scholl: *Zeit. wiss. Photogr.*, 4, 1 (1906).

<sup>5</sup> W. Wilson: *Ann. Phys.*, (4) 23, 107 (1907).



All these works suggested the idea that the galvanic resistance of the light-sensitive layer of the photographic plate might decrease under the influence of light, and that the appearance of the latent image could be reduced to a purely physical phenomenon—the increase of the number of free electrons (in parts of the plate exposed to light). For the definitive resolution of this question the change of conductivity of the sensitive emulsion under the influence of light had to be studied experimentally. The present work was undertaken for this purpose.

The resistance was measured by means of a method proposed by W. Siemens<sup>1</sup> developed by H. Meyer<sup>2</sup> and carefully studied by us.<sup>3</sup> This method allowing the measuring of enormous resistances by means of instruments of relatively low sensitivity, consists in charging a condenser through the resistance under test during a given time and in the following discharge of the same condenser through a ballistic galvanometer. In the course of improvement of this method principal weight had to be laid on the elimination of the sources of accidental irregularities as e. g., thermo-currents from the hands of the observer, residual charge of the condenser, polarization of the resistance, dissymmetry of deflections, inconstancy of contacts, etc. After the removal of all these causes of errors the method allowed to measure resistances of about  $10^9$ – $10^{10}$  ohm with an accuracy of 0.5–1.0%.

As the glass plate bearing the layer presented too high a conductance, light-sensitive films were studied where the conductivity of the celluloid film is only one-twentieth of that of the layer. Contacts consisted of tin-foil and Hofman's chemical clips. To exclude the conductance by the gelatine layer covering the back-side of certain films it was isolated from tin-foil by thin ebonite plates. The electrical conductivity of such a film "Premo" Kodak Ltd. of the size  $5 \times 10$  mm. at  $18^\circ$ – $20^\circ$  C was of the order of magnitude  $10^{-11}$  ohm<sup>-1</sup> cm<sup>-1</sup>.

<sup>1</sup> W. Siemens: *Wissenschaftliche und technische Arbeiten*, 1, 137 (1889).

<sup>2</sup> H. Meyer: *loc. cit.*

<sup>3</sup> It will be described in another paper.

The first experiments showed that this value depends in a high degree on the temperature and on the hygrometric state of the atmosphere. To protect the film from these external influences and from light, we placed it with the contacts in a black wooden box with a glass window which could be closed tightly by a card-board cover pasted over with black velvet. Two wires entered this box through paraffin and ebonite insulators and were connected with the contacts by means of the above-mentioned clips. A thermometer divided into fifths of a degree and allowing fiftieths to be read was introduced into the same box. As the exposure to light always heated the film the temperature coefficient of its electrical resistance was measured first. For this purpose the box was heated from outside to  $1^{\circ}$ - $2^{\circ}$  by means of a hot-air current from an electrical fan "Foen."

All readings on the thermometer and galvanometer were taken every three minutes. The results are given in Table I and on the one curve (Fig. 1), where values of time in minutes are plotted as abscissae and those of temperature  $t$

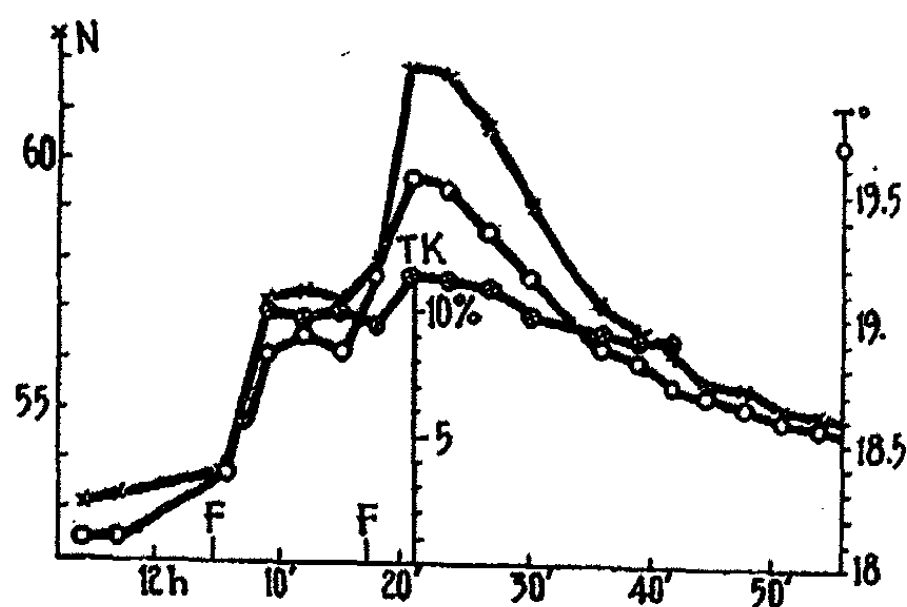


Fig. 1

in degrees for the one curve (circles) and those of galvanometer deflections in mm on the scale for the other (crosses) are plotted as ordinates. Two short lines with the inscription F show the moments, where heating with the "Foen" has been applied to the whole apparatus.

TABLE I

Reading at	Deflection N	Temp. t degree	Mean temp. t degree	Mean temp. coef. percent	M. t. c. of exp. percent
11h. 54'	+53.1	—	18.09	—	—
57'	-53.3	—	18.09	—	—
12h. 5' Heating of the box during 30" by a hot air current from "Foen"					
6'	+53.8	18.18-18.50	18.34	—	—
9'	-57.2	18.80-18.86	18.83	10	13
12'	-57.4	18.90-18.90	18.90	9.7	5.6
15'	+57.2	18.85-18.83	18.84	10.0	6.2
17' Heating during 30" "Foen"					
18'	-58.0	18.90-19.22	19.06	9.5	6.8
21'	+62.0	19.50-19.54	19.52	11.5	16
24'	-61.8	19.53-19.47	19.50	11.4	18.8
27'	+60.8	19.37-19.30	19.34	11.0	11.3
30'	-59.2	19.20-19.11	19.15	10.0	15
36'	-57.2	18.90-18.85	18.88	9.3	13
39'	+56.7	18.82-18.80	18.81	9	13
42'	-56.3	18.73-18.71	18.72	9	8
45'	-55.7	18.70-18.68	18.69	—	—
48'	+55.6	18.65-18.63	18.64	—	—
51'	-55.2	18.60-18.60	18.60	—	—

From the data of this experiment the mean temperature coefficient<sup>1</sup> has been found to be approximately 10% per degree (cf. Table I and the curve in Fig. 1—circles with crosses inside). This is an extraordinarily high value exceeding from three to five times the same coefficient for liquid conductors. After this, films were exposed to light. To protect them from heating by red and infra-red rays, bearing the greater part of the energy of the spectrum, the glass window of the box was covered with a cobalt glass, which absorbed these rays and allowed the most actinic blue and violet rays to pass.

<sup>1</sup> For this calculation changes of N and T° from the initial state (N = 53.1, t° = 18.09°) to the respective reading were used. In the last column (U. t. c. of exp.) mean temperature coefficients are given calculated from changes of N and t° from one reading to the next one. This method, more sensitive than the first one, gives figures which depend in a high degree on the accidental inaccuracies of every reading. Therefore only the mean temp. coef. from the initial state are tabulated in further tables and represented graphically.

Sun was taken as the source of light. Its rays were deflected by two mirrors into the box and fell upon the film. Readings on the thermometer and the galvanometer were made every 3 min., beginning a certain time before the exposure to light and continuing for some time after its action has ceased. The results of a typical experiment are given in Table II and the Fig. 2.

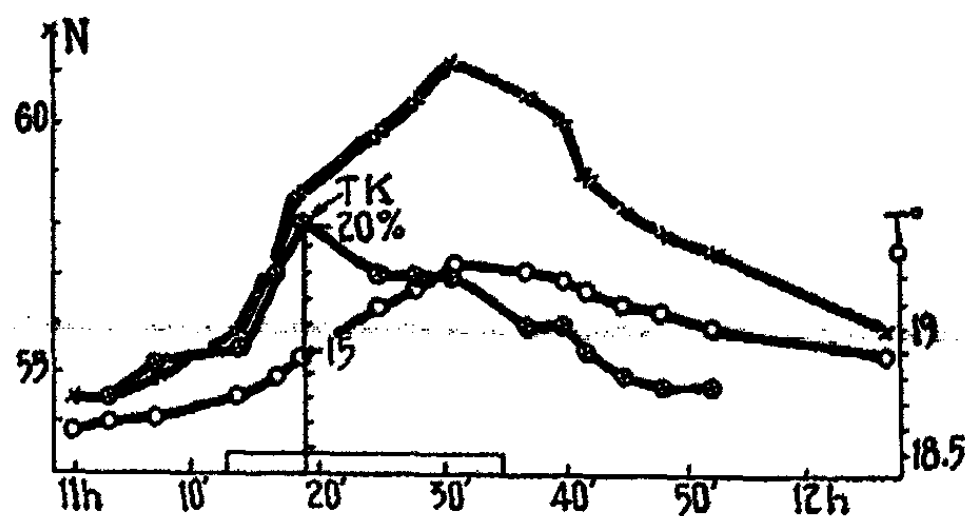


Fig. 2

TABLE II  
28-IV 1917. Battery—200 el.  
C = 1/2 MF. High sensitivity

Reading at	Deflection N	Mean temp. t degree	mean temp. coeff. percent
10h. 32'	+51.8	18.21	—
11h.	+54.5	18.57	—
11h. 3'	-54.5	18.60	13
11h. 7'	+54.9	18.62	14.3
13'	Beginning of the exposure: mirrors and cob. glass		
14'	+55.8	18.71	15
17'	-57.2	18.83	18
19'	+58.6	18.87	20
25'	+59.8	19.06	18
28'	-60.5	19.15	18
31'	+61.3	19.24	18
35'	End of exposure; box closed		
37'	+60.6	19.23	16
40'	-60.1	19.19	16
42'	+59.0	19.14	15
45'	-58.4	19.09	14
48'	+57.9	19.06	13.6
11h. 52'	-57.5	19.00	13.6
12h. 7'	+56.0	18.89	

It can be seen from these data that the curve of galvanometer deflections (nearly proportional to the conductivity) rises, following closely the curve of temperature increase i. e., the same as in Fig. 1, where heating was not accompanied by the action of the light.

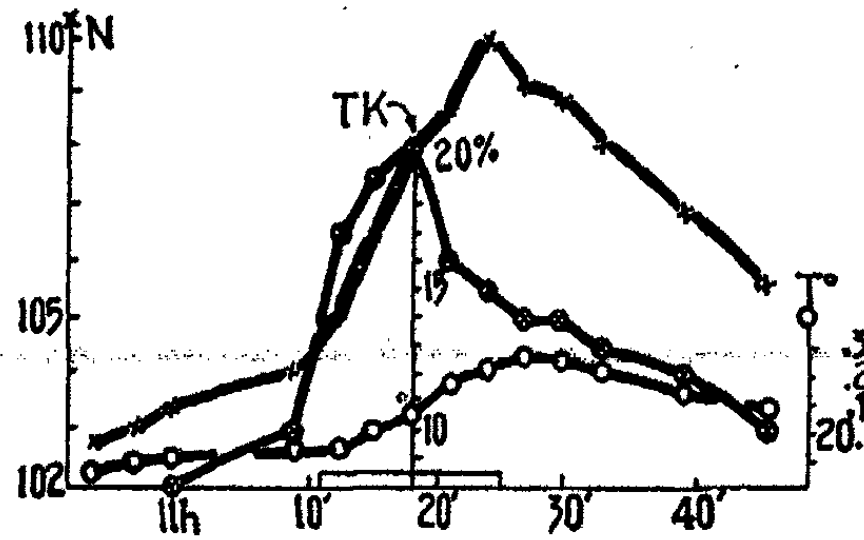


Fig. 3

TABLE III  
12/V 1917. Same conditions as in Table II

Reading at	Deflection N	Mean temp. t degree	Mean temp. coeff. percent
10h. 48'	+102.6	19.80	—
54'	+102.8	19.85	—
57'	-103.0	19.88	—
11h.	+103.4	19.90	8
9'	-104.0	19.93	10
11' Beginning of the expos. to sun-light: cob glass			mirrors and
12.5'	+105.0	19.94	17
15'	-106.4	20.00	19
18'	+107.9	20.06	20
21'	-108.6	20.17	16
24'	+110.0	20.22	15
25' End of exposure. Box closed			
27'	-109.1	20.26	14
30'	+108.9	20.25	14
33'	-108.1	20.22	13
39'	+106.9	20.14	12
45'	-105.6	20.08	10

For comparison we give in the Table III and Fig. 3 the results of similar observations made over an exposed developed and fixed film, which is no longer light-sensitive.

The form of the curve is quite analogous to that in Fig. 2. Light-sensitiveness does not affect the conductivity. Table IV and Fig. 4 represent a similar experiment with a fresh un-

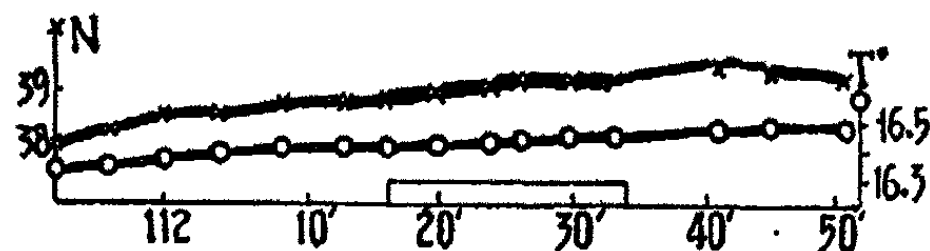


Fig. 4

exposed film with the only difference that the film received no direct sun-light, but diffused light from the clouds on a dull day.

TABLE IV  
3/V, 1917. Same conditions. Diffused light

Reading at	Deflection N	Mean temp. t degree
10h. 52'	+38.0	16.31
56'	-38.3	16.33
11h.	+38.6	16.35
4'	-38.6	16.38
8'	+38.8	16.40
13'	-38.8	16.40
16'	+38.9	16.40
Begin of the exposure. Mirror and cob. glass		
Diffused light from clouds		
20'	-39.0	16.41
24'	+39.1	16.42
26.5'	-39.2	16.43
30'	+39.2	16.45
33'	-39.2	16.45
End of exposure, box closed		
41'	+39.5	16.47
45'	-39.4	16.48
51'	+39.3	16.48

Here the heating is insignificant, and the conductivity increase is very small. The action of light cannot be stated,

as before. The same result has been obtained (the 30/17 Apr. 1917) with an exposed and developed film on a very dull day. No heating took place—the temperature and conductivity were quite constant.

If we calculate the mean temperature coefficient (as described above and plot them in curves 1-3 (in these figures) the values of the mean temperature coefficient (T.C.) are designated by crosses in circles) we can see that when heating only is applied (without action of light) the changes of T.C. are small (see Table I and Fig. 1). If the film be exposed to light, the T.C. increase very rapidly (see Table II and Fig. 2), but decrease again after the action of light has ceased. These facts could be interpreted as a proof of an influence of light on conductivity. However, this is wrong, because the same phenomenon was observed when a developed and fixed film, which is no longer light-sensitive, was exposed to light (see Table III and Fig. 3). It follows from this that the observed action of light is of secondary origin; it is caused by the greater heating of the film, which absorbs the light, in comparison with the surrounding air and the thermometer, which notes its temperature changes. The observed effect is a bolometric one and is not connected with the light-sensitiveness of the film.

In the preceding tables the abnormally large values of the mean temp. coeff. of conductivity attract our attention. They amount in some instances to 20% never falling lower than 10% per degree. These abnormally high values depend possibly, on the separation of a part of the water from the sensitive layer (presenting a gel from the standpoint of colloidal chemistry) under the influence of heat, the gel being at higher temperatures in equilibrium with a smaller quantity of water.

To protect the film from the influence of humidity, it was covered (together with the contacts) with sandarac-benzene-varnish. After drying, the conductivity under the action of heating and light was measured. The temp. coeff. decreased to 5% per degree, the general form of the curve remaining the same as above. Only the increase of conductivity did not follow the heating so quickly and became not quite reversible

(a phenomenon analogous to hysteresis). The conductivity of a varnished film is *not affected by light*.

As the determinations with dry films did not give the expected results, new experiments were undertaken with a liquid and a jelly-form emulsion, to facilitate the migration of electricity-bearers, if these would appear under the action of light. In preparing the emulsion I followed with insignificant modifications the prescription of Eder:<sup>1</sup>

A.  $\text{NH}_4\text{Br}$ -2 gr, gelatine-2 gr, water 20 cc.

B.  $\text{AgNO}_3$ -3 gr, distilled water 12.5 cc.

C. Gelatine 2-5-gr, water 20 cc.

Solution B was poured into A under shaking, the liquid was boiled, poured into C, and the whole stirred. After solidification the mass was pressed through a metal gauze and washed many hours in running water. All these operations were made in the dark or under faint red light.

The carefully washed emulsion was melted and introduced into an Arrhenius vessel for conductivity measurements. From outside it was covered with black asphalt-varnish except the lower part containing the emulsion and two platinum electrodes. The vessel was suspended on a flat metallic ring, to which a cylindrical metal screen could be pressed tightly from below by means of an india-rubber ring. When light had to act upon the emulsion, the screen slid down on special rails and opened the lower part of the vessel, which had not been blackened.

The conductivity of the emulsion was much larger than that of the dry layer—about  $5 \cdot 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ . All measurements could be made therefore by the well-known method of Kohlrausch-Ostwald—by means of alternating current, using a wire bridge and a telephone. The vessel was placed in an Ostwald thermostat with transparent glass walls. As the source of light, a Tungram  $\frac{1}{2}$  watt lamp of 400 HK at a distance of 20 cm was used, or sun-light, reflected by means of a mirror.

---

<sup>1</sup> L. M. Eder: *Ausf. Handbuch der Photographie*, III, 216.



The same facts were observed as in the dry layer; the emulsion was heated rapidly by light, and the change of conductivity was greater than could be expected from the temperature change, because the thermometer was immersed in the surrounding water of the thermostat, not in the emulsion itself. This made all temperature coefficients too large.

Table V and Fig. 5 represent the results of an experiment, when reflected sun-light fell on the emulsion.

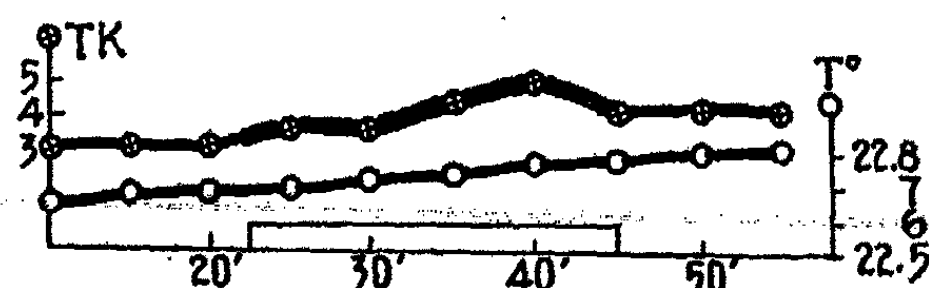


Fig. 5

TABLE V  
29/VII-1917. Kohlrausch's method  
Liquid AgBr—gelatine emulsion

Reading at	Temp. of thermostat deg.	Spec. cond. $K_t$	Mean temp. coeff. percent
11h. 50'	22.50	$8.087 \times 10^{-4}$	
12h. 10'	22.63	$8.120 \times 10^{-4}$	3
15'	22.66	$8.126 \times 10^{-4}$	3
20'	22.67	$8.130 \times 10^{-4}$	3.1
Sun-light reflected by a mirror			
25'	22.69	$8.143 \times 10^{-4}$	3.6
30'	22.71	$8.159 \times 10^{-4}$	3.6
35'	22.73	$8.169 \times 10^{-4}$	4.4
40'	22.76	$8.181 \times 10^{-4}$	5.0
45'	22.78	$8.194 \times 10^{-4}$	4.8
End of exposure, vessel covered by screen			
50'	22.80	$8.194 \times 10^{-4}$	4.4
55'	22.81	$8.192 \times 10^{-4}$	4.2

The mean temp. coef. increase twofold under these conditions. To prove the bolometric origin of this effect pure gelatine solution without AgBr was taken, but gave no result as absorbing too small a quantity of light. To increase the absorption of light, an "emulsion" (rather, a suspension) of

barium sulphate in gelatine was prepared where the conditions of light diffusion and absorption are the same as in the bromogelatine silver emulsion. This mixture showed under the action of light a similar (even a larger) increase of temp. coef. of conductivity, not being light-sensitive at all (see Table VI and Fig. 6). Here also the effect was found to be a bolometric one.

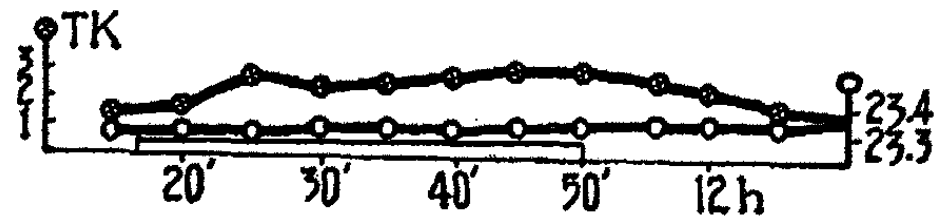


Fig. 6

TABLE VI  
(31-VIII, 1917) Kohlrausch's method  
Gelatine with suspended BaSO<sub>4</sub>

Reading at	Temp. of thermostat degree	Spec. cond.	Mean temp. coeff. percent
11h. 5'	23.23	$3.602 \times 10^{-4}$	—
15'	23.27	$3.604 \times 10^{-4}$	1.4
Exposure: sun-light reflected by mirror			
20'	23.28	3.605	1.7
25'	23.28	3.607	2.8
30'	23.30	3.608	2.4
35'	23.30	3.608	2.6
40'	23.30	3.609	2.9
45'	23.31	3.611	3.1
50'	23.32	3.612	3.1
End of exposure			
56'	23.32	3.611	2.8
12h. 5'	23.33	3.610	
10'	23.35	3.609	

Experiments with dry and liquid photographic emulsions showed that their electrical resistance does not change within the limits of experimental errors when they are exposed to light. The interest of this fact is especially great if we compare it with the stated change of resistance of pure halide silver salts under the action of light. It is probable that the same changes

occur in the silver bromide of the photographic emulsion, but they cannot influence its general resistance as the propagation of these changes is paralysed by the gelatine surrounding the separate granules of AgBr.

Therefore, the determinations of conductivity with the degree of accuracy now attainable do not give the possibility to follow those changes and to resolve the question about the nature of the latent image.

The subject of this paper was suggested to me by Prof. N. P. Kasterine, to whom I express my sincere thanks.

*Physical Laboratory*

*Odessa University*

1917

## NEW BOOKS

**A Comprehensive Treatise on Inorganic and Theoretical Chemistry.**  
*Vol. 1. By J. W. Mellor. 24 × 16 cm; pp. xv + 1065. New York and London: Longmans, Green and Co., 1922. Price: \$20.00 per vol.*—In the preface the author says: "With due regard to the law *humanum errare est*, this work aims at giving a complete description of all the compounds known in Inorganic Chemistry, and, where possible, these are discussed in the light of the so-called Physical Chemistry. The separation of Organic from Inorganic Chemistry is nothing more than a conventional convenience; it is probable that the sharper the line of demarcation, the greater the loss which each of these divisions of chemistry will suffer. In the analysis of inorganic compounds, for example, some extraordinarily sensitive tests are available, and some extraordinarily clean separations can be effected by utilizing the properties of certain organic compounds of the metals."

"Much of the material of this work was compiled in card-index form long before my Modern Inorganic Chemistry appeared; and that work was really an abridgment of this one. The references which were not included in the scheme of that work will be found here. It was not originally intended to make the larger work assume the exhaustive character which this book has now acquired. Rightly or wrongly, I came to the conclusion that it is a mistake to load up a student with facts as if he were going to be a specialist in all branches of inorganic chemistry. In addition to the general principles, the salient features of certain type-compounds should be taught, and anything further should be left for works of reference, where full information may be obtained—to be absorbed or forgotten as may be expedient. Consequently, in the ideal case, a work of reference should not only give the authorities for statements of fact, but it should also indicate what knowledge has been gleaned on the particular subject in question. To do this in a practicable manner, attention must be directed to the original publications on the subject. This naturally makes the work of compilation extremely laborious; in some cases, indeed, it happens that scores of independent references are involved in the statement of one particular fact."

"I think it was P. J. Macquer who apologized for the alphabetic form of the subject-matter of his *Dictionnaire de chimie* (Paris, 1766), by stating that chemistry was little more than a collection of facts scarcely entitled to the name of science, or capable either of synthetic or analytic explanation; and hence he concluded that the dictionary form was the best mode of arranging the facts. The dictionary thus belongs to a primitive stage in the development of a science in that it is but a collection of facts to be employed in building up the science.

"We now flatter ourselves that the periodic law has given inorganic chemistry a scheme of classification which enables the facts to be arranged and grouped in a scientific manner. The appearance of order imparted by that guide is superficial and illusory. Allowing for certain lacunae in the knowledge of the scarcer elements prior to the appearance of that law, the arrangements employed by the earlier chemists are just as satisfactory, and in some cases, indeed, more satisfactory than those based on the periodic law.

"The arrangement of the subject-matter of inorganic chemistry according to the periodic scheme is justified solely by expediency and convention. It has a tendency to make teachers over-emphasize unimportant and remote analogies, and to under-estimate important and crucial differences. I imagine that when we have found a truer basis of classification, such differences as are displayed between, say, *ferrosum* and *ferricum* compounds will be exhibited as if two different elements are involved, and that iron alone appears as the stable form when separated from these compounds. Similar remarks apply to other multi-valent elements. The difference between the higher and lower valent forms of an element with a given acid are often greater than between the compounds of two totally different elements with the same acid.

"The first volume of this work is mainly introductory, and in it the atom is considered to be the chemist's unit, or the unit of chemical exchange. The newer work on the structure of atoms, and the so-called elements with variable atomic weights will be introduced in the third volume, as a sequel to the radioactive elements. The collection in the first volume of most of the generalizations required for application to special cases in subsequent volumes has simplified many explanations. This applies, for example, to thermal diagrams, equilibrium diagrams for ternary systems, etc. The general historical sketches in this volume facilitate the reviews of the histories of the elements and their compounds which appear in subsequent volumes.

"Hydrogen and oxygen, and the compounds of these two elements, have been worked in with the introductory volume. The second volume includes the halogens and the alkali metals. The ammonium compounds are included with the compounds of the alkalies. The other elements will appear mainly in the order of the periodic law. The metal hydrides, oxides, halides, sulphides, sulphates, carbonates, nitrates and phosphates are included with the metals; the other compounds are described with the acids, or the acidic elements. With the complex salts and intermetallic compounds of an element are included analogous compounds of ammonium, hydrazine, and hydroxylamine, as well as of all those elements which have been previously discussed. It should therefore be possible to locate a desired compound from an inspection of the backs of the volumes, which are lettered to show what elements are discussed inside. The indexes and cross-references are also available."

The chapters are entitled: the evolution and methodology of chemistry; combination by weight, hydrogen and the composition of water; the physical properties of gases; combination by volume; the classification of the elements; hydrogen; oxygen; water; solutions; crystals and crystallization; thermodynamics and thermochemistry; the kinetic theory of atoms and molecules; ozone and hydrogen peroxide; electrolysis and the ionic hypothesis; electrical energy.

This is a tremendous undertaking and a very successful start. It seems scarcely possible that the author can carry out his programme single-handed; but everybody will wish him success in his self-appointed task. One does not know which to admire most, the knowledge which makes such a work possible, the skill in presentation, or the courage and persistence which carries the author through the awful drudgery involved in getting such a mass of facts into final form.

In the first chapter on the evolution and methodology of chemistry,

it is interesting to note, p. 9, that "about 150 A. D., the Egyptian astronomer Claudius Ptolemy measured the angles of incidence and refraction of a beam of light passing from air into water, but more than fourteen hundred years elapsed before W. Snell (1621) detected the law of refraction hidden in Ptolemy's data."

The reviewer was much interested in the remarks on inductive and deductive reasoning. Sir William Hamilton was quite frank when he said, p. 9, that "in physical science the discovery of new facts is open to every blockhead with patience, manual dexterity, and acute senses; it is less effectively promoted by genius than by co-operation, and more frequently the result of accident than of design." It would be well if people were to take to heart Newton's statement, p. 18, that "no great discovery was ever made without a bold guess" and the similar one by Whewell, p. 172, that "advances in knowledge are not commonly made without the previous exercise of some boldness and license in guessing."

The admiration for exact measurements as such is nowadays so great that probably relatively few people will agree with the first paragraph on p. 10. "It cannot be doubted that science in its higher work, requires a supple and well-developed imagination which T. Gomperz says is the instrument of genius, no less for scientific discovery than for artistic creation. The secret charm of scientific discovery is not in the facts *per se*, but rather in the extrication of natural relations among the facts one with another. Particular groups of facts must be unified or generalized into a system—the so-called law. Science begins with facts and ends with laws. Law is the essence of facts. As pointed out elsewhere, Newton's celebrated law epitomizes in one simple statement how bodies have always been observed to fall in the past. Immortal Newton did not discover the cause or the why of the falling of the apple, but he did show that it was due to the operation of the same forces which hold the earth, the plants, and their satellites in their appropriate orbits. Newton's simple and comprehensive law epitomizes in one single principle the many and varied phenomena associated with falling bodies, planetary motions, etc., and generally, the scientific generalization explains the operations of nature by showing the elements of sameness in what at first sight appears to be a confused jumble of phenomena. Generalization is the golden thread which binds many facts into one simple description. That peculiar type of genius, that rare quality of mind required for the work of generalization, is found only in a Newton or a Darwin. Plato said that if ever he found a man who could detect the one in many he would follow him as a god."

For those who want numerical data, such a chapter as the one on the physical properties of gases, pp. 147-170, will be enthralling. For those who want a theoretical problem, one can recommend a critical study of Callendar's theory of osmosis, p. 559, or of the effect of heat of dilution on osmotic pressure, p. 547. Those interested in catalysis will find distraction if they read the paragraphs in regard to the effect of oxides of the metals on ozone, hydrogen peroxide, chlorate, etc., pp. 350, 359, 887, 901, 937, 942 and elsewhere. The magnetic behavior of colloidal iron salts, p. 648, is also well worth studying.

The author is not very enthusiastic over the present status of the electrolytic dissociation theory, pp. 994, 999, 1006. "The present position of the theory of ionization discussed at the Faraday Society (1919) made it very clear

that in spite of twenty years' labor, there is something fundamentally wrong in the application of the mass law to ionization excepting in the case of weak electrolytes and of very dilute solutions of the stronger electrolytes. The general conclusion to be drawn from the work is that electrical conductivity is not an accurate measure of ionic concentration. . . . . Stieglitz finds that the solubility product must be treated as an approximate, empirical principle without a theoretical foundation. . . . . F. P. Worley has emphasized that instead of the rate of hydrolysis of ethereal salts and cane sugar being proportional to the concentration of hydrogen ions the two properties are altered in different directions by changes of concentration. . . . . Consequently, the catalytic activity of the acids is not proportional to the concentration of the hydrogen ions; and, adds F. P. Worley, if hydrogen ions and un-ionized molecules are both active chemically, . . . . . in time, the extreme supporters of the ionic hypothesis may admit that both ions and un-ionized molecules may be concerned in electrolytic conductivity!"

In one point, the author seems to have slipped up. When discussing Hittorf's migration experiments on silver nitrate between silver electrodes, p. 985, he says, p. 990, that "W. Hittorf's results can be deduced from the assumption that both the solvent and the solute conduct the current, for if, say, silver nitrate conducts the whole current, free acid appears only at the anode; if the water conducts the whole current free acid appears only at the cathode; and if both salt and solvent conduct the current, free acid appears at both electrodes, and the current can be portioned between the solvent and solute so as to make the observed facts fit the hypothesis. Hence, W. Hittorf's migration data do not prove that ions travel at unequal rates, for the observed facts can be explained by at least two plausible hypotheses."

The weak point about this argument is that, under the conditions of the experiment, free acid does not appear at either electrode.

The reviewer was sorry to see the old fallacy about the commercial importance of the oxygen or hydrogen standard of the atomic weights, p. 201. "This question of a standard is not of mere academic interest, because in buying and selling ores on the percentage amount of contained metal, a difference in the atomic weight selected may involve appreciable differences in the estimated value of the ore. For instance if oxygen be taken as 16, the corresponding atomic weight of antimony is 119.9 and of uranium 239.61; if hydrogen be taken as unity, these values become, respectively, 118.9 and 237.65—differences of one and two units." If one took oxygen as 100, the atomic weight of antimony would become about 750; but that would not change the price of antimony ore nor do we analyze ores as a means of determining atomic weights.

It would be untrue to say that there are no misprints; but the number is surprisingly small considering the kind of book. *Wilder D. Bancroft*

*Some Physico-Chemical Themes. By Alfred W. Stewart. 22 X 15 cm; pp. xii + 419. New York and London: Longmans, Green and Co., 1922. Price: \$7.00.*—In the introduction the author says: "The present volume is not intended to survey the whole field of physical chemistry, nor does it even profess to describe all the more interesting parts of the subject: for any attempt to carry out either of these plans would have expanded the book far beyond

:  
:  
t  
B



the limits which seem desirable. The intention has been rather to select for treatment several interesting branches of physical chemistry and to throw some light upon their general outlines, in the hope that the descriptions given may arouse the interest of the reader sufficiently to make him consult the original literature or to look up other books in search of further information."

The final paragraph in the introduction, p. 6, is also of distinct interest. "In concluding this introduction, it may be well to mention a point which has been kept in view during the writing of the book. A volume of this kind is intended to encourage the reader to do two things: (1) acquire a knowledge of facts and (2) form his own opinions on the subjects treated, apart from the hypotheses suggested by other people. For this reason wherever it has been possible, the facts have been kept entirely separate from any theories on the subjects. It cannot be too often impressed upon a student that it is only by forming his own individual views upon chemical problems that he can become really a master of the subject. By this it is meant that he should be intellectually satisfied that a theory is firmly based before he accepts it; he should not encourage himself to take refuge behind the fact that "so-and-so says it is true." It is not necessary to evolve new theories of one's own, but it is equally unnecessary—and much more undesirable—to accept blindly anything which happens to find its way into print on one side or other of a controversy."

The subjects treated are: residual affinity and some physical properties; double salts; the problem of the oceanic salt deposits; complex salts and complex ions; the pseudo-acids; the theory of indicators; non-aqueous ionizing media; colloids; the Brownian movement; Perrin's researches on the distribution of particles in emulsions; Avogadro's constant and some molecular dimensions; adsorption; some hypotheses of the colloidal state; catalysis; the spectra of the elements; chemical affinity; the developments of the Periodic Law; the atoms and the periodic system; some views of atomic structure.

The book covers a wide field and is extremely well written. There will of course be points which do not appeal to one man so much as to another. The author recognizes that himself, p. vi, and suggests that, in case a critical reader laments the omission of topics in which he himself is keenly interested, he should repair the error by writing a book on these subjects himself. Fortunately the criticisms that the reviewer wishes to make are so limited in range and number that they would not fill a pamphlet, to say nothing of a book.

On pp. 118, 126, and elsewhere, the author says that the facts destroy completely Ostwald's explanation of the action of indicators. It is absolutely true that Ostwald's explanation of the color change with phenolphthalein, etc., was wrong; but the author does not give Ostwald the credit, to which he is entitled, for putting the theory of indicators on a scientific basis. It is comparatively unimportant whether the color change is due to the forcing back of the dissociation, or to some rearrangement which is connected with and follows from the change of dissociation. Ostwald adopted the simplest hypothesis and the phenomena proved to be more complex than he had assumed. It is desirable to know to what the color changes are due; but it seems to the reviewer that the really essential part of the theory of indicators was worked out by Ostwald and not by the organic chemists. Incidentally it is interesting to note that the author's knowledge of organic chemistry is apparently not sufficient



to keep him from following Ostwald into the error, p. 125, of classifying methyl orange as a strongly acidic instead of as a weakly basic indicator.

The reviewer, of course, turned at once to the chapter on colloids. He was a little grieved to find the author, p. 164, admitting that freezing-point measurements prove that the molecular weight of albumin is probably at least 14000. This is the more remarkable because, in the very next sentence, the author says that "these measurements depend upon the assumption that we are dealing with a true solution." On p. 170 the author is apparently worried by the fact that a suspension of petroleum in water acquires a negative charge although the petroleum has no positive or negative radicals in its structure. The explanation is that the drops of petroleum adsorb hydroxyl ions from the water.

On p. 177 the author points out that "Svedberg, by direct observation, found that, in the case of a silver sol to which aluminum sulphate was added, there was no change in the amplitude of the vibration of the particles on the addition of the electrolyte; but that, as the particles coalesced, the amplitude of vibration diminished with each increase in size of the aggregates. This proves that the change in the velocity of the particles is the result and not the cause of the coagulation." This is perfectly satisfactory in itself. On p. 188, however, we read that "Svedberg believes that the Brownian movement is independent of electrical charges; but the evidence of the effect of electrolytes is so extensive that it can hardly be brushed aside merely on this account." There is no contradiction between Svedberg's conclusions and the experimental results of anybody else. Svedberg showed that the addition of electrolytes did not affect the Brownian movement directly. In so far as the electrolyte causes agglomeration of the particles, it cuts down the Brownian movement indirectly. The other people assumed that the change in the Brownian movement preceded the agglomeration; but there was nothing in their experiments to prove it.

The author has said in the preface that he has made no attempt to include the work published in last month's journals, which is quite as it should be. In a book intended to stimulate research and to prevent people from taking statements on authority, it would have been well to have commented critically upon Perrin's work on the distribution of mastic particles in suspensions, p. 207. Extrapolating roughly from Perrin's data, we find that in a vertical distance of less than 0.1 mm., the concentration should drop from 1880 to one. A bottle of a colloidal gold solution, approximately uniform in color, should therefore represent a state very far from equilibrium, which is not what experiment seems to show us. Critical comment would have been more desirable in view of the fact that Burton seems to have shown what is wrong with Perrin's theory.

It is apparently impossible to get anybody to appreciate that the Gibbs theory for change of concentration in the surface film, p. 243, holds for true solutions, p. 243, and can only be applied with great caution to colloidal solutions. On p. 256 the author concludes that a catalyst cannot affect the final state of equilibrium of the system into which it is introduced unless the laws of thermodynamics are to be rejected. The author has overlooked the fact that the laws of thermodynamics do not apply to systems in which there are what we call passive resistances to change. It is in these systems that the catalyst changes the apparent equilibrium. As an organic chemist, the author must know that we cannot treat organic chemistry under the phase rule as a system of car-

bon, hydrogen, and oxygen, which it is theoretically. This does not cause anybody to weep over the laws of thermodynamics. Why not use common-sense in other cases?

The section on flame spectra, p. 276, is years behind the times. Weiser's work on the green and blue copper flames would have interested the reader. The work on triboluminescence and crystallo-luminescence might well have been included somewhere.

The presentation of the situation in regard to Newlands, Mendeleeff, and Lothar Meyer, is admirable and the reviewer was much interested in the author's views in regard to the position of the elements of the rare earths in the periodic table, p. 356.

While the reviewer has pointed out what seem to him shortcomings in the text, and while it is probably inevitable that each reader will be impressed most by the parts about which he knows least, the reviewer wishes to repeat what he has said, so far as he can remember, about every book by the author, that it is an admirable type of book and that the presentation is as good as can be expected of anybody. Any man who tries to cover a wide field is bound to make minor slips; but these are of no real importance. We do want broad, inspiring books and the author has a real talent for that sort of thing.

Wilder D. Bancroft

**Colloid Chemistry of the Proteins. Part I.** By Wolfgang Pauli. Translated by P. C. L. Thorne. 21 × 15 cm.: pp. xi + 120. Philadelphia: P. Blakiston's Son and Co., 1922. Price: \$2.25.—The chapters are entitled: colloid chemistry and the general chemistry of the proteins; conditions of stability in protein solutions; the electric charge of natural soluble albumin; properties of proteins in iso-electric reaction; salts of albumin and acids; salts of albumins and bases; alterations in state of the alkali proteins with lapse of time; salts of the globulins and migration velocity of the protein ions.

It is not clear what Pauli means by a colloidal solution. On p. 4 he says that "Wolfgang Ostwald is the author of the very suitable terms *dispersion medium* (continuous phase) and *disperse phase* for the component parts of a colloidal system." That is an explicit recognition that a colloidal solution is a two-phase system and yet he says, on p. 5, that "solutions of colloidal character are obtained when substances of very high molecular weight are dissolved in water. The tendency of the large molecules to associate and polymerise can still further increase the colloidal properties of these solutions. Albumin, starch, glycogen, etc., are included in this group of substances, whose main characteristic is that they occur exclusively in the colloidal condition."

If a substance dissolves, it is not colloidal. While it is very possible that albumin polymerizes, the reviewer knows of no proof of this. It is this vagueness and inaccuracy as to premises that plays havoc with so much of the work in biological chemistry, because it is hopeless to build upon shifting sands. It is rather sad to read, p. 16, that peptization really depends on the formation of complex salts.

Pauli says, p. 11, that "addition of water occurs on the particles of many colloids and is described as hydration in the wider sense, and as imbibition when the adding of water occurs together with penetration of water into a large aggre-

gate. The indications of hydration of a disperse phase are a proportionally great viscosity of the solution, the decreased activity of the movement of the particles as displayed in diffusion or in an electric field, and an alteration in volume or density in the direction of compression of the medium. . . . . We shall see that hydration of particles of albumin solutions has been demonstrated, and, consequently, dissolved proteins are classed among hydrated (solvated) colloids."

On p. 16 we read: "Some proteins are hydrophobe, some have hydrated particles; and the conditions under which they are stable are different in the two cases. Proteins of the first group exhibit Hardy's law of instability at the neutral point when treated with electrolytes. To this group belong heat-coagulated albumin, casein, salt-free globulin, acid albumin, etc. On the other hand, gluten, natural albumin, and the other proteins of the second group are stable in solution, even when the particles are not electrically charged. The electric charge is, however, quite an important factor in the stability of the lyophile or hydrated proteins, for it is an accepted fact that only neutral particles are precipitated from solution by electrolytes. Accordingly, all means of displacing albumins from solution will show an optimum at the point of electric neutrality, a condition which will be dealt with in detail later on. Generally, the difference between lyophobe and lyophile albumins lies in the fact that in the first case mere discharge of the particles (*e. g.*, by an electric field) leads to precipitation, while in the second case discharge must be combined with effects which lead to an alteration in the relation of the particles to the solvent, so that their lyophile character is reduced or lost altogether. Saturation of the solution with certain alkali salts, the addition of alcohol or phenols, etc., bring about the latter conditions."

Of course Pauli believes firmly that albumin and other proteins form definite compounds with acids and bases, p. 55. "The plain fact that proteins combine both with acids and bases has been known for a long time. On the other hand, quantitative measurements of the extent of combination awaited the clear conception of the terms acid and base which only physical chemistry could furnish. The results of the application of titrimetric methods to the determination of the capacity of proteins for combination with acids and bases (Spiro and Pemsel) were only made clear by the progressive understanding of the function of indicators (W. Ostwald, H. Friedenthal, E. Salm and others). Certain proteins, such as casein, have been shown to form approximately neutral salts when titrated with strong alkalis, using phenolphthalein as indicator, the point of colour change in this instance being near the true point of neutrality in the physico-chemical sense (Laqueur and Sackur). Many other indicators, such as phloroglucin—vanillin, give an idea of the maximum combination of acids with albumin, which, although only rough, is sufficient for many purposes (J. Christiansen). The work of S. P. L. Sørensen, in particular, has shown that, in order to arrive at useful conclusions as to hydrion concentrations by the use of indicators, special precautions must be taken when proteins are present. Our exposition of the combination of albumin with acids, and of the physico-chemical properties of the products formed thereby, will be based mostly on recent researches, which, without disturbing the equilibrium between protein and acid have led, on the basis of direct determination of hydrion concentrations, to a pretty comprehensive view of the phenomena which occur."

It has been said that colloid chemists foam at the mouth when anybody

mentions the possibility of a protein forming a compound with an acid or a base, and this is true to some extent. In so far as a protein is an amino-acid there is no theoretical reason why it should not form a compound either with a base or with an acid; but it does not follow that a compound is formed in any given case. The physical chemist has been through the mill with solid solutions and basic salts. He knows that the literature is full of mythical compounds whose only claim to existence was that the constituents happened to be present in stoichiometric proportions which did not seem improbable to the man making the analyses. The colloid chemist does not propose to go through the same experience if he can help it. The biological chemist can have all the compounds he wishes if he will show some proof of their existence; but the colloid chemist is not going to accept compounds merely because the biological chemist does not know of any other way to account for the phenomena. It may perfectly well be that caseine is a tribasic acid; but it is not safe to deduce this from titrations with phenolphthalein and with litmus.

The case of the globulins is interesting, p. 121. One equivalent of hydrochloric acid or nitric acid is said to dissolve twice as much globulin as one equivalent of sulphuric acid or oxalic acid while one equivalent of caustic soda or of ammonia dissolves twice as much globulin as one equivalent of barium hydroxide. This is accounted for in terms of the theory by saying that the globulins can only neutralize one hydrogen or one hydroxyl in a molecule; but this is an assumption *ad hoc* and we are not told why. We are told that the reason why acetic acid is so much less effective than hydrochloric acid is because it is a weaker acid but we are not told why the weak base, ammonia, should be just as effective as caustic soda. The only statement made is, p. 123, that ammonium globulinate does not suffer an appreciable hydrolytic dissociation which reflects the very acidic character of globulin. This is merely re-stating the facts in terms of the theory and does not explain why the strongly acid globulin can only neutralize one hydroxyl in barium hydroxide. There was a wonderful opportunity here for talking about steric hindrances.

This is an interesting book and it is very important to know definitely the views of the man who has the first-hand knowledge of the subject; but the use made of colloid chemistry seems practically negligible to the reviewer.

*Wilder D. Bancroft*

**Organic Chemistry for the Laboratory.** By *W. A. Noyes*. Fourth edition. 23 X 15 cm; pp. xii + 293. Easton: The Chemical Publishing Co., 1920. Price: \$3.50.—The chapters are entitled: analysis of compounds of carbon; general operations; hydrocarbons; alcohols and phenols; ether; aldehydes, ketones and their derivatives; acids; derivatives of acids; hydroxy- and ketonic acids; carbohydrates; halogen compounds; nitro compounds; amines; diazo, hydrazo, nitroso, and other nitrogen compounds; sulphur compounds; qualitative examination of carbon compounds.

It is very important for an organic chemist to have manipulative skill and for the physical chemist to have more knowledge of organic chemistry than is usually the case. Consequently we welcome the existence and popularity of a book like this one. The question comes up whether this is the best possible book and to that the reviewer must give a negative answer. Let us take one of

the very simple cases, that of ethyl bromide, p. 199. The yield as given is not over eighty percent referred to potassium bromide and very much less when referred to alcohol. There is nothing to show why the yield is no higher and yet that is an important thing. The physical chemist will probably recall something about reversible equilibrium and will think that it would be profitable to cut down the water content. He will wonder why 30 cc of water are to be added in making up the mixture and the reviewer does not know where the student could find out that the hydrobromic acid is oxidized by hot concentrated sulphuric acid. The reviewer believes that such information should be given.

*Wilder D. Bancroft*

**An Introduction to the Physics and Chemistry of Colloids.** By Emil Hatschek. Fourth edition. 18 × 13 cm; pp. xiii + 172. Philadelphia: P. Blakiston's Son and Co., 1922. Price: \$2.25.—The third edition appeared three years ago (23, 588). This new one has been rewritten and enlarged. It is much better than the preceding ones though it still falls far short of what the reviewer thinks it might be. Adsorption comes in casually at the end of the book and the author finds it difficult to explain, p. 75, why addition of a calcium salt should reverse a sodium soap emulsion. Throughout, the book is not clear. On p. 37 the author states that the Brownian movement is a factor which counteracts sedimentation; but that it is not the only one because it is not affected directly by factors which destroy the stability of suspensoid sols, namely the addition of electrolytes. He then states that the electrical charge on the particles is another factor intimately connected with the stability of sols on the one hand and the irreversible character of the transformations they undergo on the other. Statements like that are confusing to the beginner and irritating to everybody else. The real truth is that the electrical charge prevents coalescence while the Brownian movements counteract the sedimentation. Further the presence of an electrical charge has nothing necessarily to do with the irreversibility of the coagulation.

On the same page the author says that the origin of the electric charge is still a subject of controversy. He therefore postpones the discussion of it to p. 154, where he is non-committal.

*Wilder D. Bancroft*

11314  
1737

## ELECTRONIC STRUCTURES OF ATOMS<sup>1</sup>

BY MAURICE L. HUGGINS

Although the Lewis theory of valence and atomic structure<sup>2</sup> has met with remarkable success<sup>3</sup> when applied to chemical facts, Lewis was able to apply it in its entirety only to some of the elements, chiefly those of lowest atomic weight, from hydrogen to scandium. Among those of higher atomic weight, although some fitted in perfectly with the system, others did not, and it was evident that in order to include all, the theory must be modified or extended in some way.

Langmuir<sup>4</sup> has attempted to do this, but he was forced to leave still unexplained many valence relationships and other physical and chemical facts. In this and following papers, the author attacks the problem.

### The Lewis Theory

Lewis' main assumptions are the following:

1. An uncombined neutral atom has in its outermost shell a number of electrons corresponding to the column of the Periodic Table in which that element belongs.

2. A single bond consists of a pair of electrons holding two atoms together; in a double bond two pairs of electrons join two atoms; and in a triple bond two atoms are connected by three electron pairs.

3. Each atom tends to obtain an even number of electrons in its outer shell, and also to complete its group of eight electrons, or "octet," by bonding with other atoms or otherwise.

---

<sup>1</sup> This paper, except for minor changes, was written in 1920, but unavoidable circumstances have delayed its publication. A short outline of the theory has recently been published in *Science*, 55, 459 (1922).

<sup>2</sup> G. N. Lewis: *Jour. Am. Chem. Soc.*, 38, 762 (1916).

<sup>3</sup> Cf. for example, I. Langmuir: *Ibid.*, 41, 868, 1543 (1919); 42, 274 (1920); Latimer and Rodenbush: *Ibid.*, 42, 1419 (1920).

<sup>4</sup> Langmuir: *Ibid.*, 41, 868 (1919).

**"Cubical Atom" Versus "Tetrahedral Atom"**

Although in the original development of his theory Lewis considered the valence electrons as being approximately at the corners of a cube, in his paper referred to above he proposed, at least for organic compounds, an arrangement in which each pair of electrons acting as a bond is drawn together and occupies one of the four corners of a tetrahedron, the atomic kernel<sup>1</sup> being the center. That the tetrahedron of pairs is the stable arrangement for the valence shells of all of the lighter electronegative atoms, Lewis has believed for some time, and this view will be adopted in this paper. It might be well to briefly consider some of the arguments in favor of this conception.

The cubical arrangement is quite inadequate for the representation of organic compounds. It not only gives no opportunity for the formation of a triple bond, such as must often be assumed between carbon and carbon, carbon and nitrogen, and nitrogen and nitrogen, but is also incompatible with the well-known principle of free rotation about a single bond, for such free rotation could hardly exist if the electrons composing the bond were widely separated from each other.

Whenever an atom of some other element is attached to one of carbon or of nitrogen, the only logical assumption is that the bond connecting the two is here also a pair of electrons which are quite close together. In such a case it would seem very improbable that two of the eight electrons in the shell of this other atom are close together as in a tetrahedral atom, and the other electrons relatively far apart, spaced according to the cubic arrangement. And in the case of an oxygen atom, for instance, doubly bonded to a carbon or nitrogen atom, is it not much simpler to assume that the four electrons not acting as bonds are also paired off than to give them any other less symmetrical positions?

The fact that an atom (of one of the elements considered

<sup>1</sup> This term, introduced by Lewis, is used to denote everything inside of the valence shell.



by Lewis) with an *odd* number of electrons in its outer shell always shows a great tendency to react with other atoms so as to have an *even* number of valence electrons around it,<sup>1</sup> whereas an atom with an *even* number of valence electrons, even though they are not all acting as bonds, is often quite unreactive, is another very potent argument in favor of the pair, rather than the single electron, being the unit (both of bond electrons and of those which are not acting as bonds) in the outer shells of these atoms.

In order to satisfactorily account for the atomic arrangements which have been found to exist in crystals, it seems to be quite necessary to assume that the valence electrons are drawn together in pairs, usually at the corners of a tetrahedron for the lighter elements. Many of the results obtained with this idea as a basis are given in other papers by the writer.<sup>2</sup>

#### The Law of Force between Electrons

This pairing of electrons may be readily accounted for by assuming the proper kind of a law (or laws) of force at small distances, as will be shown by an example in the latter part of this paper. The chief requirement of such a law, for this purpose, is that, *as two electrons approach each other, the repulsion between them reaches a maximum at a distance of the order of magnitude of 1 Å. (1 Ångstrom unit =  $10^{-8}$  cm), the force then decreasing for a considerable proportion of the remaining distance at least (Fig. 1). The repulsion may or may not change to an attraction. Any of a number of laws of this type will result in the pairing of electrons in atomic shells when they are drawn in, by the attraction of the nucleus, until somewhat closer together than this distance of maximum repulsion.*

A law of this type would similarly result in the formation of groups of three electrons, or triplets, when two pairs, or a pair and a single electron, are forced sufficiently close together. In some atoms, moreover, we might expect two or more electronic

<sup>1</sup> Cf. Lewis' discussion of "odd molecules," *loc. cit.*, p. 770.

<sup>2</sup> Huggins: *Phys. Rev.*, [2] 19, 346, 354, 363, 369 (1922); *Jour. Am. Chem. Soc.*, Sept. 1922.



arrangements to be stable, differing in the numbers of pairs and triplets in the various shells.

Before proceeding to a more complete discussion of the laws of force at small distances, let us see whether the above assumption leads us to atomic structures which are in conformity with the periodic system and the properties of the elements.

#### **Atomic Structures; Hydrogen to Neon**

A hydrogen atom possesses one electron which can pair off with a single electron in the shell of another atom, of hydrogen or of some other element. A helium atom contains two electrons outside of the nucleus. These are drawn in so close to the latter that they cannot act in a bond-forming capacity.

A neutral lithium atom possesses three electrons.<sup>1</sup> These we might expect to be arranged symmetrically around the nucleus, giving a trivalent element; but the fact that lithium is monovalent leads us to infer that two electrons tend to be closer to the nucleus (and so, probably, to each other) than the third. Such an arrangement, as will be shown later, may be accounted for by the type of law of force we have assumed, two of the electrons being pulled in by the nucleus until the distance between them ( $d$ , Fig. 2) is somewhat less than the distance of maximum repulsion. Because of this fact these two are forced still closer to each other and to the nucleus (represented by a plus sign in the figure), the third electron being at the same time pushed further away from the nucleus.

Increasing the nuclear charge to four, in beryllium, and five in boron, draws the two electrons which are paired closer to the nucleus (and so closer to each other). In carbon, with a nuclear charge of six, the pair has been pulled in so close that the remaining four electrons arrange themselves in tetrahedral fashion, practically as though the inner pair were a part of the nucleus. This pair then persists as the innermost "shell" in the atoms of all of the heavier elements.

In the nitrogen atom we have a case similar to that in

---

<sup>1</sup> In the following pages, whenever electrons are mentioned, only those outside of the nucleus are considered.

lithium. Five electrons, if placed as symmetrically as possible around the central unit, would be so close to each other that this arrangement would be unstable, and two of the five would be drawn closer together, and the pair thus formed would at the same time be pulled in closer to the nucleus. The resulting arrangement may be looked on as a somewhat distorted tetrahedron, with a pair of electrons at one corner, a single electron at each of the other three corners, and the nucleus and two electrons near the center.

Three more pairs are formed, in like manner, in the next three elements, oxygen, fluorine, and neon. The last has as its outer shell four pairs of electrons at the corners of a regular tetrahedron.

#### Sodium to Argon

As the nuclear charge increases, the most stable positions for additional electrons are obviously opposite the centers of the faces of the kernel tetrahedron. Even after the four faces are occupied by single electrons, the repulsions of the pairs in the inner shell for the valence electrons are strong enough to cause the latter to form pairs opposite the tetrahedron faces, except in a few compounds<sup>1</sup> in which the valence electrons are pulled so far away from the kernel that they are more influenced by their own repulsions and by the repulsions between the other atoms than by the arrangement of the kernel pairs.

The argon atom consists of a tetrahedron of pairs outside of another tetrahedron of pairs, with a nucleus and two electrons in the center. If these two tetrahedra are the same size, that is, if the electron-pairs are all equidistant from the atomic center, they form a perfect cube. Whether or not this is the case is yet to be determined; it makes little difference in the present theory.

The structures considered up to this point are almost identical with those assumed by Lewis. The properties of the corresponding elements and their compounds have been shown

<sup>1</sup> E. g.,  $\text{H}_2\text{SiF}_6$ ,  $\text{PCl}_5$ ,  $\text{SF}_6$ .

by him and by others to be very strikingly in accord with these structures. It is unnecessary, therefore, to consider them in further detail here.

#### Potassium to Krypton

As the nuclear charge continues to increase, the atom is able to hold additional electrons. These, when the kernel charge becomes great enough to pull them in close to the next inner shell, tend to arrange themselves opposite the faces of the underlying cube or near-cube.<sup>1</sup> The greater the central charge the closer to the nucleus and to each other both the kernel pairs and the valence electrons are drawn. As soon as the distance between two pairs or between a pair and a single electron becomes sufficiently less than the distance of maximum repulsion, a triplet is formed, one electron dropping in from the valence shell to the kernel cube. This increases the repulsion between groups (in the shell containing the triplet) and they are pushed further apart. Another increase in the charge on the nucleus again draws the electron-pairs and the valence electrons closer, another electron drops in from the valence shell, etc. It is quite conceivable that there might be two or more stable arrangements of electrons around a given atomic nucleus, differing in the number of triplets formed in this way, and so in the number of valence electrons. Certainly external conditions, such as the presence of other atoms which tend to hold electrons in the valence shell, can greatly affect the number of valence electrons which drop in from valence shell to kernel. Hence it is but the logical result of this theory that these elements should exhibit considerable variability of valence.

As the number of triplets increases, the repulsion, acting on the remaining pairs, increases and they are forced further and further away from the nucleus. This results, when the nuclear charge is large enough, in the stability of another

<sup>1</sup> It is important that the reader bear in mind throughout this discussion that a *tetrahedron* has 4 corners and 4 faces, a *cube* has 8 corners and 6 faces, and an *octahedron* has 6 corners and 8 faces.

arrangement—that of an octahedron with a tetrahedron outside of it, the corners of the tetrahedron being opposite four of the eight faces of the octahedron. This may be regarded as being derived from the cube by having two of the original pairs forced out of the inner shell, the remaining six groups (at least four of which must be triplets) rearranging themselves to form the octahedron. The two pairs forced out, together with two others, form the outer tetrahedron:

Before proceeding further, it seems best to present a system which has been worked out by the author for the purpose of affording a means of simply representing the structures of complicated atoms. It may be readily understood by a few examples. Atoms of the elements from helium to fluorine in the Periodic Table will be represented by the formula

$$(+N)(2 \times 1)(n)$$

where "N" is the nuclear charge or atomic number and "n" is the number of valence electrons—0 for He, 4 for C, 7 for F. Elements from neon to chlorine are similarly

$$(+N)(2 \times 1)(4 \times 2)(n)$$

in which  $(4 \times 2)$  represents four pairs of electrons at the corners of a tetrahedron, and the first of those in the third row,

$$\begin{aligned} & (+N)(2 \times 1)(4 \times 2)(4 \times 2)(n) \text{ or} \\ & (+N)(2 \times 1)(8 \times 2)(n) \end{aligned}$$

If the two tetrahedra  $(4 \times 2)(4 \times 2)$  have the same dimensions, they together form a cube  $(8 \times 2)$ . Although a true cube may actually not be obtained for these elements, as already explained, for the sake of simplicity the latter formula will be used in the remainder of the article.

Table I is a compilation of atomic formulae for the elements in their commonest valences. Table II contains formulae representing various typical or unusual compounds, to many of which reference will be made in the discussion which follows.

Titanium and the elements immediately following it show a variability of valence which can be very satisfactorily explained by assuming a falling in of electrons, one by one,

TABLE I  
Atomic Structures of the Elements.

H	(+1)(1)	Mg	(+12)(2×1)(4×2)(2)
He	(+2)(2×1)	Al	(+13)(2×1)(4×2)(3)
Li	(+3)(2×1)(1)	Si	(+14)(2×1)(4×2)(4)
Be	(+4)(2×1)(2)	P	(+15)(2×1)(4×2)(5)
B	(+5)(2×1)(3)	S	(+16)(2×1)(4×2)(6)
C	(+6)(2×1)(4)	Cl	(+17)(2×1)(4×2)(7)
N	(+7)(2×1)(5)	A	(+18)(2×1)(4×2)(4×2)or (+18)(2×1)(8×2)?
O	(+8)(2×1)(6)	K	(+19)(2×1)(8×2)(1)
F	(+9)(2×1)(7)	Ca	(+20)(2×1)(8×2)(2)
Ne	(+10)(2×1)(4×2)	Sc	(+21)(2×1)(8×2)(3)
Na	(+11)(2×1)(4×2)(1)		
Ti	(+22)(2×1)(8×2)(4)		and
	(+22)(2×1)(x×3+y×2)(4-x)		x=1(or 2?); y=8-x
V	(+23)(2×1)(8×2)(5)		and
	(+23)(2×1)(x×3+y×2)(5-x)		x=1, 2 or 3; y=8-x
Cr	(+24)(2×1)(8×2)(6)		and
	(+24)(2×1)(x×3+y×2)(6-x)		x=3 or 4; y=8-x
Mn	(+25)(2×1)(8×2)(7)		and
	(+25)(2×1)(x×3+y×2)(7-x)		x=1, 3, 4, or 5; y=8-x
Fe	(+26)(2×1)(x×3+y×2)(4×2)(4-x)		x=2; y=4; and
	(+26)(2×1)(x×3+y×2)(8-x)		x=2, 4, 5, or 6; y=8-x
Co	(+27)(2×1)(x×3+y×2)(4×2)(5-x)		x=3; y=3; and
	(+27)(2×1)(x×3+y×2)(9-x)		x=5, 6 or 7; y=8-x
Ni	(+28)(2×1)(x×3+y×2)(4×2)(6-x)		x=2, 3 or 4; y=6-x and
	(+28)(2×1)(x×3+y×2)(10-x)?		x=6, 7 or 8; y=8-x
Cu	(+29)(2×1)(x×3+y×2)(4×2)(7-x)		x=5 or 6; y=6-x
Zn	(+30)(2×1)(6×3)(4×2)(2)		
Ga	(+31)(2×1)(6×3)(4×2)(3)		
Ge	(+32)(2×1)(6×3)(4×2)(4)		
As	(+33)(2×1)(6×3)(4×2)(5)		
Se	(+34)(2×1)(6×3)(4×2)(6)		
Br	(+35)(2×1)(6×3)(4×2)(7)		
Kr	(+36)(2×1)(6×3)(4×2)(4×2)		or
	(+36)(2×1)(6×3)(8×2)		
Rb	(+37)(2×1)(6×3)(8×2)(1)		
Sr	(+38)(2×1)(6×3)(8×2)(2)		
Y	(+39)(2×1)(6×3)(8×2)(3)		
Zr	(+40)(2×1)(6×3)(8×2)(4)		and
	(+40)(2×1)(8×3)(6×2)(2)?		In ZrH <sub>2</sub> ?
Cb	(+41)(2×1)(6×3)(8×2)(5)		and
	(+41)(2×1)(8×3)(6×2)(3)?		In trivalent Cb?
Mo	(+42)(2×1)(6×3)(8×2)(6)		and
	(+42)(2×1)(34+x)(6-x)		Structure uncertain. x=1, 2 or 3
—	(+43)(2×1)(6×3)(8×2)(7)		and

Ru	(+43)(2×1)(34+x)(7-x) (+44)(2×1)(6×3)(8×2)(8) (+44)(2×1)(34+x)(8-x)	Structure uncertain In RuO <sub>4</sub> and Structure uncertain. x=1, 2, 4, 5, or 6
Rh	(45)(2×1)(34+x)(9-x)	Structure uncertain. x=6
Pd	(+46)(2×1)(34+x)(10-x)	Structure uncertain. x=6, 8, or 9?
Ag	(+47)(2×1)(8×3)(6×2)(4×2)(1)	
Cd	(+48)(2×1)(8×3)(6×2)(4×2)(2)	
In	(+49)(2×1)(8×3)(6×2)(4×2)(3)	and
Sn	(+49)(2×1)(6×3)(8×2)(6×2)(1) (+50)(2×1)(8×3)(6×2)(4×2)(4) (+50)(2×1)(6×3)(8×2)(6×2)(2)	and
Sb	(+51)(2×1)(8×3)(6×2)(4×2)(5) (+51)(2×1)(6×3)(8×2)(6×2)(3)	and
Te	(+52)(2×1)(8×3)(6×2)(4×2)(6) (+52)(2×1)(6×3)(8×2)(6×2)(4)	and
I	(+53)(2×1)(8×3)(6×2)(4×2)(7) (+53)(2×1)(6×3)(8×2)(6×2)(5)	and In I <sub>3</sub> <sup>-</sup> , ICl <sub>3</sub> , etc.
Xe	(+54)(2×1)(8×3)(6×2)(4×2)(4×2) (+54)(2×1)(8×3)(6×2)(8×2)	or
Cs	(+55)(2×1)(8×3)(6×2)(8×2)(1)	
Ba	(+56)(2×1)(8×3)(6×2)(8×2)(2)	
La	(+57)(2×1)(8×3)(6×2)(8×2)(3)	
Ce	(+58)(2×1)(8×3)(6×2)(8×2)(4) (+58)(2×1)(8×3)(1×3+5×2)(8×2)(3)	and
Pr	(+59)(2×1)(8×3)(1×3+5×2)(8×2)(4) (+59)(2×1)(8×3)(2×3+4×2)(8×2)(3)	In PrO <sub>3</sub> and
Nd	(+60)(2×1)(8×3)(3×3+3×2)(8×2)(3)	
-	(+61)(2×1)(8×3)(4×3+2×2)(8×2)(3)	
Sa	(+62)(2×1)(8×3)(5×3+1×2)(8×2)(3)	
Eu	(+63)(2×1)(8×3)(6×3)(8×2)(3)	
Gd	(+64)(2×1)(8×3)(6×3)(1×3+7×2)(3)	
Tb	(+65)(2×1)(8×3)(6×3)(2×3+6×2)(3)	
Dy	(+66)(2×1)(8×3)(6×3)(3×3+5×2)(3)	
Ho	(+67)(2×1)(8×3)(6×3)(4×3+4×2)(3)	
Er	(+68)(2×1)(8×3)(6×3)(5×3+3×2)(3)	
TmI	(+69)(2×1)(8×3)(6×3)(6×3+2×2)(3)	
Yb	(+70)(2×1)(8×3)(6×3)(7×3+1×2)(3)	
Lu	(+71)(2×1)(8×3)(6×3)(8×3)(3)	
TmII	(+72)(2×1)(8×3)(6×3)(8×3)(4)	
Ta	(+73)(2×1)(8×3)(6×3)(8×3)(5)	
W	(+74)(2×1)(8×3)(6×3)(8×3)(6) (+74)(2×1)(66+x)(6-x)	and structure uncertain. x=1, 2(?) or 4(?)
-	(+75)(2×1)(8×3)(6×3)(8×3)(7) (+75)(2×1)(66+x)(7-x)	and Structure uncertain
Os	(+76)(2×1)(8×3)(6×3)(8×3)(8)	and

TABLE I continued  
Atomic Structures of the Elements

	(+76)(2×1)(66+x)(8-x)	Structure uncertain. x=2 (?), 4(?), 5(?), or 6(?)
Ir	(+77)(2×1)(66+x)(9-x)	Structure uncertain. x=5, 6 or 7
Pt	(+78)(2×1)(66+x)(10-x)	Structure uncertain. x=6 or 8
Au	(+79)(2×1)(66+x)(11-x)	Structure uncertain. x=8
and	(+79)(2×1)(8×3)(6×3)(8×2)(6×3)(1)	
Hg	(+80)(2×1)(8×3)(6×3)(8×2)(6×3)(2)	and
	(+80)(2×1)(8×3)(6×3)(8×3)(6×2)	or
	(+80)(2×1)(8×3)(6×3)(8×2)(6×2)(4×2)	
Tl	(+81)(2×1)(8×3)(6×3)(8×2)(6×3)(3)	and
	(+81)(2×1)(8×3)(6×3)(8×3)(6×2)(1)	or
	(+81)(2×1)(8×3)(6×3)(8×2)(6×2)(4×2)(1)	
Pb	(+82)(2×1)(8×3)(6×3)(8×2)(6×3)(4)	and
	(+82)(2×1)(8×3)(6×3)(8×3)(6×2)(2)	or
	(+82)(2×1)(8×3)(6×3)(8×2)(6×2)(4×2)(2)	
Bi	(+83)(2×1)(8×3)(6×3)(8×2)(6×3)(5)	and
	(+83)(2×1)(8×3)(6×3)(8×3)(6×2)(3) ?	or
	(+83)(2×1)(8×3)(6×3)(8×2)(6×2)(4×2)(3) ?	
Po	(+84)(2×1)(8×3)(6×3)(8×2)(6×3)(6)	and
	(+84)(2×1)(8×3)(6×3)(8×3)(6×2)(4) ?	or
	(+84)(2×1)(8×3)(6×3)(8×2)(6×2)(4×2)(4) ?	
-	(+85)(2×1)(8×3)(6×3)(8×2)(6×3)(7)	and
	(+85)(2×1)(8×3)(6×3)(8×3)(6×2)(5) ?	or
	(+85)(2×1)(8×3)(6×3)(8×2)(6×2)(4×2)(5) ?	
Nt	(+86)(2×1)(8×3)(6×3)(8×3)(6×3)	
-	(+87)(2×1)(8×3)(6×3)(8×3)(6×3)(1)	
Ra	(+88)(2×1)(8×3)(6×3)(8×3)(6×3)(2)	
Act	(+89)(2×1)(8×3)(6×3)(8×3)(6×3)(3)	
Th	(+90)(2×1)(8×3)(6×3)(8×3)(6×3)(4)	
-	(+91)(2×1)(8×3)(6×3)(8×3)(6×3)(5)	
U	(+92)(2×1)(8×3)(6×3)(8×3)(6×3)(6)	and
	(+92)(2×1)(8×3)(6×3)(8×3)(6×2)(4×2)(4)	

to the kernel, making triplets out of pairs, in the manner described above. In different compounds the same element may have different numbers of electrons falling in to the inner shell, the number and arrangement of the valence electrons and of surrounding kernels exerting a great deal of influence. Surrounding the atom in question by oxygen, as in the chromates and permanganates, for instance, tends to keep electrons from dropping in. On the other hand, the max-

TABLE II

Formulae representing Certain Compounds

$\text{BF}_4^-$	(+5) (2×1) (4×2) (4F) <sup>-</sup>
$\text{Fe}(\text{CN})_6^{----}$	(+26) (2×1) (6×3 + 2×2) (6×2) (6CN) <sup>----</sup>
$\text{Fe}(\text{CN})_6^{---}$	(+26) (2×1) (5×3 + 3×2) (6×2) (6CN) <sup>---</sup>
$\text{Co}(\text{NH}_3)_6^{+++}$	(+27) (2×1) (6×3 + 2×2) (6×2) (6NH <sub>3</sub> ) <sup>+++</sup>
$\text{Co}(\text{NO}_2)_6^{----}$	(+27) (2×1) (6×3 + 2×2) (6×2) (6NO <sub>2</sub> ) <sup>----</sup>
$\text{Ni}^{++}$	(+28) (2×1) (4×3 + 2×2) (4×2) <sup>++</sup>
$\text{Ni}(\text{CN})_4^{--}$	(+28) (2×1) (4×3 + 2×2) (8×2) (4CN) <sup>--</sup>
$\text{Ni}(\text{CO})_4$	(+28) (2×1) (6×3) (8×2) (4CO)
$\text{Cu}(\text{NH}_3)_4^{++}$	(+29) (2×1) (5×3 + 1×2) (8×2) (4NH <sub>3</sub> ) <sup>++</sup>
$\text{Cu}(\text{NH}_3)_2^+$	(+29) (2×1) (6×3) (6×2) (2NH <sub>3</sub> ) <sup>+</sup>
$\text{Zn}(\text{NH}_3)_4^{++}$	(+30) (2×1) (6×3) (8×2) (4NH <sub>3</sub> ) <sup>++</sup>
$\text{Ag}(\text{NH}_3)_2^{++}$	(+47) (2×1) (8×3) (6×2) (6×2) (2NH <sub>3</sub> ) <sup>+</sup>
$\text{ICl}_3$	(+53) (2×1) (6×3) (8×2) (6×2) (4×2) (3Cl)
$\text{I}_3^-$	$\left[ \begin{array}{l} (+53) (2 \times 1) (8 \times 2) (6 \times 2) (8 \times 2) \\ (+53) (2 \times 1) (6 \times 3) (8 \times 2) (6 \times 2) (4 \times 2) \\ (+53) (2 \times 1) (8 \times 3) (6 \times 2) (8 \times 2) \end{array} \right]^-$
$\text{PtCl}_2$	(+78) (2×1) (8×3) (6×3) (4×3 + 4×2) (6×2) (2×2) (2Cl)
$\text{AuCl}_3$	(+79) (2×1) (8×3) (6×3) (4×3 + 4×2) (6×2) (3×2) (3Cl)
$\text{HAuCl}_4$	(+79) (2×1) (8×3) (6×3) (4×3 + 4×2) (6×2) (4×2) (3Cl; ClH)
$\text{Au}(\text{CN})_4^-$	(+79) (2×1) (8×3) (6×3) (4×3 + 4×2) (6×2) (4×2) (4CN) <sup>-</sup>
$\text{Hg}_2^{++}$	$[(+80) (2 \times 1) (8 \times 3) (6 \times 3) (8 \times 2) (6 \times 3)]_2^{++}$

imum number of electrons which can drop in seems to be reached in the simple positive ions, where there are no other atoms bonded to the atom in question. The number of electrons "drawn in" per atom for each of these elements in its various valences is tabulated in Table IIIA. Note the regularity with which the number drawn in the most stable positive ions increases with an increase in the nuclear charge.

It seems probable that for the first elements, from titanium on, the basic structure is the cube ( $8 \times 2$  or  $3$ ), somewhat distorted of course, while at the end of the list the most stable arrangement is the octahedron ( $6 \times 2$  or  $3$ ), four of the faces of which are occupied by pairs, which are then arranged at the corners of a tetrahedron ( $4 \times 2$ ). Crystal structure evidence indicates that iron, cobalt and nickel kernels in some



TABLE III  
Electrons drawn in from Valence Shell to Kernel

A.

Ti	0	1	2?	-	-	-	-	-	-	-	-	-	-
V	0	1	2	3	-	-	-	-	-	-	-	-	-
Cr	0	-	-	3	4	-	-	-	-	-	-	-	-
Mn	0	1	-	3	4	5	-	-	-	-	-	-	-
Fe	-	-	2	-	4 <sup>1)</sup>	5	6	-	-	-	-	-	-
Co	-	-	-	-	-	5 <sup>1)</sup>	6	7	-	-	-	-	-
Ni	-	-	-	-	-	-	6 <sup>1)</sup>	7	8	-	-	-	-
Cu	-	-	-	-	-	-	-	-	9	10	-	-	-
Zn	-	-	-	-	-	-	-	-	-	10	-	-	-
Ga	-	-	-	-	-	-	-	-	-	10	11	12?	-
Ge	-	-	-	-	-	-	-	-	-	10	-	-	12

B.

Zr	0	-	2?	-	-	-	-	-	-	-	-	-	-
Cb	0	-	2?	-	-	-	-	-	-	-	-	-	-
Mo	0	1	2	3	-	-	-	-	-	-	-	-	-
—													
Ru	0	1	2	-	4	5	6	-	-	-	-	-	-
Rh	-	-	-	-	-	-	6	-	-	-	-	-	-
Pd	-	-	-	-	-	-	6	-	8	9?	-	-	-

C.

W	0	1	2?	-	4	-	-	-	-	-	-	-	-
—													
Os	0	-	2?	-	4?	5?	6?	-	-	-	-	-	-
Ir	0	-	-	-	-	5	6	7	-	-	-	-	-
Pt	-	-	-	-	-	-	6	-	8	-	-	-	-
Au	-	-	-	-	-	-	-	-	8	-	10	-	-

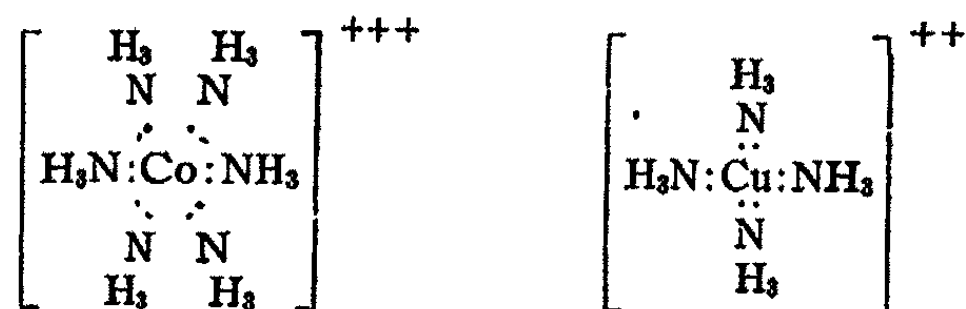
compounds are surrounded by six valence electron-pairs at octahedron corners, indicating a cubical arrangement underlying, and in other compounds by four pairs, probably the result of an octahedron-tetrahedron kernel structure. In most nickel compounds, and in practically all those of copper and the following elements, there are four or a smaller number of pairs in each valence shell. This we may take as indicating a kernel containing a tetrahedron outside of an octahedron. Thus we arrive at the atomic formulae given in Table I.

<sup>1</sup> Evidence from crystal structures indicates that in certain minerals iron, cobalt, and nickel atoms have four electrons each in the valence shell, besides those furnished by other atoms.

The "auxiliary valence" of these elements is merely their tendency or ability to add on compounds with "lone pairs" of electrons (valence pairs not acting as bonds or parts of bonds)

such as trivalent nitrogen compounds  $\begin{array}{c} R \\ \vdots \\ :N: \\ \vdots \\ R \end{array}$ , cyanide ion  $\begin{array}{c} R \\ \vdots \\ :C \vdots N: \\ \vdots \\ R \end{array}$ , water  $\begin{array}{c} \vdots \\ :O:H \\ \vdots \\ H \end{array}$ , halide ion  $\begin{array}{c} \vdots \\ :X: \\ \vdots \end{array}$ ; etc. These lone pairs

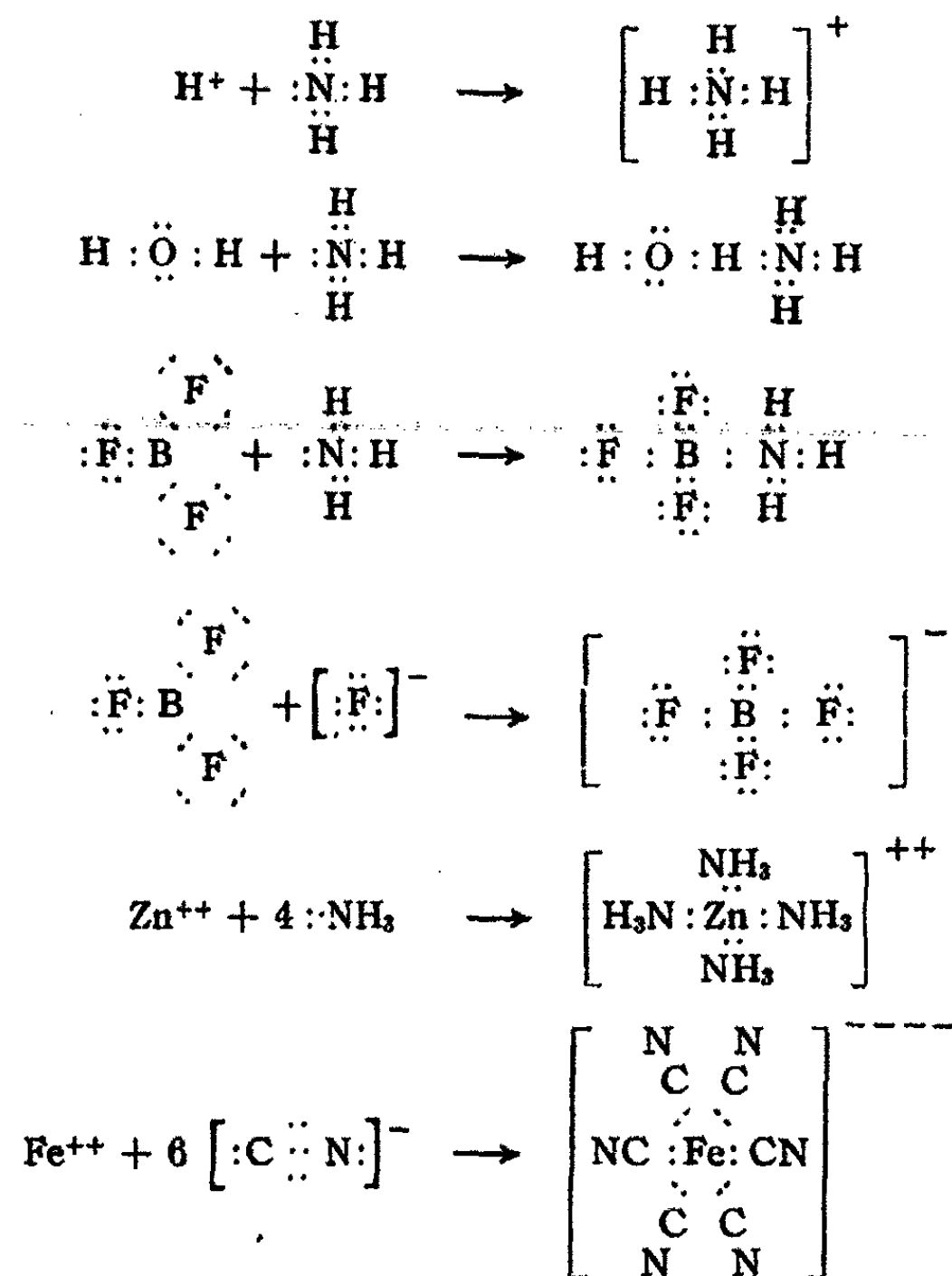
occupy positions opposite the centers of the faces of the underlying structure (cube or octahedron), forming, in the case of the iron and cobalt complexes, a valence octahedron, and in the case of the copper, zinc, and some of the nickel complexes, a (distorted) cube consisting of four valence pairs and four kernel pairs, outside of the underlying octahedron. To illustrate this a few of the "kernel formulae" of these compounds are given in Table II. Where it is only desired to indicate the valence electrons, formulae like the following will also sometimes be found useful:



Single bonds, it may be noted here, may be formed in either of three different ways: (1) by the union of two atoms each of which contains a lone (unpaired) electron, (2) by the union of an atom containing a lone pair with another atom capable of holding onto that pair, and (3) by the breaking up of a polyatomic polyelectronic bond, which bond is often formed as the result of the addition of two simple diatomic bonds, but, being usually quite unstable, exists only momentarily as an intermediate step in the reaction.<sup>1</sup>

<sup>1</sup> It is important that the reader bear in mind throughout this discussion that a tetrahedron has four corners and four faces, a cube has eight corners and 6 faces, and an octahedron has 6 corners and eight faces.

We are concerned at this point in the development of the present theory, only with reactions of the second type given above. Of these, the following are typical examples:



As one modification of the above reaction we have the reaction of a positively charged kernel containing no electrons in its valence shell with an atom containing a lone valence pair. The bond formed is here often very weak, since the attraction of the positive kernel for electrons is usually small.

This type of reaction is of major importance in crystal formation. In this process each atom or molecule is acted on by several forces tending to form bonds in this way. Indi-

vidually these forces may be quite weak, but collectively they are quite sufficient to pull the atom or molecule into its proper position in the crystal. Once formed, these new bonds may be just as strong as, and even identically the same as, some of the bonds which originally (in the liquid or gaseous state) held the atoms of the molecule together.

It is also this kind of reaction which often produces polymerization and the formation of molecular aggregates (e. g., of  $H_2O$ ).

The "simple" or first order compounds of elements (Cu, Zn, etc.) which are capable of adding lone pairs in this way have, as a general rule, high melting points, and often are very insoluble, both in water and other solvents, indicating that their crystal structures are very stable and hard to disrupt.

From cuprous copper to krypton, valence electrons occupy positions opposite the four faces of the inner octahedron which are not already occupied by pairs. They thus tend to form another tetrahedron, which is complete in bromide ion and krypton. This and the tetrahedron already there form a cube.

The elements copper, zinc and gallium, although mono-, di-, and trivalent, respectively, show a much greater tendency to add electrons and a much smaller tendency to give up their own (forming simple positive ions) than do potassium, calcium and scandium. The reason is that in atoms of the former elements the valence electrons can assume positions around the kernel octahedron which are but slightly farther from the nucleus than the electron-pairs in the kernel tetrahedron; this tetrahedron may then almost be considered as a part of the valence shell; and the *effective* kernel charge—a rough measure of the restoring force acting on a valence electron-pair pulled out slightly from its equilibrium position in a radial direction—is then much greater than in atoms of the alkali or alkaline earth metals.

There seems to be a very slight tendency in di- (and mono-?) valent gallium, and perhaps in divalent germanium, for two

more electrons to be drawn into the kernel, forming, presumably, two more triplets.

#### Rubidium to Xenon

The elements immediately following krypton, (+ 36)  $(2 \times 1) (6 \times 3) (8 \times 2)$ , are in every way similar to those following argon, a new shell being gradually built up on the outside of the krypton kernel. It is possible, although not necessary to the theory, that, under the influence of external forces, the cube and the octahedron may in some compounds (e. g.,  $\text{MoO}_4^-$  and  $\text{RuO}_4$ ) exchange places, each corner of the cube passing, in the shift, through a face of the octahedron, and each corner of the octahedron through a face of the cube.

As with the elements following scandium, as soon as the nuclear charge becomes great enough, electrons are pulled in from the valence shell to change pairs to triplets in the next inner shell. This process may begin with zirconium, in its dihydride, and columbium, in its trivalent compounds; most certainly it takes place in molybdenum compounds, the number of electrons drawn in varying from zero in  $\text{MoO}_4^{--}$  and  $\text{MoF}_6$ , to three, in  $\text{MoCl}_3$ , etc.

Table IIIB gives the number of electrons which are apparently drawn in per atom for the elements from Zr to Pd. It will be noticed that there is somewhat less regularity here than in the former case (Table IIIA). This and the fact that somewhere in the process the most stable arrangement becomes one of three shells (besides the innermost two electrons)—cube, octahedron and tetrahedron—makes an attempt to give an exact kernel structure for each of these elements in each valence little more than a guess. Hence kernel formulae are not given for these substances in Table I.

By the time silver is reached, however, the rearrangement has been completed and valence electrons begin to form a new shell on the outside of a kernel which we may represent as  $(+ N) (2 \times 1) (8 \times 3) (6 \times 2) (4 \times 2)$ . These valence electrons take up positions opposite the unoccupied faces of the octahedron,  $(6 \times 2)$ , completing the cube around it in

iodide ion and xenon. This is exactly what we found took place in the elements copper to krypton; and the properties of the two groups of elements are strikingly parallel.

Beginning with indium, another kernel arrangement is stable, the formula for which is  $(+N) (2 \times 1) (6 \times 3) (8 \times 2) (6 \times 2)$ , or, possibly,  $(+N) (2 \times 1) (4 \times 3 + 4 \times 2) (6 \times 3) (4 \times 2)$ . The kernels of monovalent indium and divalent tin are probably of this type. Iodine, in such substances as  $I^-_3$  and  $ICl_3$  seems to exist in a form in which there are only five electrons in the valence shell, hence we may give it also this kernel formula; and we *may* also be justified in doing the same for trivalent antimony and tetravalent tellurium.

#### Cesium to Uranium

Xenon, cesium, barium, lanthanum and tetravalent cerium all have kernel structures  $(+N) (2 \times 1) (8 \times 3) (6 \times 2) (8 \times 2)$ . The properties of these elements correspond closely to those of the elements krypton to zirconium. At cerium the nuclear charge is again great enough to draw in electrons from the valence shell. Cerium is both tri- and tetravalent, and the next thirteen elements (the rest of the rare earths) are invariably trivalent, with the probable exception of praseodymium in the compound  $PrO_2$ , indicating that the increase on the charge on the nucleus from one element to the next is just sufficient to cause one more electron to fall in and make another triplet. This regularity may be attributed to the fact that no intra-kernel rearrangement occurs other than the formation of triplets from pairs, and that the kernel has not a great attraction for electrons and hence is but slightly affected by atoms and electrons outside of it, which was not so true in the other cases where the electrons were drawn in.

When fourteen electrons have fallen into the kernel, all of the pairs have become triplets; further increase in nuclear charge must therefore result in an increase in the number of valence electrons. Thulium II should have a valence of four; tantalum, we know, is pentavalent like columbium; tungsten

is in many of its compounds hexavalent; and osmium is octavalent in the tetroxide.

But here we find that electrons are once more drawn in to the kernel, this time irregularly (Table IIIC), indicating, as before, some sort of a rearrangement of shells. Again the present theory does not enable us to give to each element in each of its valences a definite structure which we can reasonably be sure is correct, until we come to gold.

In its trivalent form the gold kernel is like that of divalent platinum (see Table II). In its monovalent compounds it has, no doubt, either of the two following structures:

$(+79) (2 \times 1) (8 \times 3) (6 \times 3) (8 \times 2) (6 \times 3) (1)$  or  $(+79) (2 \times 1) (6 \times 3) (8 \times 3) (6 \times 3) (8 \times 2) (1)$ .

If, as seems likely, the continuity of the curves obtained when the square roots of the frequencies of the L series of X-radiations are plotted against atomic numbers, means that the second shell out from the nucleus remains essentially the same for all elements from zinc to uranium, then the second of these structures is eliminated.<sup>1</sup> Hence we shall provisionally assume the former arrangement.

The addition of two more electrons to the kernel makes the structure  $(+N) (2 \times 1) (8 \times 3) (6 \times 3) (8 \times 3) (6 \times 2)$  (or perhaps,  $(+N) (2 \times 1) (8 \times 3) (6 \times 3) (8 \times 2) (6 \times 2) (4 \times 2)$ ) possible. Mercury, in the liquid and gaseous states, has no doubt this structure. Were it not for the possibility of shifting to the other form  $(+N) (2 \times 1) (8 \times 3) (6 \times 3) (8 \times 2) (6 \times 3) (2)$ , we might find mercury a member of the inert gas group of elements. In all of its compounds the mercury atom possesses two valence electrons, two metal atoms being bonded together in all mercurous compounds, as shown for mercurous ion  $(\text{Hg}_2)^{++}$ , in Table II.

Thallium, lead, and bismuth each form two series of compounds, corresponding to the two possible kernel arrange-

<sup>1</sup> If this assumption is correct, monovalent indium, divalent tin, etc., should each show a different L series spectrum from that obtained from these elements in compounds in which they exhibit their higher valences. To the author's knowledge, this has not been tested experimentally.

ments. In its monovalent compounds thallium has the properties of an alkali metal, which is striking evidence of the fact that its kernel is structurally very similar to those of the rare gases.

Niton, atomic number 86, has the structure (+ N)  $(2 \times 1) (8 \times 3) (6 \times 3) (8 \times 3) (6 \times 3)$ ; and since there is no other stable arrangement to which it can shift (as there is in the case of mercury), it is one of the inert gases, having no tendency either to give up or to add on electrons.

Radium, thorium and uranium, in their compounds, show that they have two, four, and six valence electrons, respectively, indicating that they each have a kernel like that of niton. Uranium in its tetravalent compounds may have either a lone valence pair, or, as seems more likely, the structure  $(+ 92) (2 \times 1) (8 \times 3) (6 \times 3) (8 \times 3) (6 \times 2) (4 \times 2) (4)$ .

#### Laws of Force

We shall now return to the consideration of the laws of force between electrons and between nuclei and electrons. Although no attempt will be made in this paper to ascertain just what the true laws of force are at small distances, still it should be of interest to show, by a simple example, how the formation of pairs and triplets is the direct result of the type of law assumed.

In Fig. 1 are shown some curves representing laws of force. Each of these, except *h*, possesses a maximum followed by a decrease in the force as the distance decreases from that corresponding to the maximum. Curves *a* to *g*, inclusive, represent the following equations, in order:

$$f = \frac{ee'}{r^2} \epsilon^{-\frac{2}{r}}, \quad f = \frac{ee'}{r^2} \epsilon^{-\frac{1}{r^2}}, \quad f = \frac{ee'}{r^2} \epsilon^{-\frac{2}{r} + \frac{0.1}{r^2}}, \quad f = \frac{ee'r}{r^3 + 1},$$

$$f = \frac{ee'r^2}{r^4 + 1}, \quad f = \frac{ee'(r^2 + 0.02)}{r^4 + 1}, \quad f = ee' \left( \frac{1}{r^2} - \frac{0.667}{r^3} \right).$$

In each of the above, *r* is the distance between the two charges *e* and *e'* the magnitude of the charges,  $\epsilon$  is the base of natural logarithms. In plotting the curves, *e* and *e'* were taken as unity. Curves *a* and *h* are of types suggested by Lewis;<sup>1</sup> *g* is

<sup>1</sup> G. N. Lewis: *Science*, 46, 297 (1917).



of a type used by J. J. Thomson<sup>1</sup> Langmuir<sup>2</sup> and others;  $j$  represents Coulomb's law.

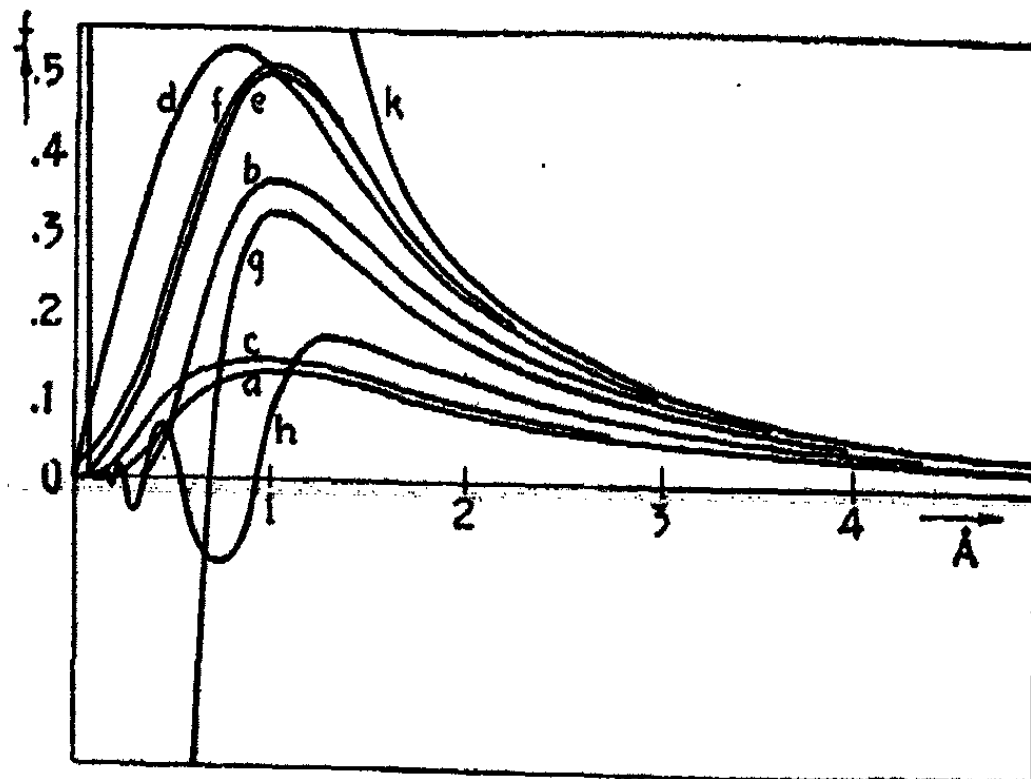


Fig. 1

Let us now assume that both repulsion between two electrons and attraction between a nucleus and an electron obey the law represented by curve  $e$ .

#### Lithium

From the equation

$$\frac{3r^2}{r^4+1} = \frac{2 \times 0.866 \times 1.732^2 r^2}{1.732^4 r^4 + 1}$$

we can obtain  $r = 0.564 \text{ \AA}$ . as the equilibrium distance of each of three symmetrically placed electrons from the nucleus. By a rather laborious combined graphical and analytical method it may be shown that if one electron is displaced *slightly* toward one of the others, the resultant force acting on it will tend to return it to its previous symmetrical position; but if two electrons approach each other closer than about  $0.37 \text{ \AA}$ ., the resultant force tends to force them still closer together, until, as a matter of fact, they are coincident.

<sup>1</sup> Phil. Mag., 41, 510 (1921).

<sup>2</sup> Science, 53, 290 (1921).

If we assume a slightly different law, say  $f = \frac{ee'(r^2 + 0.02)}{r^4 + 1}$

(Curve *f*, Fig. 1), coincidence will not result. There will then be two equilibrium arrangements, one with the three electrons at the corners of an equilateral triangle, each



Fig. 2

at a distance of 0.548 Å., the other with two electrons 0.39 Å. from the nucleus and 0.10 Å. from each other and the third electron at a distance of 0.61 Å. from the nucleus. (Fig. 2.)

#### Beryllium and Boron

It may similarly be shown that in an atom of beryllium or boron, were the same law of force acting, there would be two equilibrium configurations, one the symmetrical arrangement, the other an arrangement in which two of the electrons are paired. The distances between the charges in these assumed structures may be computed, but for our present purpose they are unimportant.

It is easy to see how the actual law of force might make only the unsymmetrical disposition stable, or how even with the assumed law, oscillations of the electrons might have the same result.

#### Carbon and Nitrogen

If we assume that the inner pair of electrons in carbon acts in every way as though a part of the nucleus, the computation for carbon is just like that for beryllium and there are again two stable arrangements for the four outer electrons. For some reason, however, the unsymmetrical configuration is rarely, if ever, assumed. This may be because of the two inner electrons tending to prevent the shift, or merely because we have not made the right assumptions with regard to the law of force.

In nitrogen, because of the fact that the nuclear charge is greater and because in the most symmetrical disposition five electrons must be much closer to each other than four, pairing of two of the valence electrons must occur.

### Other Elements; Triplets; Four-electron Groups

Pairing in other elements occurs in the same way, and for similar reasons as in the elements just considered. In a corresponding manner also, if two pairs in the same or different atomic shells are forced close enough together, one of the electrons in one pair will join the two in the other pair, forming a triplet. This leaves a single electron, which immediately pairs off with another (usually one from the valence shell). Also, if a single electron in the valence shell is drawn within the distance of maximum repulsion from a pair in the outermost kernel shell, the single valence electron will drop into the kernel, forming a triplet.

In case two triplets, or a pair and a triplet, were pulled sufficiently close to each other, we should expect from similar reasoning that a group of four electrons would be formed; but the author has been unable to work out a concordant system of structures on such a basis, hence we may assume that even in the heaviest elements the nuclear pull on electrons is not strong enough to accomplish such a result.

### The Three-electron Bond

There is nothing contrary to this theory in the idea of a three-electron bond. Such a bond between two atoms, however, could only be stable if the three electrons joined two kernels which both had a strong attraction for electrons but which did not repel each other with too great a force. Such a condition is met with in the compound NO. Although both kernels maintain a strong hold on the bond between them, their mutual repulsion causes them to be forced closer to the remaining electrons. Because of the strong attraction of each kernel for these they are drawn in so close that if they were arranged at the points of tetrahedra, as in most nitrogen and oxygen compounds they would be somewhat closer to each other than the distance of maximum repulsion. Hence triangles of electron-groups are formed around both kernels. The compounds might be represented in this way:



Similarly we might give

$\text{NO}_2$  the structure  $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{N} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$ . The addition of the second

oxygen atom to the compound increases the distance between the points of the triangle around the nitrogen, and also around the oxygen. The whole structure is less stable and more reactive; the electrons of the lone pairs are less firmly held in position at the corners of the triangles. Hence the substance is colored and tends to polymerize to  $\text{N}_2\text{O}_4$ .

There seems to be little or no evidence of three electrons acting as a single bond between any other two elements, but evidence is presented elsewhere by the author<sup>1</sup> of bonds joining more than two atoms which consist of three, four, five, six, seven, or even eight electrons.

#### The Stability of the Pair

The fact that a large majority of known compounds contain (outside of the atomic nuclei) a total number of electrons which is even, and that among those compounds which contain only elements of comparatively small atomic weight, an "odd molecule" is almost invariably colored, reactive and unstable, has led many to believe that there is something inherently stable about the *pair* of electrons both in chemical bonds and in atomic kernels. But the theory developed in this paper shows that this is not necessarily the case. Under certain conditions—in the inner shells of atoms with large nuclear charges—the triplet is stable and the pair is unstable. In all of the lighter atoms and in the valence shells of all atoms, it is true, the pair tends to form rather than triplet. Away from the influence of positive charges, electrons show no tendency even to pair.

Since triplets exist mainly, if not entirely, in the kernels of the heavier atoms, and since the stable shells of triplets are those containing an even number (6 or 8) of groups, in compounds of these elements also the total number of electrons is

<sup>1</sup> Huggins: Jour. Am. Chem. Soc., August, 1922; Science, July, 1922.

even, *except* where the process which has been styled the "dropping in" of electrons is taking place—where shells of pairs are but partly changed to shells of triplets. Whenever an *odd* number of electrons has "fallen in" to the kernel—that is, when the kernel contains an *odd* number of triplets—the total number of electrons in the compounds of that element in that particular valence will be odd, unless, of course, there are two such elements in the compound. In these cases the odd number of electrons is not accompanied by instability, reactivity, and intense color, unless these are due to other causes.

This theory, then, not only explains the cause of an even total number of electrons in so many compounds, but specifies in what compounds there will be an odd number, and whether or not the odd molecule will be unstable, highly colored and very reactive.

#### Electronic Positions; Spectroscopy

The "positions" of electrons in the various atoms which have been presented in this paper should of course be considered merely as equilibrium positions, about which there may be oscillation or rotation of the electrons or electron groups.

Since the actual laws of force acting between the elementary positive and negative charges are still unknown to us, we cannot at the present time compute the distances between electrons in the pairs and triplets and the radii of the various shells in the atoms of each element. For the same reason this theory in its present form cannot be checked up by means of spectroscopic facts. It is to be hoped, however, that the limitations which the theory seems to place on the variations of the force laws at small distances, will aid in the search for the truth regarding them.

#### Summary

The Lewis theory of valence and atomic structure is assumed to be correct for the lighter atoms. The evidence in favor of a tetrahedron of electron-pairs, rather than a cube of single electrons, being the most stable arrangement for the valence shell in these atoms—an idea also proposed by Lewis—

is presented. It is shown how the stability of such an arrangement may be the result of the deviation of the force law between two electrons from Coulomb's law at small distances. The chief requirement for this purpose is "that as two electrons approach each other, the repulsion between them reaches a maximum at a distance of the order of magnitude of 1 Å., the force then decreasing, for a considerable proportion of the remaining distance, at least." As result of a law of this type, whenever two electrons, forming part of an atomic shell, are forced close enough together, they come still closer to each other—that is, they pair off—and when two pairs, or a pair by the attraction of an atomic nucleus and the repulsion of other electrons, a triplet is formed. Based on this assumption and on the idea that the electrons in an atomic shell tend to place themselves opposite the centers of the faces of the imaginary polyhedron formed by the electron groups in the next underlying kernel shell, an arrangement of electrons is obtained for each element in each of its valences (with a very few exceptions, not yet completely worked out) which conforms to the known properties of that element. For these arrangements Table I may be consulted. Periodic relationships are also simply and logically accounted for.

The author wishes to here express his grateful appreciation of the kindly criticism and advice received from other members of this Department, especially Professors G. N. Lewis and Wm. C. Bray.

*Chemical Laboratory  
University of California  
Berkeley, California*

91-0911

## THE MELTING AND FREEZING POINT OF SODIUM CHLORIDE<sup>1</sup>

BY JOHN BRIGHT FERGUSON

The melting or freezing point of sodium chloride is usually relegated into the category of a secondary thermometric point. However, there is much to commend the use of this point to workers in chemical laboratories where the pure salt and suitable containers<sup>2</sup> are readily obtained. For this reason, we desire to place on record some determinations of this point, which we were led to make by a somewhat unsatisfactory calibration of a thermo-element at this point.

### Thermo-couple and Calibration

A platinum: platinum-rhodium thermo-element was used. The wires were 0.5 mm in diameter and from pre-war German stock.

The electrical measuring apparatus consisted of a Williams double potentiometer, set up essentially as given by White.<sup>3</sup> The galvanometer was of such sensitivity, that a reading of 50 divisions on the scale corresponded to 10 microvolts.

A properly insulated alundum tube, wound with nichrome wire, served as a heating unit. Inside the alundum tube a large silica test-tube was placed and the crucible containing the metals were so placed in this test-tube as to be in the region of uniform temperature in the furnace.

Crucibles turned from Acheson graphite rods were used as containers for the cadmium, zinc, antimony, copper-silver and copper samples. Lids and graphite powder were also prepared from the same rods.<sup>4</sup>

<sup>1</sup> Contribution from the Chemical Department of the University of Toronto.

<sup>2</sup> Nickel crucibles have been recommended. Bur. Standards, Circ., 66, 10 (1917).

<sup>3</sup> W. P. White: Jour. Am. Chem. Soc., 36, 1880 (1914).

<sup>4</sup> Day and Sosman: Am. Jour. Sci., 29, 125 (1910). Bur. Standards, Circ., 66, 11 (1917); 7, 5 (1920).

The silver point was determined by the wire method; the bare element was placed in a clean silica test-tube like that in which the crucibles were placed but free from carbonaceous material and the tube evacuated. Silica tubing was used both to insulate the parts of the element and also to protect it when necessary.

The cadmium, zinc and antimony were from a stock of Kahlbaum's best pre-war chemicals. The copper consisted of carefully selected bright chips of electrolytic copper from the same source. The silver was obtained from the mint at Ottawa through the courtesy of the Director and was certified 999.9 fine.

The results obtained at these fixed points are given in Table I. For comparison, the values given by Adams<sup>1</sup> for a standard element are given and also the corresponding temperatures in degrees centigrade upon the thermodynamic scale.

TABLE I  
Values obtained in the calibration at the fixed points

Material	Freezing point	Melting point	Standard element	Temperature deg. cent.
Cadmium	2506.4	2509.4	2503	320.9
Zinc	3429.6	3430.5	3430	419.4
	3428	3428.3	—	—
Antimony	5539.1	5541.7	5530	630
Copper-silver Eutectic				
Sample 66% Silver	7106.5	7123.2	7102.1	779
	7108	7121.4	—	—
Silver Vacuum Wire				
Method	—	9161	—	—
	—	9159	9111	960.2
Copper	10574	10586.5	10534	1082.8
	10575.5	10585.4	—	—

The results given in the previous table would indicate that our element gave slightly greater E. M. F. values at tem-

<sup>1</sup> L. H. Adams: Jour. Am. Chem. Soc., 36, 65 (1914). The value for the copper-silver eutectic is not given by him but is easily derived from his table assuming the value 779° given by the Bureau of Standards.



peratures above that of the zinc point, than did the standard element. The results cannot all be considered of equal weight since the experimental errors would tend to lower the copper value (oxidation) whereas in the case of the silver value they would raise it (wire method). The copper-silver eutectic value may be low if other than the eutectic composition be used.<sup>1</sup> The freezing points taken by us with this material were sharp, showing the slight under-cool with subsequent slow heating mentioned by Waidner and Burgess. In one case prior to the break, the cooling was at the rate of 10 microvolts per minute; at the break the temperature first rose 1 microvolt in two minutes, remained constant 1 minute and then fell 1 microvolt in three minutes ( $1 \mu v = 0.09$  degrees). This break would seem to leave nothing to be desired. However, in view of the work of Waidner and Burgess, we think that the melting point determinations probably correspond closer to the true eutectic temperature than do our freezing determinations.

A deviation curve,<sup>2</sup> for calibration purposes, was drawn by plotting the differences in microvolts between our values at the fixed points and those of the standard element, against the temperatures in degrees centigrade. The differences chosen were: zinc 0, antimony 10, copper-silver eutectic 20, silver 49, and copper 52. The curve was drawn so as to lie midway between the two latter values. This curve indicates that our element gives a reading 22 microvolts higher than the standard element at 800 degrees and this deviation appears to be as great a deviation as can be consistently deduced from our results.

#### **Sodium Chloride Determinations**

The sodium chloride determinations were carried out in the silica test-tube used for the silver determinations. The salt was first melted in a platinum crucible over a blast-lamp, care being taken to avoid the reduction of the salt. The

<sup>1</sup> Waidner and Burgess: *Bur. Standards, Bull.*, 62, 149 (1909).

<sup>2</sup> R. B. Sosman: *Am. Jour. Sci.*, (4) 30, 7 (1910).

bare thermo-element was then allowed to freeze in place and the crucible and element transferred to the silica test-tube in the resistance furnace. The crucible held about 15 cc and was, unless otherwise stated, filled three quarters full of the molten salt. The freezing point of the salt was taken as the highest temperature to which the salt heated up after the slight under-cool. The melting point was taken as the upper break on the melting curve.

The results are given in Table II. The temperatures given were calculated from the deviation curve and are in degrees centigrade on the thermo-dynamic scale.

TABLE II  
Melting and Freezing Point Determinations for Sodium Chloride

Material	Melting point		Freezing point		Remarks
	Micro-volts	Average in °C	Micro-volts	Average in °C	
Kahlbaum's purest salt from pre-war stock	7389.3	803.4	7386.4	803.1	Element in centre of charge
	7388.8	—	7387.3	—	
	—	—	7384.6	—	Small charge element in surface
	7387.8	—	7379.2	—	
7382.8	—	7376.2	—	Element at side near top	
J. T. Baker C. P.	7386.1	803.1	7381.6	802.7	Element in centre of charge
Squibb's C. P.	7388.8	803.4	7387.2	803.2	Element in centre of charge
Merck C. P.	7391.1	803.6	7387.4	803.1	Element in centre of charge
	7391.3	—	7385.5	—	

Discussion of Results

These results would indicate that the pure salt freezes at  $803^{\circ} \pm 1^{\circ} \text{C}$ . The generally accepted value is  $801^{\circ} \text{C}$ . The values given by the following workers<sup>1</sup> also support a higher value than that now accepted: Plato, 804.1; Arndt,

<sup>1</sup> Landolt-Börnstein, Roth: Physikalisch-chemische Tabellen, page 222 (1912).

805; Sardonini, 806; and Menge, 803. Griffiths' value<sup>1</sup> of 801, obtained with a salt 99.98% pure, made for dairy purposes, would seem also to favor a higher value since such salt could hardly be of the same purity as our best reagent chemicals.

*Toronto, Canada*

---

<sup>1</sup> Ezer Griffiths: "Methods of Measuring Temperatures," page 75.

3-18-27

## CATALYTIC PREPARATION OF AZOBENZENE AND ANILINE. II

BY C. O. HENKE AND O. W. BROWN

### Introduction

In our previous work we have shown that nitrobenzene is reduced by hydrogen to azobenzene in the presence of suitable catalysts.<sup>1</sup> Of a large number of catalysts studied, lead and bismuth were found to be the only catalysts which gave azobenzene in large amounts. Small amounts of azobenzene were secured with chromium, antimony and manganese while with the other catalysts a colored product was obtained, the color possibly being due to azoxybenzene and azobenzene. We have secured this formation of azobenzene with thallium as catalyst.

### Experimental Details

The apparatus used was the same as that described in our previous papers with the exception of the following minor changes. A glass combustion tube was used instead of the  $\frac{1}{2}$ " iron pipe. Also the thermometer capillary extended farther into the combustion tube than the T tube through which the hydrogen and the capillary are led into the combustion tube. This eliminates the probability of any nitrobenzene vapors being entrapped between the T tube and the combustion tube.

In our previous work the hydrogen (which was obtained in steel cylinders) was purified by passing through a heated tube filled with pieces of copper, bubbling through concentrated sulphuric acid and then passing over sticks of caustic. It then passed through the flowmeter and into the furnace. It was found, however, that small particles of sulphuric acid were mechanically carried out of the sulphuric acid bottle, through the tower containing solid caustic, through the flowmeter and

<sup>1</sup> Henke and Brown: Jour. Phys. Chem., 26, 324 (1922).

into the furnace. Not all of the sulphuric acid particles reached the furnace. Most of them were deposited in the rubber and glass tube connections and in the caustic tower. Some, however, were deposited in the flowmeter capillary and some passed into the furnace. The small amount of acid deposited in the capillary of the flowmeter would cause it to read a little too high. It was found that these minute particles of sulphuric acid could be stopped by introducing between the caustic tower and the flowmeter a U tube filled with glass wool. The glass wool seems to effectually remove the sulphuric acid particles, for after a flowmeter had been used in this way for about three months not a trace of acid could be detected in the capillary of the flowmeter.

The method of procedure and the methods of analysis were the same as described in our previous papers.

#### **Experimental Results**

To purify the metallic thallium it was dissolved in sulphuric acid. This solution was heated to boiling and then saturated with  $H_2S$  to precipitate any Bi, Sb, As, etc., which might be present. After standing for some time it was filtered and then boiled to remove excess  $H_2S$ . An excess of ammonia was then added to the filtrate to throw down iron and alumina and the solution again boiled and filtered. If the filtrate was not almost colorless this operation was repeated. From the clear, nearly colorless filtrate  $TlCl$  was precipitated by  $HCl$ . This was filtered out and digested with  $H_2SO_4$  with the addition of  $HNO_3$  and  $HCl$  until all the thallium was oxidized to the thallic condition. Then the digestion was continued until free from chlorine. Pure thallium hydroxide was then precipitated with ammonia, washed, filtered and dried. Twenty-one grams of the dried oxide was used as catalyst which was placed in the same part of the tube as in our previous work.

The thallic oxide was reduced by a slow current of hydrogen (1.7 liters hydrogen per hour), the temperature being raised gradually. The reduction of the oxide by hydrogen is an exothermic reaction. The heat evolved causes an increase in

temperature at that point of the catalyst column where the reduction is taking place. The reduction begins at that end of the catalyst column where the hydrogen first strikes it. As the reduction proceeded the temperature indicated by the thermocouple was kept below 250°. When, however, after about two hours, the reduction zone reached the thermocouple the temperature indicated by the thermocouple suddenly rose to 278° and after a few minutes dropped again to about 250°.

The results of experiments with this catalyst are given in Table I. In each experiment 2 cc of nitrobenzene was used, the same as in our previous work.

TABLE I.  
Temperature of catalyst—260° C.  
Rate of flow of nitrobenzene—4.1 grams per hour.

Experiment number	Hydrogen in liters per hour	Excess of hydrogen in % <sup>1</sup>	Material yield of aniline in % of theory	Material yield of azobenzene in % of theory	Total material yield in % of theory
6J4-2	14	830	2.4	68.6	70.9
7J4-2	14	830	2.0	65.3	67.3
8J4-2	7	370	2.7	78.9	81.6
9J4-2	7	370	3.4	76.0	79.4
10J4-2	3.5	130	3.4	89.9	93.3
11J4-2	3.5	130	4.0	85.5	89.5
12J4-2	1.7	13	4.3	90.2	94.5
13J4-2 <sup>2</sup>	1.7	13	2.0	51.8	53.8

From the above results thallium is a catalyst producing azobenzene almost to the exclusion of aniline. The aniline yields are without exception very low. Besides azobenzene, azoxybenzene was also produced. The amount of azoxybenzene produced was not determined.

The results of Table I are shown graphically in Fig. 1. In curve A are plotted the results of the first experiment at

<sup>1</sup> The excess of hydrogen is calculated from the amount that would be required to produce azobenzene.

<sup>2</sup> In experiment 13J4-2, 10 cc of nitrobenzene was used instead of 2 cc.

each rate of flow of hydrogen while in curve B are plotted the results of the second experiment at each rate of flow of hydrogen. The result of experiment 13J4-2 is not plotted in the figure because a 10 cc portion instead of a 2 cc portion was

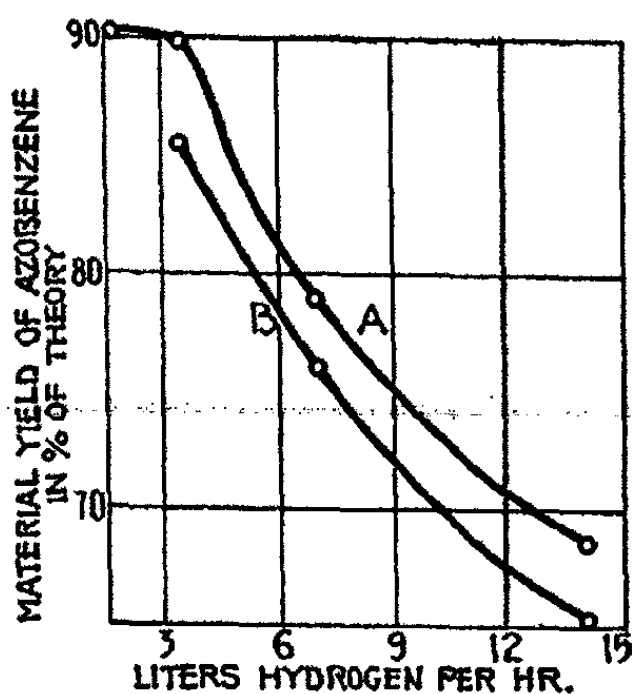


Fig. 1

used in this experiment and hence is not comparable to the others. Both curves show that each time the rate of flow of hydrogen was decreased the yield increased even to the point where the excess of hydrogen was very low. Curve B is lower than curve A. That is, the second experiment at any given rate of flow of hydrogen was lower than the first experiment. This indicates that the catalyst loses its activity with use. Then one would expect that if the first experiment had been carried out with the rate of flow of hydrogen at 1.7 liters per hour a higher total material yield than 94.5% would have been obtained.

This decrease in activity with use is probably due to the fact that thallium melts and runs together. The melting point of thallium as reported in the literature is about 301°. It was stated above that the reduction of thallic oxide by hydrogen was an exothermic reaction. With the slow rate of 1.7 liters hydrogen per hour the temperature rose from 260° to 276° when the zone of reduction reached the thermocouple. With a previous thallium catalyst in which the rate of flow of hydrogen for the reduction was 5.2 liters hydrogen per hour the temperature as indicated by the thermocouple rose from 240° to 304°. Probably with the slow rate of hydrogen each little particle when it was reduced became heated to a higher temperature than indicated by the thermocouple, probably above the melting point of thallium. Also the reduction of nitrobenzene

is an exothermic reaction. Hence when used as a catalyst probably the little particles were frequently heated above the melting point of the thallium for a short time.

This melting and running together was not encountered to such a great extent with the lead and bismuth catalysts as was pointed out in a previous paper. The lead and bismuth catalysts were frequently used  $30^{\circ}$  and even more above their melting points. Sometimes they would melt and sometimes they would not melt, probably depending on the physical condition of the oxide from which it was reduced. Of the three, thallium melts the most easily and lead the least. In this connection it is interesting to note that thallium produced practically no aniline while lead gives high yields of aniline, bismuth being intermediate. If lead adsorbs hydrogen strongly one might suppose that this adsorbed layer of hydrogen prevented the particles of lead from running together. Likewise if thallium does not adsorb hydrogen (except in small amounts) one might assume that as being sufficient reason for its melting and running together. This could be explained in an exactly similar manner if one assumed the formation of a hydride.

Our previous work with lead showed that the physical condition of the oxide from which the catalyst was made determined to a great extent whether or not it would run together. The catalyst from a coarse crystalline oxide did not run together into globules as easily as the one from a fine amorphous oxide. Thinking that this same thing might hold true in the case of thallium, some precipitated thallic oxide was treated with nitric acid and ignited, the temperature being allowed to rise to  $450^{\circ}\text{C}$ . The resulting oxide was a coarse heavy oxide, 50 grams being required to fill the trough for putting the catalyst in place while only 21 grams of the precipitated oxide were required. This catalyst after reduction was used under the same conditions as experiment 6J4-2 and gave an 89.5% yield of azobenzene and 3.5% yield of aniline. The second experiment, carried out like experiment 10J4-2,



gave an 89.9% yield of azobenzene and 6.4% yield of aniline, a result very similar to that of experiment 10J4-2. Upon examining the catalyst it was found to have melted and run together as the previous thallium catalysts.

Sabatier<sup>1</sup> states that under certain conditions platinum, when used as a catalyst in the reduction of nitrobenzene, gives some white crystals of hydrazobenzene. We have secured high yields of azobenzene with thallium, lead and bismuth as catalysts. This suggests an analogy between atomic weight and catalytic activity for when arranged in the order of their atomic weights Tl, Pb and Bi fall together, one after the other, while Pt precedes Tl by only two elements, mercury and gold. If the analogy holds these two metals should act as catalysts producing azobenzene or hydrazobenzene.

TABLE II

Rate of flow of nitrobenzene—4.4 grams per hour.  
Rate of flow of hydrogen—14 liters per hour.  
Excess of hydrogen—480%.

Experiment number	Temperature degrees C	Material yield of aniline in % of theory
7K2 <sup>2</sup>	260	85.9
8K2	260	54.8
10K2 <sup>3</sup>	279	90.9
11K2	298	93.2
18K2	317	90.3
19K2	336	98.3
20K2	355	99.7

A gold catalyst was prepared by dissolving 5 grams of gold in aqua regia, adding 4 grams of asbestos, and evaporating and drying. When this catalyst was used at 260° some solid red azobenzene appeared in the condenser but there was practically no aniline. In the attempt to get a more active cat-

<sup>1</sup> Sabatier: "La Catalyse," p. 112 (1913).

<sup>2</sup> In this experiment the rate of flow of nitrobenzene was 1.9 grams per hour.

<sup>3</sup> Previous to this experiment the catalyst was heated in hydrogen to 342° C.

alyst 6 grams of gold were dissolved in aqua regia as before and then boiled down several times with nitric acid. However this treatment did not remove all the chlorine. Four grams of asbestos were then added and the resulting mass dried at about 50°. This catalyst was put in the furnace and reduced at 260°. Some of the results with this catalyst are given in Table II.

In the first experiment (No 7K2) 0.185 gram of a white crystalline solid appeared in the condenser. It had a melting point of about 194° C. It was soluble in alcohol, water and dilute NH<sub>4</sub>OH and dilute HNO<sub>3</sub>. When dissolved in NH<sub>4</sub>OH it gave a white precipitate upon the addition of H<sub>2</sub>SO<sub>4</sub>, which was soluble upon the addition of more ammonia. However the original white solid would dissolve and give a clear solution in dilute H<sub>2</sub>SO<sub>4</sub>. When dissolved in HNO<sub>3</sub> it gave a white precipitate upon the addition of AgNO<sub>3</sub> which was soluble in NH<sub>4</sub>OH. When burned on a platinum wire it left no ash. It was probably a chlorazo or hydrazo compound.

In the second experiment only a small amount of this compound was formed. Also the aniline yield decreased a great amount indicating a decrease in activity. The first gold catalyst also decreased in activity with use, solid red azobenzene being formed in the first experiment but not in the second experiment. This indicates that gold is capable of producing small amounts of azobenzene and thus fits in the analogy, although its activity in this direction is very low.

Mercury was also tried but probably due to the fact that it is liquid at room temperature no catalytic effect was obtained. At most this analogy between atomic weight and catalytic activity is probably only one factor, for a lead catalyst can be prepared which will give 97% yields of aniline at 310° and on the other hand one can be prepared which will give 55% yields of azobenzene at 290°.

Gold is moreover capable of giving high yields of aniline, in fact almost theoretical yields, experiment 20K2 giving a 99.7% yield of aniline. However it loses its activity with use.

Thus experiment 18K2 is a little lower than 11K2 while if it had followed 11K2 it would probably have been higher.

#### Summary

1. Thallium has been shown to be an excellent catalyst for reducing nitrobenzene to azobenzene, giving very little aniline.

2. The activity of the thallium decreases very rapidly with use, probably caused by its melting and running together.

3. With thallium at 260° C and 13% excess of hydrogen a material yield of 90.2% azobenzene was obtained.

4. An analogy between atomic weight and the property of acting as a catalyst in the formation of azobenzene has been pointed out.

5. Gold has been shown to have high catalytic activity for producing aniline which decreases with use. With gold as catalyst the yield of aniline at 355° C is almost quantitative.

*Laboratory of Physical Chemistry  
Indiana University, Bloomington*

## THE RÔLE OF HYDROGEN- AND HYDROXYL-ION DIFFUSION IN NERVE AND MUSCLE ACTION

BY ELLIOT Q. ADAMS

*Resemblances of Nerve and Muscle.*—Many points of resemblance between the working of nerve and of muscle have been noted by physiologists. The same mechanical, thermal, electrical or chemical stimuli induce activity of both. While the necessary duration and intensity of stimuli are different for muscle and for nerve, such differences exist to a lesser degree also between different nerves and between different muscles. Both exhibit at the moment of activity a change in electric potential<sup>1</sup> of from 20 to 80 millivolts—the “negative variation” of duBois-Reymond. The activity of both kinds of tissue is diminished by cooling, and destroyed by heating to temperatures even lower than the coagulation point of any of the tissue proteins. These similarities have suggested to many observers the identity of fundamental basis of the activity of nerve and of muscle.

*Chemistry of Muscle, and—by Inference—of Nerve.*—The assumption of similarity in action allows the chemistry of the action of nerve to be inferred from the more patent chemistry of muscle action. All muscles contain a reserve supply of *carbohydrate*, glycogen. Most voluntary muscles, and cardiac muscle among involuntary muscles, contain a pigment similar to, or identical with, haemoglobin, permitting *oxygen* storage. When the blood supply of a muscle is cut off, a state of “rigor” develops, more rapidly if the muscle is heated or stimulated, sooner in muscles which do not contain respiratory pigment, and more slowly, or not at all, in an atmosphere of oxygen. In rigor the muscle contains *lactic acid*, and the production of this same acid may be detected immediately after normal activity. Exercise during partial asphyxia, more precisely anoxemia, leads to excretion of lactic acid. Finally

<sup>1</sup> Frequently miscalled the “action current.”

"red" muscle tissue in the presence of oxygen can in some manner dispose of lactic acid. The production of heat consequent on muscular activity consists of two nearly equal parts, one of which is developed during activity, the other—only when oxygen is present—during recovery from fatigue. These facts have been summarized in the hypothesis that in muscular activity glucose, supplied in part by the glycogen, is converted to lactic acid, which during recovery is removed in the presence of oxygen, by a reaction which converts part of the acid back to glucose and oxidizes a part to carbon dioxide and water. In the absence of sufficient oxygen the lactic acid is excreted. Since nervous tissue, like unstriated muscle, appears not to contain respiratory pigment, nerve activity is assumed to result from the enzymatic conversion of glucose (or galactose<sup>1</sup>) into lactic acid, within the fibers. In recovery the lactic acid is neutralized by the surrounding plasma into which it diffuses, while the supply of carbohydrate is similarly replaced by diffusion.<sup>2</sup>

*Purpose of Paper.*—The purpose of this paper is not to offer the foregoing as a new theory of nerve and muscle action—for muscle, at least, the hypothesis has wide acceptance—but to give the results of certain calculations, based on the theory as to the limits of variation of the "reaction"<sup>3</sup> both within and without the fiber.

*Donnan Equilibrium.*—When two solutions containing electrolytes are separated by a membrane permeable to some, but not all, of the ions present, an equilibrium will be reached

---

<sup>1</sup> Reasons will be stated later for supposing that in the *medullated* nerves galactose is the sugar metabolized.

<sup>2</sup> The erroneous statement is often made that diffusion is too slow a process to be concerned in rapid actions like that of nerve. The time required for diffusion varies inversely as the *square* of the linear dimension of the system concerned, so that in a system whose diameter is a few *micra* diffusion is 100,000,000 times as rapid as in a similar system whose diameter is a few centimeters.

<sup>3</sup> The term "reaction" is used by chemists to denote the *state* of acidity or alkalinity of a solution. Unfortunately the same word is used also for the *process* of chemical change.

as described by Donnan<sup>1</sup> with, in general, a potential difference between the solutions. This potential difference will have, at equilibrium, such a value that while each of the diffusible ions will differ in concentration on the two sides in a ratio whose logarithm is proportional to the potential and to the electrochemical valence of the ion—due account being taken of sign—the aggregate concentrations of anions and of cations in each solution will be equivalent.

The total concentration of electrolytes in mammalian blood is somewhat less than 0.2 normal, the principal cations being sodium, potassium and calcium, and the principal anions chloride and bicarbonate. The equivalent concentration of ionized colloids is a small fraction of this, while the ions of water have concentrations a million-fold smaller. (Compare Table I.)

From measurements by Loeb,<sup>2</sup> slightly extrapolated, the potential difference between 10% gelatine hydrochloride and M/6 NaCl (containing M/128 HCl) is 2 millivolts. From this it may be concluded that the concentrations of protein ions present under physiological conditions will cause potential differences of not more than a few hundredths of a unit of  $P_H$  (i. e., of 61 millivolts at 37°).

The plasma membranes are not completely impermeable to all of the five principal ions, nor to water, hence *when time is given for diffusion* osmotic equilibrium will be reached and the concentrations of some, at least, of the ions will differ on the two sides of the membrane in the ratio appropriate to the existing (Donnan) potential. Comparison of analyses of cells and plasma suggests that the membranes are impermeable to *cations* but permeable to anions.<sup>3</sup> Now the ratio of chloride

<sup>1</sup> F. G. Donnan: Zeit. Elektrochemie, 17, 572 (1911). Other references will be found in "The Origin of the Potential Differences Responsible for Anomalous Osmosis," J. Loeb: Jour. Gen. Physiol., 4, 220 (1921-22).

<sup>2</sup> J. Loeb: Jour. Gen. Physiol., 3, 678 (1920-21).

<sup>3</sup> It will be shown in another paper that a membrane at a potential of 125 millivolts positive with respect to *both* the solutions which it separates will have a permeability for cations only 0.010% of that for anions. The high relative concentration of bicarbonate in cells is due to the circumstance that carbonic acid is a product of metabolism; hence diffusion equilibrium with respect to it will not be attained.

ion concentrations is always much less than 10, hence *in any steady state* the potential will be a small fraction of that corresponding to one unit of  $P_H$ . On the other hand, the magnitude of the action potentials in nerve and in muscle shows that the diffusion of chloride and of water is not so rapid as to prevent potentials greater than 61 millivolts ( $\Delta P_H = 1$ ) existing for short periods of time.

In the calculations to follow it will be assumed that, on the one hand, anionic diffusion is adequate to prevent any appreciable (Donnan) potential in resting tissue; and that, on the other hand, the diffusion of buffers,—i.e., bicarbonate and phosphate since protein ions will not diffuse through the membrane,—is so slow that it can be neglected in comparison with that of hydrogen and hydroxyl ions.<sup>1</sup> It is furthermore assumed that the ratio of the diffusion mobilities of hydrogen ion and of hydroxyl ion is the same<sup>2</sup> as in pure water.

*Simple Case.*—For simplicity consider a fiber, unit volume of which is bounded by unit area (e. g., 1 cubic micron by 1 square micron) and containing unit concentrations of enzyme and of carbohydrate. Let  $D_H$  represent the diffusion mobility of hydrogen-ion and  $D_{OH}$  that of the hydroxyl ion, and  $K_{cat}$  the ratio of the rate of production of acid<sup>3</sup> to the existing hydrogen-ion concentration. If  $(H^+)$  and  $(OH^-)$  be the concentrations of the ions within the fiber and  $(H^+)_0$

<sup>1</sup> The plasma membranes are much more permeable to the ions of water than to other ions. This is probably to be explained as a species of convection by lipoid-soluble electrolytes, such as lecithin. The inaccuracies of these assumptions will tend to compensate one another, as the establishment of a potential will facilitate the reaching of the critical acidity within the membrane, while the diffusion of buffers will hinder it.

<sup>2</sup> The presence of a membrane will not prevent this condition from being satisfied if the membrane contributes only a small part of the diffusion resistance, or if its electrical resistance varies with "reaction" in the same manner as that of water.

<sup>3</sup> In reactions catalyzed by acid, the simplest relation and also the relation oftenest observed, is that of simple proportionality of the rate of reaction to the hydrogen-ion concentration and to the concentration of "substrate." This relation, and constancy of concentration of enzyme has been assumed. No assumption as to the relation between enzyme concentration and reaction is needed.

and  $(\text{OH}^-)_0$  their concentrations in the surrounding medium, the rate of loss of acid from the fiber by diffusion is

$$-\dot{(\text{H}^+)_{\text{diff}}} = D_{\text{H}} [(\text{H}^+) - (\text{H}^+)_0] + D_{\text{OH}} [(\text{OH}^-)_0 - (\text{OH}^-)], \quad (1)$$

the rate of production of acid by the enzyme, since the reaction is assumed autocatalytic, is

$$(\dot{\text{H}^+})_{\text{cat}} = K_{\text{cat}}(\text{H}^+), \quad (2)$$

and the total rate of change of hydrogen-ion concentrations if the diffusion of buffers can be neglected is

$$(\dot{\text{H}})_{\text{total}} = [K_{\text{cat}} - D_{\text{H}}](\text{H}^+) - \frac{[D_{\text{OH}}(\text{OH}^-)_0 - D_{\text{H}}(\text{H}^+)_0]}{D_{\text{OH}}(\text{OH}^-)} + \quad (3)$$

For constancy of "reaction"

$$(\dot{\text{H}}) = 0 = [K_{\text{cat}} - D_{\text{H}}](\text{H}^+) - \frac{[D_{\text{OH}}(\text{OH}^-)_0 - D_{\text{H}}(\text{H}^+)_0]}{D_{\text{OH}}(\text{OH}^-)} + \quad (4)$$

In dilute aqueous solutions the product of the concentrations of hydrogen and hydroxyl ion is a constant  $K_w$  which at 37° C has the value  $2 \cdot 10^{-14}$ . Multiplying (4) by  $(\text{H}^+)$ :

$$[K_{\text{cat}} - D_{\text{H}}](\text{H}^+)^2 - [D_{\text{OH}}(\text{OH}^-)_0 - D_{\text{H}}(\text{H}^+)_0](\text{H}^+) + D_{\text{OH}}K_w = 0 \quad (5)$$

In order that excitability be present it is necessary that the nerve be capable both of remaining at a "reaction" only slightly more acid than that of the surroundings and (at a higher acid concentration) of producing acid more rapidly than it diffuses away. Mathematically this means that the equation (5) must have two real (positive) roots. This in turn requires the first term to be positive and the second negative.<sup>1</sup> That is:

$$K_{\text{cat}} > D_{\text{H}} \quad (6)$$

$$D_{\text{OH}}(\text{OH}^-)_0 > D_{\text{H}}(\text{H}^+)_0 \quad (7)$$

That is, at the "reaction" of the surroundings both the rate of catalytic production of acid and that of diffusion of hydroxyl ion must exceed the rate of diffusion of hydrogen ion. Since hydrogen ion is more mobile than hydroxyl ion, this requires a distinctly alkaline "reaction."

*General Case.*—From inspection of equation (6) it can be seen that the equation involves only concentrations of hydro-

<sup>1</sup> The third term is always positive, since diffusion coefficients and concentrations cannot have negative values.



gen and hydroxyl ion, diffusion velocities and a constant expressing the rate of the catalytic reaction as compared with diffusion. Changes in the shape and size of the system will affect in equal ratio the diffusion of the two ions, hence allowance for the dimensions of the system, and similarly for the unit in which  $D_H$  and  $D_{OH}$  are expressed, can be made in the constant  $K_{cat}$ .

In the following discussion the electrolytic mobilities of the ions at 37° C, 422 for hydrogen and 245 for hydroxyl, will be used for the diffusion constants  $D_H$  and  $D_{OH}$ . The normal "reaction" of human blood at 37° C is taken as  $P_H = 7.35$ .

*Numerical Solutions.*—Equation (5) becomes:

$$[K_{cat} - 422](H^+)^2 - [245 \times 5_{-7}63 - 422 \times 0_{-7}477](H^+) + 245 \times 2_{-14}5 =$$

$$[K_{cat} - 422](H^+)^2 - 1191_{-7}(H^+) + 611_{-14} = 0$$

$$580(H^+)^2 - 1191_{-7}(H^+) + 611_{-14} = [1002 - K_{cat}](H^+)^2$$

$$(H^+)^2 - 2_{-7}054(H^+) + 1_{-14}054 = [1.728 - K'_{cat}](H^+)^2$$

Since  $K_{cat}$  is already in arbitrary units, the quantity  $K_{cat} + 580$  has been represented by  $K'_{cat}$ .

$$(H^+) - 1_{-7}027 = \pm \sqrt{1.728 - K'_{cat}} (H^+)$$

$$(H^+) = \frac{1_{-7}027}{1 \mp \sqrt{1.728 - K'_{cat}}} \quad (8)$$

Inequality (6) becomes

$$K'_{cat} > 0.728 \quad (9)$$

If the rate of catalytic production of acid does not exceed the rate of diffusion of hydrogen ion, no stimulus, however great, will initiate a propagable disturbance. Whence

$$(H^+) > \frac{1_{-7}027}{1 + 1} = 0_{-7}513 \quad (10)$$

For roots of equation (8) to remain real

$$K'_{cat} < 1.728 \quad (11)$$

When the rate of catalytic production of acid attains this value in the course of recovery from excitation, any stimulus, however

<sup>1</sup> Calculated from the following data: for hydrogen ion  $A_{18^\circ} = 315$ , logarithmic coefficient + .0154 per ° C, for hydroxyl ion  $A_{18^\circ} = 174$ , logarithmic coefficient + .0180 per ° C. (Landolt & Börnstein, Meyerhoffer, Roth: Tabellen.)

small, will be effective. This is, therefore, the threshold of spontaneous or "automatic" action.

Whence  $(H^+) \geq 1.027$  (12)

That is, the "reaction" before stimulation must be less acid than  $(H^+) = 1.027$ ; after stimulation, more acid.

Finally inequality (7) gives

$$245 \frac{2.145}{(H^+)_0} > 422(H^+)_0 \quad (13)$$

Whence  $(H^+)_0 < \sqrt{\frac{245 \times 2.145}{422}} = \sqrt{1.14451} = 1.0705$  (14)

Unless the plasma "reaction" is more alkaline than this, recovery from stimulation is impossible. These two modes of failure of nerve or muscle activity are typified by diastolic and systolic arrest of the heart, respectively.

These results are summarized in Table I.  $X_H$  is the hydrogen-ion potential relative to pure water at the same temperature (37° C).<sup>1</sup>

TABLE I

	(H <sup>+</sup> ) concentration	P <sub>H</sub> = co - log (H <sup>+</sup> )	X <sub>H</sub> (1) 6.80 - P <sub>H</sub>
Normal blood (human, at 37° C)	0.45	7.35	-0.55
Lower limit <sup>(2)</sup> resting nerve	0.51	7.29	-0.49
Upper limit <sup>(2)</sup> resting nerve	1.03	6.99	-0.19
Lower limit <sup>(2)</sup> acting nerve			
Observed limit of blood acidity <sup>(3)</sup>	1.12	6.95	-0.15
Calculated limit of blood acidity	1.20	6.92	-0.12
Pure water at 37° C	1.58	6.80	-0.00

Measurements on experimental animals and one clinical observation by G. E. Cullen give according to Van Slyke<sup>3</sup> the value 6.95 for the most acid P<sub>H</sub> compatible with life. (The animals and the patient were in deep coma when the observations were made.)

<sup>1</sup>Cf. E. T. Wherry: Jour. Wash. Acad. Sci., 9, 305 (1919); E. T. Wherry and E. Q. Adams: Ibid., 11, 197 (1921). The unit of the X<sub>H</sub> scale is the same as that of the P<sub>H</sub>, namely, a ten-fold change in hydrogen-ion concentration.

<sup>2</sup>These figures depend on the plasma reaction assumed, normal blood reaction has been used.

<sup>3</sup>D. D. Van Slyke: Jour. Biol. Chem. 48, (1) 154 (1921).

It may be objected that studies have been made by Adrian<sup>1</sup> and others of the behavior of nerve and muscle in *acid* solutions. But no claim is made by Adrian that the reaction *inside the tissue* has become acid, relative to pure water. In the case of cardiac muscle exposure for an hour to solutions of  $P_H < 6.0$  abolishes activity. The greater resistance of nerve to acidity of the solution may well be accounted for by lower permeability, better buffering, or both.

#### Summary

1. Calculations have been made based on the assumptions that nerve and muscle action depend on an autocatalytic conversion of glucose (or of galactose) to lactic acid, kept in check by diffusion, and that the significant factors in the *initiation* of a response are the autocatalytic reaction and the diffusion of hydrogen ion and hydroxyl ion.

2. In plasma whose "reaction" is that of normal blood, ( $(H^+) = 0.745$ ;  $P_H = 7.35$ ;  $X_H = -0.55$ )<sup>2</sup> the "reaction" within the excitable nerve or muscle fiber is calculated to lie between  $(H^+) = 0.751$  ( $P_H = 7.29$ ;  $X_H = -0.49$ ) and twice that concentration ( $(H^+) = 1.703$ ;  $P_H = 6.99$ ,  $X_H = -0.19$ ).

3. For effective stimulation the "reaction" must be acidified locally within the fiber to a critical value which depends on the concentration of enzyme (lactacidase) present in the fiber, and which must be more acid than the last-named figure. ( $(H^+) > 1.703$ ;  $P_H < 6.99$ ;  $X_H > -0.19$ ).

4. It is calculated that a plasma "reaction" of  $P_H = 6.92$  ( $(H^+) = 1.720$ ;  $X_H = -0.12$ ) will abolish the response of nerve or muscle.

5. This is in agreement with the observation of Van Slyke<sup>3</sup> that the most acid reaction during life (in deep *coma*) is  $P_H = 6.95$ ;  $(H^+) = 1.712$ ;  $X_H = -0.15$ ).

Nela Research Laboratories,  
Nela Park, Cleveland, O.

<sup>1</sup>"The Recovery Process of Excitable Tissues," Part I, E. D. Adrian: Jour. Physiol., 54, 1 (1920).

<sup>2</sup>See footnote 1 on page 645.

<sup>3</sup>See footnote 3 on page 645.

40-8-21

## THE ABSORPTION OF WATER BY SOIL COLLOIDS

BY W. O. ROBINSON<sup>1</sup>

Investigations on soil colloids have been conducted by the Bureau of Soils for the last two years. The method of separating the colloidal matter, called "ultra clay," from the rest of the soil has been described by Moore, Fry and Middleton,<sup>2</sup> the significance of the ultra clay has been pointed out by Whitney,<sup>3</sup> and a tentative method for estimating the total amount present in soils has been proposed in the paper first mentioned.

The separation of all the colloidal material from the rest of the soil is exceedingly difficult. The method of estimation proposed in the above paper was, therefore, based on one of the most characteristic properties of the colloidal matter—absorption. A sample of the ultra clay was extracted from the soil; the absorption of dye and ammonia by this sample and by the unextracted soil was determined; the ratio of the two specific absorptions, that of the soil and that of the ultra clay, multiplied by 100 was suggested as giving the total amount of colloidal matter present in the soil.

The degree of accuracy with which the values obtained by this method represent the amounts of colloid actually present in different soils depends, as pointed out in the paper, on the extraction of a representative sample of the ultra clay, and on the larger particles in the soil absorbing only a negligible amount compared with the absorption of the colloid. The method is also based on the assumption that the colloidal material after extraction and concentration absorbs to the same extent that it does in the unextracted soil.

Determinations of the specific water-absorption of ultra clays (grams of water absorbed per gram of material) indicate

<sup>1</sup> Published by permission of the Secretary of Agriculture.

<sup>2</sup> Jour. Ind. Eng. Chem., 13, 527 (1921).

<sup>3</sup> Science, 54, 653 (1921).

that a measurement of the amount of water absorbed by the soil may possibly show the amount of colloid present more accurately than the absorption of dye or ammonia. The specific water-absorptions of ultra clays extracted from 34 soils, differing widely in texture, origin, mode of formation and chemical composition, were fairly constant, the extreme values varying from the mean value by only 19 and 17 percent. The specific absorptions of the colloid for malachite green and ammonia, on the other hand, varied greatly, the highest values being, respectively, 6 and 4 times the lowest. Insofar as accurate values by an absorptive method are dependent upon securing a representative sample, a determination of the water-absorption seems, on account of its relative constancy, to offer advantages over determinations of dye or ammonia absorptions.

The constancy of the specific water-absorptions of the various ultra clays also indicates that the colloidal matter in soils might be closely estimated by merely determining the water-absorption of the soil and then dividing the results by the average water-absorption value of the ultra clays. While this method might give slightly less accurate results in some cases than the method first proposed, it would have a distinct advantage in not requiring an extraction of a sample of the colloid. This extraction is a time-consuming operation and involves the use of an expensive supercentrifuge.

The colloids used in this work were separated by Mr. Anderson of this Bureau by treating the soil with five times its weight of water, agitating thoroughly in a barrel churn, letting settle over night, then decanting the supernatant liquid and passing it slowly through a supercentrifuge giving a centrifugal force seventeen thousand times that of gravity. The liquid passing through contains the colloid which will remain in suspension for an indefinite period of time. The colloid was then collected by filtering off through Pasteur-Chamberland tubes. It can be seen that this process reduces the soluble salts in the colloid to a minimum.

#### **Method of Determining the Water-Absorption**

In theory the determination of the water-absorption is extremely simple, though the technique is somewhat difficult and for concordant results the manipulation must be carefully done. The earlier method as proposed by Hilgard was indeterminate because pure water was the liquid used in the absorption chamber. A moment's reflection will show that the vapor pressure of pure water will always be higher than the water condensed on the soil which will have in solution salts dissolved from the soil. Theoretically the distillation from the pure water to the soil would then go on forever or until the pure water was exhausted.

Mitscherlich<sup>1</sup> introduced an important modification by allowing the absorption of water vapor to take place over a 10% solution of sulphuric acid. Under these conditions the water absorption is a determinate quantity and practical equilibrium is established in a vacuum desiccator in a few days.

A modification of the Mitscherlich method was used in this work. In order to get as high a vapor pressure of water as possible 2% sulphuric acid was substituted for the higher concentration Mitscherlich used.

For the determination about 2 grams of the air-dry colloid which had been passed through a 100-mesh sieve was weighed out in a shallow weighing dish of 50 mm. diameter, provided with a well-fitting, ground-glass stopper. The uncovered dish, with the colloid spread evenly over the bottom, was placed in a vacuum desiccator containing a large amount of 2% sulphuric acid. The desiccator was then covered and evacuated to 50 mm. or less mercury, put in a thermostat at 30° C and kept there for 5 days. The desiccator and contents were then taken from the thermostat, dry air slowly let in, the cover of the desiccator removed, the dishes quickly covered, put into an empty desiccator and weighed as soon as cooled to room temperature. After weighing, the uncovered dishes were put in a drying oven and kept there for 18 hours at 110°

<sup>1</sup> E. A. Mitscherlich: "Bodenkunde," p. 56, Paul Parey, Berlin (1905).

C. The dish was then immediately covered, cooled and weighed. It is very important to cover the dish in the desiccator containing the saturated atmosphere preliminary to the first weighing and to cover the dish, after drying, in the oven as soon as possible. Two grams of soil colloids saturated over 2% sulphuric acid will lose 10 mg. when exposed to, say, 25% saturated air, for less than one minute. The taking up of moisture from the laboratory air after drying is likewise rapid. The difference between the weight of the material when saturated and when dried at 110° gives the water absorbed.

The degree of subdivision of the ultra clay when absorption of water vapor takes place appears to have little effect on the result. For instance, the colloid when granulated absorbed the same amount of water as it did when finely powdered.

It will be noted that the soil was in the air-dry condition before the absorption was allowed to take place. Some other workers have dried their soils at 100° over phosphoric pentoxid prior to absorption of water vapor in order to have all soils in a uniform condition. It has been pointed out that such procedure might alter the absorption of some colloids, and it therefore seemed better to start with a substance that had not been heated or thoroughly dried out.

All determinations given in this paper were made in duplicate. Abnormal results were confirmed by repetition. With carefully controlled conditions duplicates were considered satisfactory when they did not vary more than 2%, though in general closer results were obtained. The results are given in Table I.

#### **Water-Absorption as an Indication of the Colloidal Content of Soils**

It is a striking fact that the ultra clays, regardless of their source, possess nearly the same capacity to absorb water. The extreme specific absorptions are .240 and .348; the average value is .298; and the mean deviation from the average value

TABLE I  
Specific Water-Absorptions of Ultra Clays

Soils from which colloid was extracted	Gram water vapor absorbed per gm. colloid	Variations from mean
Carrington loam soil	.320	+.022
Carrington loam subsoil	.337	+.039
Cecil clay loam soil	.336	+.038
Cecil clay loam subsoil	.287	-.011
Chester loam soil	.240	-.058
Chester loam subsoil	.273	-.025
Clarksville silt loam soil	.239	+.041
Clarksville silt loam subsoil	.315	+.017
Clyde loam soil	.309	+.011
Hagerstown loam soil	.253	-.045
Hagerstown loam subsoil	.258	-.040
Huntington loam soil	.274	-.024
Houston black clay soil	.348	+.050
Huntington loam subsoil	.298	.000
Manor loam soil	.293	-.005
Manor loam subsoil	.340	+.042
Marshall silt loam soil	.294	-.004
Marshall silt loam subsoil	.300	+.002
Miami silty clay loam soil	.302	+.004
Miami silty clay loam subsoil	.308	+.010
Norfolk fine sandy loam soil	.243	-.055
Norfolk fine sandy loam subsoil	.276	-.022
Ontario loam surface soil	.241	-.057
Ontario loam subsoil	.320	+.022
Orangeburg fine sandy loam soil	.263	-.035
Orangeburg fine sandy loam subsoil	.305	+.007
Sassafras silt loam soil	.266	-.032
Sassafras silt loam subsoil	.310	+.012
Sharkey clay soil	.308	+.010
Stockton clay adobe soil	.341	+.043
Stockton clay adobe subsoil	.337	+.039
Wabash silt loam soil	.333	+.035
Wabash silt loam subsoil	.309	+.011
Susquehanna clay subsoil	.261	-.037
Mean	.298	.027

is .027, or 9 percent of the average. Ultra clays differing most from the mean are somewhat unusual in composition. The Ontario loam surface soil colloid, for instance, contains two to four times as much organic matter as the other colloids, while



the Stockton clay adobe and the Houston black clay soils are rather unusual soils, noted for their colloidal properties when wet.

Chemical analyses indicate that the ultra clays consist chiefly of a hydrated silicate of aluminum, with varying amounts of one or more of the following substances: ferric hydroxide, silicic acid, organic matter and possibly aluminum hydroxide. It is, therefore, significant that dried samples of silicic acid, aluminum hydroxide, and ferric hydroxide gels<sup>1</sup> had specific absorptions of .202, .351, and .256, respectively—values close to those yielded by the ultra clays.

If the colloidal matter in a soil were estimated by dividing the absorption of the soil by the average absorption of the ultra clays, the result should approximate the results obtained through dividing the soil by the specific absorption of the ultra clay actually present. Where the latter, longer method might show 30 percent of colloid, use of the average factor might show 24 percent to 35 percent in extreme cases, but in general the results should fall within 27 percent and 33 percent. As already pointed out, the absorption of non-colloidal particles in the soil would affect the accuracy of absorption methods for determining the colloidal matter. Work which is being prepared for publication, on the absorption of water vapor by ground soil minerals, indicates that the coarser mineral particles absorb so little water that the error due to this cause does not materially affect determinations in most soils.

Work on the accuracy with which the amount of colloidal matter in soils may be measured by absorption methods and the assumptions involved in such methods is still in progress in the Bureau, hence this water-absorption method is proposed only tentatively at this time.

It has been recognized by soil scientists for many years that the hygroscopic value of the soil is a valuable indication of the nature of the soil, but it has not been generally appre-

---

<sup>1</sup> The silicic acid gel was kindly furnished by the Davison Chem. Co., and the aluminum and iron gels were provided by the Chemical Warfare Service.

ciated that from the hygroscopic determination a fairly close estimation of the amount of colloid present in the soil may be calculated.

#### **Conclusions**

Samples of the colloidal matter extracted from 34 soils which differed widely in texture, origin, mode of formation and chemical composition showed a relatively constant absorption of water. The extreme absorptions were .240 gm. and .348 gm. of water per gram of colloid, and the mean value was .298. It is suggested that the colloidal matter in a soil might be fairly closely estimated by determining under certain conditions the water-absorption of the soil and dividing the result by the average factor .298.

*Bureau of Soils  
U. S. Department of Agriculture  
Washington, D. C.*

## HYDROUS OXIDES. IV

BY HARRY B. WEISER

### Hydrous Stannic Oxide

As early as 1812 Berzelius<sup>1</sup> called attention to the fact that the properties of the hydrous oxide formed by precipitation of stannic chloride with alkali were quite different from the product resulting from the action of nitric acid on tin. Berzelius thought at first that he was dealing with two degrees of oxidation but subsequent investigations by Davy, Gay-Lussac and Berzelius<sup>2</sup> himself showed that this was not the case. Thus, Berzelius was led to conclude that the two preparations having widely different properties were simply modifications of the same oxide. In this way the term isomer or isomeric modification was introduced in chemistry.<sup>3</sup>

### Precipitated Hydrous Stannic Oxide

Since the oxides formed by precipitation of stannic salts and by the action of nitric acid on tin both give a slight acid reaction when shaken with water they are commonly designated as orthostannic and metastannic acids, respectively. The earlier chemists regarded them as distinct chemical individuals and recognized the similarities and differences between the two that are listed in Table I.

In the light of what we now know of the colloidal state of matter, the statements of earlier chemists concerning the properties of orthostannic and metastannic acids are for the most part inaccurate. Accordingly we shall consider the properties of these two so-called isomers more fully in the subsequent paragraphs. Since both substances are hydrous oxides and not acids, I shall designate them as alpha oxide and beta oxide, respectively, instead of as orthostannic acid and metastannic acid.

<sup>1</sup> Lehrbuch, 5th Edition, 2, 596 (1812).

<sup>2</sup> Liebig's Ann., [2] 5, 149 (1817).

<sup>3</sup> Abegg: Handbuch der anorganischen Chemie, [2] 3, 593 (1909).

TABLE I

	Orthostannic acid	Metastannic acid
Preparation	Precipitation from solution of stannic salt	Action of concentrated HNO <sub>3</sub> on tin
Formula	H <sub>2</sub> SnO <sub>3</sub>	H <sub>2</sub> SnO <sub>3</sub>
Action of HNO <sub>3</sub>	Easily soluble	Insoluble
Action of HCl	Easily soluble; not precipitated by excess acid	Insoluble. Product treated with concentrated acid and filtered dissolves in water but precipitates again with excess acid
Action of H <sub>2</sub> SO <sub>4</sub>	Easily soluble	Insoluble but swells in concentrated acid forming a mass that is soluble in water
Action of caustic alkalis	Easily soluble; not precipitated by excess alkali	Soluble when freshly prepared; precipitated by excess alkali
Action of SnCl <sub>2</sub>	No action	Yellow precipitate from solution in HCl

*Formation.*—The alpha oxide is prepared by precipitation of SnCl<sub>4</sub> or SnBr<sub>4</sub> with alkali<sup>1</sup> or with an excess of the carbonate of barium or calcium;<sup>2</sup> and by precipitating a solution of a soluble crystalline stannate having the formula M<sub>2</sub>Sn(OH)<sub>6</sub><sup>3</sup> with a mineral acid.<sup>4</sup> Rose<sup>5</sup> claims to get the alpha oxide by hydrolysis of a dilute solution of SnCl<sub>4</sub> at the boiling point. This is unquestionably incorrect since it has been observed repeatedly that the alpha oxide formed by hydrolysis of SnCl<sub>4</sub> at low temperatures goes over to beta oxide gradually on standing or very rapidly at the boiling point.<sup>6</sup> Similar

<sup>1</sup> Berzelius: *Loc. cit.*

<sup>2</sup> Schiff: *Liebig's Ann.*, 47, 120 (1861).

<sup>3</sup> Belucci and Paravano: *Zeit. anorg. Chem.*, 45, 142 (1902).

<sup>4</sup> Frey: *Ann. Chim. Phys.*, [3] 12, 463 (1844); 23, 385 (1848); Kuhl: *Pharm. Zeit.*, 53, 49 (1908).

<sup>5</sup> Pogg. *Ann.*, 75, 1 (1848).

<sup>6</sup> Barfoed: *Jour. prakt. Chem.*, 101, 368 (1867); Engel: *Comptes rendus*, 124, 765 (1897); 125, 464, 651, 709 (1897); Zsigmondy: *Liebig's Ann.*, 301, 368 (1898).

observations have been made with  $\text{SnBr}_4$ <sup>1</sup> and with  $\text{Sn}(\text{NO}_3)_4$ . Lorenz<sup>2</sup> obtained the alpha oxide by electrolyzing an alkali chloride, nitrate or sulphate solution using a platinum cathode and a tin anode.

The typical beta oxide is prepared by the oxidation of tin with moderately concentrated  $\text{HNO}_3$ . Weber<sup>3</sup> claimed that acid of 1.2 sp. gr. gave both the alpha and beta oxides while acid of 1.35 sp. gr. produced a clear solution from which beta oxide was obtained by warming. Hay<sup>4</sup> and Scott<sup>5</sup> likewise observed that tin dissolved completely in moderately dilute nitric acid (1 : 1) at 2° and from this solution beta oxide precipitated by warming or by standing at ordinary temperatures. The solution contained stannous nitrate, stannic nitrate<sup>6</sup> and doubtless colloidal stannic oxide<sup>7</sup> in varying amounts depending on the concentration of acid and the temperature. As before noted, beta oxide is produced whenever a dilute solution of a crystalline tin salt undergoes hydrolysis at the boiling temperature. A solution of amorphous sodium metastannate so-called, likewise precipitates beta oxide when heated.

From this survey of the methods of preparing the two hydrous oxides it is evident that either may be prepared by hydrolysis of stannic salts under suitable conditions. It is probable that alpha oxide is always the first product of this hydrolysis and that this is transformed to the beta oxide quite slowly at ordinary temperatures but with increasing rapidity as the temperature is raised.

*Composition.*—The oxide precipitated from a stannic solution in the cold has been assigned many formulas by different investigators. Thus Fremy<sup>8</sup> claims to get the hydrate  $3\text{SnO}_2 \cdot 7\text{H}_2\text{O}$  when the oxide is dried in a stream of air;  $3\text{SnO}_2 \cdot 2\text{H}_2\text{O}$

<sup>1</sup> Lorenz: *Zeit. anorg. Chem.*, 9, 371 (1896).

<sup>2</sup> *Ibid.*, 12, 436 (1896).

<sup>3</sup> *Pogg. Ann.*, 122, 358 (1864).

<sup>4</sup> *Chem. News*, 22, 298 (1870).

<sup>5</sup> *Ibid.*, 22, 322 (1870).

<sup>6</sup> Walker: *Jour. Chem. Soc.*, 63, 845 (1893).

<sup>7</sup> Mecklenburg: *Zeit. anorg. Chem.*, 64, 370 (1909).

<sup>8</sup> *Ann. Chim. Phys.*, [3] 12, 463 (1844); 23, 393 (1848).

when dried at 140°; and  $\text{SnO}_2 \cdot \text{H}_2\text{O}$  when dried in vacuum. Weber<sup>1</sup> claims to get  $\text{SnO}_2 \cdot 2\text{H}_2\text{O}$  by drying the product in the air at ordinary temperatures; and Graham<sup>2</sup> and Schaffner<sup>3</sup> find the oxide dried at 140°–160° approximates the composition  $\text{SnO}_2 \cdot \text{H}_2\text{O}$ . From similar dehydration experiments Carnelley and Walker<sup>4</sup> conclude that there are probably a large number of hydrates of the oxide that have a rather limited range of stability.

The oxide obtained by the action of nitric acid on tin has likewise been assigned numerous formulas corresponding to definite hydrates, the composition depending on the method of drying.<sup>5</sup> According to Engel<sup>6</sup> the alpha and beta acids have the respective formulas,  $\text{H}_2\text{SnO}_3 \cdot \text{H}_2\text{O}$  and  $\text{H}_2\text{Sn}_5\text{O}_{11} \cdot 9\text{H}_2\text{O}$  when dried in the air and  $\text{H}_2\text{SnO}_3$  and  $\text{H}_2\text{Sn}_5\text{O}_{11} \cdot 4\text{H}_2\text{O}$  when dried in vacuum. He also recognizes a parastannic acid  $\text{H}_2\text{Sn}_5\text{O}_{11} \cdot 7\text{H}_2\text{O}$  when dried in air and  $\text{H}_2\text{Sn}_5\text{O}_{11} \cdot 2\text{H}_2\text{O}$  when dried in vacuum. Musculus<sup>7</sup> concludes that metastannic acid is a hydrated oxide,  $5\text{SnO}_2 \cdot \text{H}_2\text{O}$ , formed by condensation of stannic acid,  $\text{SnO}_2 \cdot \text{H}_2\text{O}$ ; and that between these extremes are a number of intermediate oxides of rather instable nature. Vignon<sup>8</sup> has determined the heat evolved when hydrous stannic oxides prepared in different ways are treated with potassium hydroxide. He found that this varied from 32.7 Cal. for an alpha oxide in the presence of HCl or KCl to 0.2 Cal. for an ignited beta oxide. From these results Vignon concludes with Musculus that successive polymerization of  $\text{H}_2\text{SnO}_3$  results in the formation of a series of acids which he represents as follows:  $\text{H}_2\text{SnO}_3$ ,  $\text{H}_2\text{Sn}_2\text{O}_5 \cdot \text{H}_2\text{O}$ ,  $\text{H}_2\text{Sn}_n\text{O}_{2n} + 1 \cdot (n-1) \text{H}_2\text{O}$ .

An extended investigation of the dehydration of hydrous

<sup>1</sup> Pogg. Ann., 122, 358 (1864).

<sup>2</sup> Liebig's Ann., 13, 146 (1835).

<sup>3</sup> Ibid., 51, 168 (1844).

<sup>4</sup> Jour. Chem. Soc., 53, 89 (1888).

<sup>5</sup> Fremy: Loc. cit.; Thomson: Ann. Phil., 10, 149 (1817); Weber: Loc. cit.; Tschermak: Pogg Ann., 44, 733 (1862).

<sup>6</sup> Comptes rendus, 124, 765 (1897); 125, 464, 651, 709 (1897).

<sup>7</sup> Ann. Chim. Phys., [4] 13, 95 (1868); Comptes rendus, 65, 961 (1867).

<sup>8</sup> Comptes rendus, 108, 1049 (1889); 109, 372 (1889).

stannic oxides prepared in different ways has been made by van Bemmelen.<sup>1</sup> He demonstrated conclusively that there is no evidence of a single definite hydrate of stannic oxide. A composition corresponding to a definite hydrate was shown to be purely accidental depending as it does on the method of preparation, the method of drying, the temperature and the age of the sample. It follows, therefore, that the alpha and beta oxides are not definite hydrates,  $\text{SnO}_2 \cdot \text{H}_2\text{O}$  and  $5\text{SnO}_2 \cdot \text{H}_2\text{O}$ , respectively, but are hydrous oxides, the composition of which can vary continuously through wide limits. As a result of these important observations van Bemmelen concludes that the alpha and beta oxides are not different allotropic modifications and attributes the divergent properties to difference in structure. In support of his view he points out that there is no definite inversion point at which the alpha oxide is changed to the beta oxide but that this transformation goes on slowly but continuously at low temperature even under water. Lorenz<sup>2</sup> confirmed van Bemmelen's observation that the two oxides could exist in every conceivable degree of hydration and hence that the difference between the two products could not be a question of the amount of water each contains. Following up van Bemmelen's suggestion that the two oxides are not isomers in the usual sense of the word but are colloidal modifications of hydrous stannic oxide, Mecklenburg<sup>3</sup> arrives at the conclusion that "the alpha and beta stannic acids are hydrous oxides that are but little, if at all, soluble in water and differ from each other in the size of the particles." The evidence in support of this view is quite conclusive as will be pointed out in the subsequent paragraphs.

*Action of Hydrochloric Acid.*—The freshly prepared alpha oxide is readily soluble in dilute HCl and is not precipitated by an excess of the acid even at the boiling point; whereas the beta oxide is insoluble in both the dilute and concentrated acid.

<sup>1</sup> Die Absorption, 59, 66 (1910).

<sup>2</sup> Zeit. anorg. Chem., 9, 369 (1895).

<sup>3</sup> Ibid., 64, 368 (1909); 74, 207 (1912).

If beta oxide is treated with concentrated HCl, a gelatinous mass is formed which Engel<sup>1</sup> considers to be a hydrochloride of metastannic acid, metastanyl chloride. This product is taken up by water but is reprecipitated by boiling or by adding concentrated HCl. The difference in behavior of the solution of alpha oxide in HCl and of the beta oxide (treated with HCl) in water, has resulted in their being called alpha chloride and beta chloride, respectively. A number of suggestions have been offered to account for the difference in properties. Thus Fremy and Musculus consider beta chloride to be a polymer of alpha chloride. Rose<sup>2</sup> suggests that the so-called beta chloride is not a compound at all, the solution in HCl being simply a solution of metastannic acid without any combination taking place between the two substances. Wittstein<sup>3</sup> suggests that the alpha chloride corresponds to an amorphous oxide and the beta chloride to a crystalline. Investigators from time to time have claimed to prepare definite basic chlorides by the action of HCl on the alpha and beta oxides. Thus Weber<sup>4</sup> prepared a substance to which he assigned the formula  $\text{Sn}_4\text{O}_6\text{Cl}_4 \cdot 5\text{H}_2\text{O}$  by the action of acid on beta oxide and Engel claims to get  $\text{SnCl}_4$ ,  $\text{Sn}_5\text{O}_9\text{Cl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Sn}_5\text{O}_9\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  corresponding to his ortho, meta and para acids above referred to.<sup>5</sup> While it has been demonstrated that the action of concentrated HCl on the alpha oxide yields  $\text{SnCl}_4$ <sup>6</sup> and that  $\text{H}_2\text{SnCl}_6$ <sup>7</sup> is formed by passing gaseous HCl into a solution of stannic chloride, there is little or no evidence to support the view that the amorphous precipitates obtained from solutions of alpha and beta oxide under varying conditions, are definite compounds. Van Bemmelen<sup>8</sup> was the first to recognize the

<sup>1</sup> Loc. cit.

<sup>2</sup> Pogg. Ann., 75, 1 (1848).

<sup>3</sup> Jahresberichte, 1850, 321.

<sup>4</sup> Weber: Pogg. Ann., 122, 358 (1864).

<sup>5</sup> Cf. Tschermak: Jour. prakt. Chem., 86, 334 (1862); Mallet: Jour. Chem. Soc., 35, 524 (1879); Schürer-Kestner: Ann. Chim. Phys., [3] 58, 471 (1860); Ordway: Am. Jour. Sci., [2] 23, 22 (1857).

<sup>6</sup> Barfoed: Jour. prakt. Chem., 101, 388 (1867).

<sup>7</sup> Engel: Loc. cit.

<sup>8</sup> Die Absorption, 56, 393 (1910); Zeit anorg. Chem., 23, 111 (1900).



real nature of the solutions of alpha and beta oxides in HCl. He pointed out that it is incorrect to speak of solubility of the oxides in acid and in support of this view he showed that the acid which holds the alpha oxide in what was thought to be a true solution, may be neutralized almost entirely without the oxide precipitating; that the salt formed may be removed by dialysis without precipitation taking place; and finally, that the solution may be boiled, converting alpha oxide into beta, which likewise does not precipitate unless the boiling is continued too long.<sup>1</sup> Van Bemmelen showed further that HCl is adsorbed by both oxides. Below the concentration which causes peptization, he found that the adsorption isotherms have the usual form, indicating that the amount adsorbed depends on the concentration of acid in contact with the oxide. The adsorption was found to be less with beta oxide than with alpha and the older and denser the beta oxide the less was the adsorption.

The action of hydrochloric acid on the different oxides can now be explained. The newly formed oxide possesses a softer and looser structure than the beta oxide and so the former is readily peptized by dilute acid and the colloid is stable even in the presence of a very small amount of acid. A high concentration of acid converts it into a true solution of  $\text{SnCl}_4$ . The coarser, denser particles of beta oxide are insoluble and are not peptized by dilute HCl. Concentrated acid on the other hand, peptizes the oxide and if the excess of acid is poured off, the particles will go into solution in water (dilute hydrochloric acid) from which they are precipitated by excess acid or by boiling. Since alpha oxide changes to beta even at ordinary temperatures and in contact with water, we should expect the colloidal solution of alpha oxide formed by hydrolysis of a dilute solution of  $\text{SnCl}_4$  gradually to assume the properties of the dilute hydrochloric acid solution of beta oxide as observed by Fremy, Rose, Löwenthal<sup>2</sup> Engel and others.<sup>3</sup>

<sup>1</sup> Graham: *Liebig's Ann.*, 121, 1 (1861).

<sup>2</sup> *Jour. prakt. Chem.*, 77, 321 (1859).

<sup>3</sup> Barfoed: *Loc. cit.*; Allen: *Jour. Chem. Soc.*, 25, 274 (1872); Lorenz: *Zeit. anorg. Chem.*, 9, 369 (1895).

In the light of the experiments of van Bemmelen, it is unlikely that the amorphous masses obtained by Engel and others are definite chlorides. Further doubt is thrown on this by Biron<sup>1</sup> who has repeated and extended the experiments of Engel. Biron obtained products similar to those of Engel but found that the composition was indefinite. He concludes that the transformation of alpha oxide results in the formation of an uninterrupted series of beta oxides that differ from each other in their degree of condensation which is greater the higher the temperature.<sup>2</sup> The action of hydrochloric acid on these various beta oxides yields so-called oxychlorides which have an indefinite composition and contain a larger or smaller proportion of chloride according as the condensation of the beta oxide is large or small. These oxychlorides, showing wide differences in composition, exhibit differences in properties that are similar qualitatively to Engel's meta and parachlorides.

*Action of Sulphuric Acid.*—The action of sulphuric acid on the alpha and beta oxide is very similar to that of hydrochloric acid. The alpha oxide is peptized by very dilute acid forming a colloidal solution while concentrated acid forms a true solution from which may be obtained crystals of  $\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ .<sup>3</sup> The beta oxide is not peptized at all by dilute sulphuric acid while concentrated acid causes peptization in the cold, the product swelling to a gelatinous mass that goes into colloidal solution in water. This colloid is readily precipitated by excess acid. Hot concentrated sulphuric acid dissolves beta oxide and from this solution crystals of  $\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  are obtained.<sup>4</sup> Van Bemmelen<sup>5</sup> studied the adsorption of sulphuric acid by a number of oxides and found that the adsorption was less the older and denser the sample, confirming his observations with HCl.

<sup>1</sup> Jour. russ. phys. chem. Ges., 36, 933 (1904).

<sup>2</sup> Cf. Mecklenburg: Zeit. anorg. Chem. 74, 207 (1912).

<sup>3</sup> Ditte: Comptes rendus, 104, 172 (1887); Kraskowitz: Pogg. Ann., 35, 518 (1835).

<sup>4</sup> Allen: Jour. Chem. Soc., 25, 274 (1872); Ditte: Loc. cit.

<sup>5</sup> Die Absorption, 106, 424 (1910); Zeit. anorg. Chem., 23, 321 (1900).

*Action of Nitric Acid.*—Dilute nitric acid peptizes alpha oxide quite readily when the latter is freshly prepared; but the beta oxide is neither dissolved nor peptized by even the most concentrated acid. Jörgensen<sup>1</sup> has found, however, that beta oxide adsorbs this acid to a certain degree and that it can be removed only by prolonged washing.

*Action of Alkalis.*—Dilute caustic alkalis carry both the alpha and beta oxides into solution. Earlier workers were of the opinion that solution took place by virtue of the formation of definite alkali stannates and metastannates. This arose from the observation that if the alkali solution of the alpha oxide is evaporated, definite crystals having the formula  $M_2SnO_3 \cdot 3H_2O$ <sup>2</sup> or  $M_2Sn(OH)_6$ <sup>3</sup> are obtained.<sup>4</sup> However, if the solution of the alpha oxide in alkali is not evaporated but treated with alcohol, a precipitate is formed varying in composition from 5 to 17 moles of  $SnO_2$  to 1 mole of  $K_2O$ , depending altogether on the relative amounts of the two substances in solution. In like manner, the precipitate obtained from a solution of beta oxide in alkali was found to vary widely, depending as it does on the conditions of formation. Thus the precipitate formed by adding excess KOH to a solution of beta oxide in alkali was found by Fremy<sup>5</sup> to have the composition  $4.84 SnO_2 \cdot Na_2O \cdot 8H_2O$ . Similarly, Rose<sup>6</sup> got a precipitate containing 7  $SnO_2$  to 1  $K_2O$  and Weber<sup>7</sup> 6.7  $SnO_2$  to 1  $K_2O$ . Fremy considers metastannates to have the general formula  $M_2O \cdot 5SnO_2 \cdot 4H_2O$ <sup>8</sup> which he writes  $M_2H_8Sn_5O_{15}$  since the product is decomposed by removing water;<sup>9</sup> but Engel<sup>10</sup> writes it  $M_2Sn_5O_{11}$ .

<sup>1</sup> Zeit. anorg. Chem., 57, 353 (1908).

<sup>2</sup> Ordway: Am. Jour. Sci., [2] 40, 173 (1865); Fremy: Loc. cit.; Marignac: Ann. Mines, [3] 15, 277 (1859); Moberg: Jour. prakt. Chem., 28, 230 (1843).

<sup>3</sup> Belucci and Paravano: Loc. cit.

<sup>4</sup> Other hydrates are also known: Haefely: Dingl. poly. Jour., 144, 66 (1867); Jonas: Centralblatt, 1865, 607.

<sup>5</sup> Ann. Chim. Phys., [3] 12, 462 (1844); 23, 393 (1898).

<sup>6</sup> Pogg. Ann., 75, 1 (1848); 105, 564 (1858).

<sup>7</sup> Ibid., 122, 358 (1864).

<sup>8</sup> Cf. Musculus: Comptes rendus, 65, 961 (1867).

<sup>9</sup> Moberg: Berzelius' Jahresberichte, 22, 144 (1843).

<sup>10</sup> Loc. cit.

$4\text{H}_2\text{O}$ . The latter also recognizes parastannates of the formula  $\text{M}_2\text{Sn}_5\text{O}_{11}\cdot 3\text{H}_2\text{O}$ .

Van Bemmelen<sup>1</sup> has investigated the action of dilute alkalis on both alpha and beta oxides and has found that colloidal solutions result. He first agitated the same amounts of beta oxide with the same volumes of cold dilute KOH of various concentrations and from the amount of oxide taken up and the stability of the resulting solutions, he showed that no definite compounds were formed. When the concentration of alkali was less than 8.8 moles of  $\text{K}_2\text{O}$  to 100 of  $\text{SnO}_2$ , the peptized oxide precipitated spontaneously, carrying down with it a greater part of the alkali. As is usual the amount of KOH adsorbed by a given amount of oxide varied with the temperature and concentration and there was no indication of the formation of definite stannates. He thus accounted for the wide variation in the composition of the precipitate thrown out by alcohol from the colloidal solution of the alpha oxide in alkali, as observed by Ordway and others.

Van Bemmelen obtained similar results with the beta oxide. The first action of dilute NaOH was to produce an opalescent solution that, in itself, showed the oxide to be in the colloidal state. The relative amounts of oxide and alkali in the solution were varied widely and as in the case of the alpha oxide, spontaneous precipitation took place, the more rapidly the greater the relative amount of  $\text{SnO}_2$ . These colloids were coagulated by excess alkali which was not the case with colloidal alpha oxide. The precipitated oxides obtained in any case adsorbed alkali in widely varying amounts depending on the alkali concentration. In the light of these observations it seems altogether probable that the amorphous masses obtained by the action of alkalis on beta oxide were not definite alkali metastannates as Musculus, Weber, Fremy and others supposed but were hydrous oxides that had adsorbed definite amounts of alkali under the specific conditions of formation employed by the different investigators.

<sup>1</sup> Die Absorption, 57 (1910).

*Mordanting Action.*—It is well known that tin salts, particularly  $\text{SnCl}_4$ , are used as mordants in dyeing cotton, wool and silk with certain dyes. The salt is adsorbed by the dye fiber and subsequently hydrolyzes forming hydrous stannic oxide which forms lakes with certain dyes that are distinguished by their brilliancy.<sup>1</sup> Vignon<sup>2</sup> studied the action of both alpha and beta oxide on a basic dye, phenosafranine; and found that with the former a brilliant red lake was formed while with the latter no dye was taken up. The dye is thus readily adsorbed by the loose, finely divided particles of alpha oxide while the larger, denser particles of beta oxide have comparatively little adsorbing power. This behavior is general and has led to the statement: "The formation of metastannic acid during the preparation of tin mordants is called firing; it must be avoided since this substance has no mordanting power and its generation involves loss of tin."<sup>3</sup>

*Action of Phosphoric Acid.*—A standard analytical procedure for separating phosphoric acid from mixtures, consists in adding tin foil to the nitric acid solution, the resulting beta oxide carrying down the phosphoric acid.<sup>4</sup> A definite stannic pyrophosphate<sup>5</sup> is not formed but a mixture of variable composition.<sup>6</sup> For the complete precipitation of one mole of phosphoric acid 6 to 7 atoms of tin must be present according to Classen;<sup>7</sup> 7 according to Antony and Mondolfo;<sup>8</sup> and about 13 according to Wöbling.<sup>9</sup> Mecklenburg<sup>10</sup> showed conclusively that the removal of phosphoric acid by precipitated stannic oxide was due to adsorption. He found that the amount of

<sup>1</sup> Herzfeld: *Das Färben und Bleichen der Textilfasern*, 1, 73 (1904).

<sup>2</sup> *Comptes rendus*, 112, 580 (1891).

<sup>3</sup> Knecht, Rawson and Loewenthal: *A Manual of Dyeing*, 1, 272 (1916).

<sup>4</sup> Reyonoso: *Jour. prakt. Chem.*, 54, 261 (1851).

<sup>5</sup> Roscoe and Schorlemmer: *Treatise on Chemistry*, 2, 848 (1907).

<sup>6</sup> Reyonoso: *Loc. cit.*; Reisig: *Liebig's Ann.*, 98, 339 (1856); Girard: *Comptes rendus*, 54, 468 (1862).

<sup>7</sup> *Ausgew. Methoden analyt. Chem.*, 2, 555 (1903).

<sup>8</sup> *Gazz. chim. ital.*, [2] 38, 145 (1898).

<sup>9</sup> *Lehrbuch anal. Chem.*, 1911, 405.

<sup>10</sup> *Zeit. anorg. Chem.*, 74, 215 (1912).

phosphoric acid carried down depended not only on its concentration but on the nature of the oxide. The adsorption isotherms for five oxides prepared at different temperatures showed that the lower the temperature of formation of the hydrous oxide, the greater its adsorption capacity.

From the above survey it is clear that the so-called alpha and beta oxides differ essentially in their solubility, adsorbability and ease of peptization. The typical alpha oxide is quite soluble in concentrated acids, and alkalis forming definite salts under suitable conditions; it possesses a marked capacity for adsorption; and is readily peptized. The typical beta oxide, however, is very difficultly soluble; has a comparatively slight capacity for adsorption; and is not peptized by dilute acids or alkalis. If these two oxides are definite isomers, then any product having properties intermediate between the two might be looked upon as a mixture of these two. However, if the difference in the properties of the two is due to variation in the size of the particles and the compactness of the hydrous mass, then any product with intermediate properties must be a chemical individual and not a mixture. Moreover, if this last assumption is correct, any number of stannic oxides are possible, each differing from the others in the size of the particles, the compactness of the mass and the amount of adsorbed water.

Mecklenburg<sup>1</sup> is of the opinion that a series of definite hydrous stannic oxides are possible and has prepared five distinct ones by hydrolysis of stannic sulphate at 0°, 25°, 50°, 75° and 100°. These oxides were dried in the air and ground to a powder. Each product was different from the others and with few exceptions, the properties approached more nearly to those usually attributed to beta oxide, the higher the temperature of formation. It was observed that there was no apparent connection between the compactness of the dried powder and the temperature of preparation. Thus, the 100° oxide was much the loosest powder, the others coming in the

<sup>1</sup> Zeit. anorg. Chem., 74, 207 (1912).

order: 75°, 0°, 50° and 25°. It was further noted that there was no apparent connection between the adsorbing power of an oxide and its ease of peptization, since the 0° and 100° oxides were peptized by concentrated HCl with equal facility although the adsorbability of the former was much greater than that of the latter. Moreover, the 50° oxide whose adsorbability lay between the other two, was peptized with greatest difficulty. This and other abnormal variations in the properties of the 50° oxide were doubtless due to the fact that it was subjected to a somewhat different treatment than the other oxides during the drying. Mecklenburg arrived at the conclusion that his five preparations were chemical individuals and not mixtures of a definite alpha with a definite beta oxide, from the observation that the precipitation value of sodium sulphate for the 100° oxide peptized with HCl was increased by the presence in the colloidal solution of 0° oxide freshly prepared by hydrolysis of stannic chloride. He assumed that the oxides were all made up of "primary particles" of the same size grouped into "secondary particles" of different sizes; and attributed the difference in properties of the several preparations to differences in the sizes of the secondary groups.

#### Experimental

*The Physical Character of Precipitated Stannic Oxides.*—As noted above, Mecklenburg observed that there was no apparent connection between the temperature of precipitation of hydrous stannic oxides and the compactness of the mass when dried and powdered. Thus, the 100° oxide which contained the least water was most compact. A possible explanation of this observation is that the conditions of drying and grinding of the several products were not identical throughout. That the compactness of the precipitated oxide does depend on the temperature of formation in a perfectly regular fashion was shown by the following experiments: Thirty cubic centimeters of a solution of stannic chloride containing 1 gm. of SnO<sub>2</sub> was precipitated in a 60 cc test-tube with 20 cc of 1.3 N NaOH. After noting the temperature of the mixture, the con-



tents of the tube were centrifuged for 2 min. at 3000 r.p.m. The height of the column of precipitate was marked on the tube after which it was emptied and the volume of precipitate determined by filling the test tube to the mark with water from a burette. The results given in Table II show conclusively that the compactness of the precipitated oxide decreases appreciably as the temperature of precipitation increases. It is inconceivable that there should be no regularity in the physical condition of a series of dried oxides prepared at different temperatures, providing the conditions of drying were maintained identical throughout.

TABLE II  
Effect of Temperature of Precipitation on the Volume of Hydrous Stannic Oxides

Temperature of precipitation	Volume of precipitated oxide containing 1 g. SnO <sub>2</sub>
1°	17.7 cc
26°	15.8 cc
28°	15.5 cc
49°	12.6 cc
72°	9.4 cc
100°	7.9 cc

*Peptization of Hydrous Stannic Oxide with Nitric Acid.*— Since hydrous stannic oxide precipitated at low temperatures is much less compact than that precipitated at higher temperatures, the former should be more easily peptized than the latter. It will be recalled that Mecklenburg observed that all of his oxides were peptized with approximately equal facility with concentrated HCl except the 50° oxide which seemed to be more difficult to peptize. He found also that the precipitation concentration of Na<sub>2</sub>SO<sub>4</sub> for the 100° oxide peptized by HCl was increased by mixing with it the 0° oxide or one freshly precipitated by hydrolysis of stannic chloride. From this observation he concluded that the different oxides cannot be mixtures of definite alpha and beta isomers. Concerning the first observation, it seems to me altogether unlikely that the 0° and 100° oxides are peptized with equal facility. What



seems more probable is that the difference in peptizability is not detectable with concentrated acid. While the subsequent experiments show that Mecklenburg is probably right in concluding that his oxides are not mixtures of a definite alpha and a definite beta oxide in varying amounts, this conclusion is certainly not justified from his precipitation experiments. On the contrary, these experiments would seem to support the view that the oxides are mixtures. Thus he shows that the so-called "sulphate value" of 100° oxide is 0.04 cc and when mixed with 10 to 90 percent of a freshly prepared oxide the "sulphate value" varies from 0.15 to 1.8 cc. Since certain ones of his 50° and 75° oxides have sulphate values within the limits found for the mixtures, it might be argued that all of his preparations are mixtures. It should be noted that Mecklenburg's observations on the effect of adding a newly formed oxide to the 100° oxide are exactly what one should expect. The adsorption of the sulphate ion by the fresh oxide is so much greater than by the 100° oxide that the initial amounts added are all taken up by the former so that the precipitation of a given amount of the latter does not take place until a higher concentration is reached.

In order to determine the relative peptizability of hydrous stannic oxides formed at different temperatures, some experiments were carried out on the moist instead of the dried oxides using dilute instead of concentrated acid. In these experiments dilute nitric acid was used since it is known that this acid peptizes alpha oxide whereas it has neither a peptizing nor a solvent action on the typical beta oxide. Accordingly, the behavior with dilute nitric acid of the oxides formed under different conditions should give not only a measure of the relative peptizability but should indicate whether the oxides are definite individuals differing in solubility, adsorbability and peptizability or whether they are mixtures of a definite alpha oxide peptizable by nitric acid with a definite beta isomer not peptizable by this acid.

The method of procedure was as follows: Thirty cubic centimeters of a freshly prepared stannic chloride solution cor-

responding to 1 gm. of  $\text{SnO}_2$  were precipitated with 20 cc of 1.25 N NaOH which was slightly less than enough for complete precipitation. Before mixing, the solutions were brought to the desired temperature and the temperature after mixing was noted. The mixture was allowed to stand 1 min., after which 50 cc of water of approximately the same temperature was added. After thorough shaking, the solutions were centrifuged at 3000 r.p.m. for 2 min. The supernatant liquid was poured off and the vessel rinsed after which 100 cc of 1.25 N  $\text{HNO}_3$  was added and the contents shaken thoroughly. The interval between precipitation and addition of acid was 5 min. Observations were made on the different oxides as given in Table III.

TABLE III  
Peptization of Hydrous Stannic Oxides with Nitric Acid

Temperature of precipitation	Observations
23°	Peptized rapidly; solution cloudy after 10 min. but clear in 15 min.
40°	Peptized more slowly; solution very cloudy after 15 min.; quite cloudy after 30 min. but clear with only a slight opalescence in 45 min.
58°	Peptized very slowly; solution very cloudy after 1 hr., clearing in 2 hrs. and clear with slight opalescence after 3 hrs.
100°	Peptization far from complete after 8 hrs.

The experiment was repeated as above described except that the precipitate was allowed to stand 10 minutes before centrifuging. This aging produced oxides that were less readily peptized as indicated by the results recorded in Table IV.

The results of the above experiments are quite conclusive. In the first place they show that there is a distinct difference in the peptizability of the oxides prepared at different temperatures. The loose, finely divided and highly hydrous particles of the oxide formed at room temperature are peptized readily by nitric acid whereas the more compact, coarser and less hydrous particles formed at higher temperatures are less

TABLE IV  
Peptization of Hydrrous Stannic Oxides by Nitric Acid (2)

Temperature of precipitation	Observations
22°	Peptized slowly; solution quite cloudy after 2 hrs. and slightly opalescent after 4 hrs.
39°	Peptized very slowly; no residue but solution very cloudy after 5 hrs.; transparent but cloudy after 10 hrs.
58°	Most peptized in 15 hrs. but solution opaque.
100°	But little peptized

readily peptized. The results indicate further that each oxide is a definite individual and not a mixture of alpha and beta isomers in varying proportions. Thus the 40° and 60° oxides are not readily peptized by dilute nitric acid and so would not be designated as alpha oxides; but they *are* peptized after a time which indicates that they are not beta oxide nor mixtures of alpha and beta oxides. This behavior might be explained by assuming that colloidal alpha oxide adsorbs beta oxide and so carries the latter into colloidal solution. This is improbable as shown by the following experiment on the behavior with dilute nitric acid of a mixture of typical alpha with typical beta oxide: 0.5 gram of oxide was precipitated from a fresh solution of stannic chloride and at once was thoroughly mixed with a suspension containing 0.5 gm. of oxide prepared by the action of nitric acid on tin. After centrifuging in the usual way the mixed oxides were treated with 100 cc of nitric acid and shaken thoroughly. After 30 minutes the mixture was centrifuged, throwing down the so-called beta oxide while the freshly prepared oxide was held in colloidal solution.

That the oxides carried into solution by dilute nitric acid were in the colloidal state was shown by adding dilute sodium sulphate solution which caused complete precipitation. Moreover, spontaneous precipitation of the colloids was observed after they had stood for a day.

Before concluding this section of the paper attention should be called to the doubtful accuracy of Mecklenburg's

assumption that the different stannic oxides are made up of "secondary particles" of different sizes formed by agglomeration of "primary particles" of the same size. It seems to me altogether unlikely that the so-called primary particles are all exactly alike and I can not see what is gained by making such an improbable assumption. I should expect the individual particles of oxide formed by the action of nitric acid on tin or by precipitation at high temperatures to be considerably larger than those in the hydrous oxide precipitated from a cold stannic solution,—a circumstance that would account for the very slight peptizability and adsorbability of the former as compared with the latter.

#### Colloidal Hydrous Stannic Oxide

*Peptization Methods of Preparation.*—Colloidal stannic oxide almost free from electrolytes was first prepared by Graham<sup>1</sup> by adding alkali to stannic chloride solution or hydrochloric acid to sodium stannate solution short of precipitation and dialyzing the resulting solutions. In both cases a gel was first formed on the dialyzer but this went into colloidal solution again as the purification was continued. The colloid was negatively charged and Graham attributed the peptization to the presence of a small amount of free alkali. Excess of the latter was removed by the addition of a few drops of tincture of iodine. As noted previously, Graham found that the colloid could be boiled without precipitating, thereby forming colloidal beta oxide, so-called. His preparations were fairly pure and so were readily coagulated by salts and acids.

Schneider<sup>2</sup> prepared the colloid by peptization with ammonia. He poured very dilute stannic chloride into dilute ammonia until the precipitate first formed just failed to dissolve. The remaining precipitate disappeared on further dilution with water and the colloid was then dialyzed forming a perfectly clear solution. This colloid was precipitated by excess nitric acid and by small amounts of HCl, H<sub>2</sub>SO<sub>4</sub> and nu-

<sup>1</sup> Pogg. Ann., 123, 538 (1864).

<sup>2</sup> Zeit. anorg. Chem., 5, 82 (1894).

merous salts. The precipitate dissolved in excess HCl and H<sub>2</sub>SO<sub>4</sub> forming chloride and sulphate, respectively.

Zsigmondy<sup>1</sup> improved on the methods of Graham and Schneider by doing away with the necessity for dialysis. Two methods were employed: In the first a current of air was passed through a solution of stannous chloride containing 0.6 gm. SnCl<sub>2</sub> in 4 liters of water until oxidation was complete. A gelatinous precipitate settled out that was washed by decantation and peptized by the addition of a very small amount of ammonia. In the second method 2 gm. of SnCl<sub>4</sub> was dissolved in 4 liters of water and allowed to stand 3 days. The gelatinous precipitate obtained was washed by decantation until free from chloride and was peptized by dilute ammonia. The amount of ammonia required was very small. In one experiment a single drop containing approximately 0.03 gm. of NH<sub>3</sub> was used in the peptization of 1.45 gm. of SnO<sub>2</sub>. Any excess ammonia was removed by heating the colloid to boiling. As usual, Zsigmondy's colloids were negatively charged and were readily precipitated by electrolytes particularly those having strongly adsorbed cations. The properties of the oxides precipitated from these solutions lay between those of the typical alpha and beta oxides and Zsigmondy believed that they were not chemical individuals but were mixtures of the two forms, the usual properties of each being modified by the presence of the other. This view is unquestionably incorrect.

As previously noted, hydrous stannic oxide freshly prepared at room temperature is readily peptized by dilute HNO<sub>3</sub>, HCl and H<sub>2</sub>SO<sub>4</sub>; while the aged oxide is peptized by concentrated HCl and H<sub>2</sub>SO<sub>4</sub> under suitable conditions but not by HNO<sub>3</sub>. The colloids prepared in this way are positively charged as evidenced by the low precipitation value of SO<sub>4</sub> ion in the presence of considerable excess of H ion.<sup>2</sup>

*Preparation by Hydrolysis of Stannic Nitrate.*—Biltz<sup>3</sup> pre-

<sup>1</sup> Liebig's Ann., 301, 361 (1898).

<sup>2</sup> Löwenthal: Jour. prakt. Chem., 56, 366 (1852); Mecklenburg: Zeit. anorg. Chem., 74, 207 (1912).

<sup>3</sup> Ber. deutsch. chem. Ges., 35, 443 (1902).

pared colloidal stannic oxide by hydrolysis of a nitrate solution prepared by treating 5 gm. of  $\text{SnCl}_4$  in 50 cc with an equivalent amount of  $\text{Pb}(\text{NO}_3)_2$  in 50 cc. After filtering and diluting the solution it was dialyzed, forming a colloid that contained a considerable excess of nitrate and some lead. The solution was cloudy and coagulated when heated. Toward electrolytes it behaved like the positive colloidal hydrous oxides of iron and chromium. Biltz<sup>1</sup> studied the mutual precipitating action of negative colloidal stannic oxide prepared by Schneider's method and the positive colloidal oxides of iron, aluminum, chromium, thorium, zirconium and cerium.

*The Aging of Colloidal Stannic Oxide.*—Attention has been called to Rose's observation that the alpha oxide peptized by dilute HCl changes gradually into the so-called beta form, the change being more rapid the diluter the acid and the higher the temperature. This transformation has been followed in a number of ways, a few of which will be mentioned: Löwenthal<sup>2</sup> found that  $\text{K}_4\text{Fe}(\text{CN})_6$  could be removed from solution completely by the addition of a dilute solution of stannic chloride; but that the older the tin solution the more was necessary to precipitate a definite amount of ferrocyanide and the greater was the amount of tin in the precipitate. This is shown in Table V. Löwenthal's observations were confirmed by Lorenz<sup>3</sup> who assumed that the ferrocyanide was removed as

TABLE V

Age of $\text{SnCl}_4$ solution da.	Amount of $\text{SnCl}_4$ solution to precipitate 0.5 g $\text{K}_4\text{Fe}(\text{CN})_6$ cc	Composition of pre- cipitate Mol. $\text{Sn}(\text{OH})_4$ Mol. $\text{K}_4\text{Fe}(\text{CN})_6$
0	6	1.5
7	10	2.3
14	14	3.3
81	27	6.5
126	32	7.5
162	36	.5

<sup>1</sup> Ber. deutsch. chem. Ges., 37, 1099 (1904).

<sup>2</sup> Loc. cit.

<sup>3</sup> Zeit. anorg. Chem., 9, 369 (1895).

$\text{SnFe}(\text{CN})_6$ ; and that more old  $\text{SnCl}_4$  solution was necessary on account of the lower concentration of stannic ion resulting from slow hydrolysis. Mecklenburg<sup>1</sup> pointed out that this explanation was unsatisfactory for two reasons: first, that ionic reactions as hydrolysis take place much more rapidly than Lorenz assumed; and second, that the composition of the precipitate was not  $\text{SnFe}(\text{CN})_6$  but was variable, containing more and more tin the older the solution. The true explanation of Löwenthal's observations lies in the aging of the colloidal hydrous oxide. The addition of  $\text{K}_4\text{Fe}(\text{CN})_6$  causes coagulation of the colloid. Since the particles of a newly formed colloid are smaller and have a greater adsorption capacity than those of an older colloid, less of the former is necessary to adsorb completely a given amount of ferrocyanide and the ratio of tin to ferrocyanide in the precipitate is relatively low. As the colloid ages however, it becomes less stable and the adsorption capacity falls off so that more colloid is necessary to adsorb a definite amount of ferrocyanide and the ratio of tin to ferrocyanide becomes quite large.<sup>2</sup>

The age of colloidal stannic oxide may be determined roughly by treating with stannous chloride. The colloid prepared from freshly formed stannic oxide is not precipitated by  $\text{SnCl}_2$  whereas the aged colloid is thrown down as a yellow precipitate by this reagent. The precipitate is variable in composition,<sup>3</sup> consisting of hydrous stannic oxide that has adsorbed varying amounts of  $\text{SnCl}_2$  under the different conditions of precipitation. In this connection it may be mentioned that hydrogen sulphide precipitates  $\text{SnS}_2$  from a colloidal solution of the fresh oxide in dilute  $\text{HCl}$ ; whereas from the aged colloid, hydrogen sulphide precipitates hydrous stannic oxide that is converted only very slowly into  $\text{SnS}_2$ .<sup>4</sup> The ex-

<sup>1</sup> Zeit. anorg. Chem., 65, 372 (1909).

<sup>2</sup> Cf. Barfoed: Jour. prakt. Chem., 101, 368 (1867).

<sup>3</sup> Fremy: Ann. Chim. Phys., [3] 12, 462 (1844); 23, 393 (1848); Schiff: Liebig's Ann., 120, 4 (1861).

<sup>4</sup> Jörgensen: Zeit. anorg. Chem., 28, 140 (1901); Barfoed: Jour. prakt. Chem., 101, 170 (1867).



planation of this behavior is evident when we consider the difference in solubility of the new and old oxide. In the new colloid prepared by peptization with HCl there is some stannic ion, the removal of which by precipitation as  $\text{SnS}_2$  results in further solution and subsequent precipitation until all is thrown down as sulphide; while the aged colloid contains but a negligible amount of stannic ion and the precipitate with  $\text{H}_2\text{S}$  is almost entirely the hydrous oxide.

Löwenthal noted that the aging of colloidal hydrous stannic oxide does not take place in the presence of tartaric acid. The reason for this is that a complex is formed that can be gotten in a definite crystalline form if desired.<sup>1</sup>

Earlier in this paper I pointed out that the aging of the newly formed oxide peptized by nitric acid manifested itself by gradual spontaneous precipitation until none remained in the colloidal state.

From this survey it is evident that we may have any number of colloidal solutions of hydrous stannic oxides, each differing from the others in the size of the hydrous particles and hence in their reactivity, adsorbability and stability under given conditions. As a rule the smaller, more soluble hydrous particles are transformed into larger, less soluble and less hydrous particles but the reverse process goes on in the presence of fairly concentrated HCl or alkali.<sup>2</sup> As with the precipitated oxide, there is no ground for assuming that the different colloidal solutions are mixtures of colloidal alpha with colloidal beta particles in varying proportions.

*Behavior of Colloidal Hydrous Stannic Oxide with Colloidal Metals.*—One of the most characteristic properties of colloidal hydrous stannic oxide is its protective action on colloidal metals. It is well known that when a gold solution is treated with  $\text{SnCl}_2$  a red coloration is first produced followed by the settling out of a purple or brown precipitate known as gold purple of Cassius from its discoverer Andreas Cassius of Ley-

<sup>1</sup> Rosenheim and Aron: *Zeit. anorg Chem.*, **39**, 170 (1904).

<sup>2</sup> Rose; Weber; Löwenthal; Barfoed; Musculus: *Loc. cit.*



den. Because of its wide use as a pigment in the ceramic industry, a number of recipes have been described for its preparation. The substance varies in color and composition with the method of formation. Certain earlier investigators as Richter and Gay-Lussac believed that purple of Cassius was a mixture but Berzelius believed that it must be a definite compound. The latter view is supported by the fact that purple of Cassius is purple in color while a mixture of gold and stannic oxide is brick red; that gold is not separated from purple of Cassius with aqua regia whereas it is from a mixture; that mercury does not extract gold from the purple as it does from a mixture; and finally that the freshly prepared purple is dissolved by ammonia forming a purple liquid. In spite of this evidence we now know that Berzelius' view is incorrect. Debray<sup>1</sup> believes that gold forms a kind of color lake with stannic oxide which is soluble in ammonia. Schneider<sup>2</sup> emphasizes the colloidal character of purple of Cassius and concludes rightly that its ammoniacal solution is a mixture of colloidal gold with colloidal hydrous stannic oxide. Supporting Schneider's view Zsigmondy<sup>3</sup> points out that a mere trace of ammonia will dissolve a large amount of freshly precipitated purple and that this purple solution will not pass through parchment during electrolysis as electrolytes do. He settled the question once for all by precipitating with nitric acid suitable mixtures of colloidal gold with colloidal stannic oxide, obtaining purples almost identical with those prepared in other ways. The gold does not combine chemically with stannic oxide but the usual properties of the former are masked by the protective action of the latter.

Müller<sup>4</sup> observed that a great number of substances are colored red by colloidal gold<sup>5</sup> and Moissan<sup>6</sup> has obtained pur-

<sup>1</sup> Comptes rendus, 75, 1025 (1872).

<sup>2</sup> Zeit. anorg. Chem., 5, 80 (1894).

<sup>3</sup> Liebig's Ann., 301, 361 (1898).

<sup>4</sup> Jour. prakt. Chem., 30, 252 (1884).

<sup>5</sup> Antony and Lucchesi: Gazz. chim. Ital., [2] 26, 195 (1896).

<sup>6</sup> Comptes rendus, 141, 977 (1905).

ples by distilling gold with tin, alumina, magnesia, zirconia, silica and lime. Substances similar to gold purple have been prepared with other metals. Thus Wöhler<sup>1</sup> showed that silver purple, formed by mixing  $\text{AgNO}_3$  with  $\text{Sn}(\text{NO}_3)_2$  is analogous to the gold pigment; and Lottermoser<sup>2</sup> prepared the former synthetically in the same manner as Zsigmondy prepared the latter. Wöhler<sup>3</sup> has also made an analogous platinum combination. All of these so-called "purples" are colloidal in nature, the composition varying with the conditions of formation. Their colloid chemistry is chiefly that of hydrous stannic oxide. When freshly prepared the purples are readily peptized by ammonia or dilute  $\text{HCl}$ ; but when dried there is little or no peptizing action even by concentrated ammonia or  $\text{HCl}$ .

*Behavior of Hydrous Stannic Oxide with Other Hydrous Oxides.*—In analytical chemistry the usual method of estimating tin consists in oxidizing it to insoluble stannic oxide and weighing it as such. It is well known however that the oxide formed in this way is always contaminated by other substances present in the solution from which it separates. Thus Rose<sup>4</sup> showed that it carries down appreciable quantities of iron, bismuth, copper, and lead. Rose made the interesting observations that when iron is present in small amounts the stannic oxide precipitated from nitric acid solution is contaminated by it; but that when any considerable quantity of iron is present, both the iron and tin remain in solution. Rose's observations were confirmed and extended by Lepez and Storch.<sup>5</sup> The latter digested tin with nitric acid containing iron and obtained solutions that varied in stability depending on the relative amounts of tin and iron present. They found that solutions containing two atoms or less of tin to one of iron could be boiled and even evaporated to dryness in a vacuum. Concentrated nitric acid threw out of these solutions a yellowish

<sup>1</sup> Zeit. Kolloidchemie, 7, 248 (1910).

<sup>2</sup> Anorganische Kolloide, 1901, 53.

<sup>3</sup> Zeit. Kolloidchemie, 2, Supplement, page III (1907).

<sup>4</sup> Pogg. Ann., 112, 164 (1861).

<sup>5</sup> Monatshefte, 10, 283 (1889).

precipitate that redissolved on dilution. Sulphuric acid and sulphates caused a permanent precipitate while acetic acid and alkali chlorides and nitrates caused no precipitation. By evaporating different solutions, the authors claimed to get compounds having the following formulas:  $1.8\text{SnO}_2 \cdot \text{H}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 1.8\text{N}_2\text{O}_5$ ;  $4\text{SnO}_2 \cdot \text{H}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 1.1\text{N}_2\text{O}_5$ ; and  $6\text{SnO} \cdot \text{H}_2\text{O} \cdot \text{Fe}_2\text{O}_2 \cdot 1.6\text{N}_2\text{O}_5$ . It was further observed that when a mixture of ferric and stannic hydrates was thrown down from the mixed nitrates by a slight excess of ammonia and the precipitate washed free from  $\text{NH}_4\text{NO}_3$ , this precipitate, still containing a trace of ammonia, dissolved in water to a clear solution. Removal of ammonia by dialysis resulted in precipitation; but the addition of a trace of ammonia again caused complete solution. Chromic nitrate was observed to behave like ferric nitrate; but aluminum, uranium, cobalt, nickel and copper nitrates did not cause solution of stannic oxide.

#### Experimental

The observations of Rose and of Lepez and Storch would seem to indicate that their ferric-stannic mixtures were either colloidal solutions of hydrous ferric oxide peptized by hydrous stannic oxide or of colloidal hydrous stannic oxide peptized by ferric and hydrogen ions. In order to determine the nature of these solutions a series of experiments was carried out that will now be described.

*Action of Colloidal Hydrous Stannic Oxide on Hydrous Ferric Oxide.*—Solutions were prepared of stannic and ferric chlorides normal with respect to the metallic ion. Ten cubic centimeters of the mixed chlorides were precipitated with an equal amount of normal  $\text{NH}_4\text{OH}$  in a 250 cc bottle after which 50 cc of water was added and the mixture centrifuged 2 min. at 3000 r.p.m. The supernatant liquid was drained from the precipitate which was shaken at once with 100 cc of  $\text{N}/100 \text{NH}_4\text{OH}$ . The complete peptization of both the hydrous stannic and ferric oxides took place in a short time with the lower concentrations of iron while with higher concentrations the peptization of the latter was slower. The solutions were shaken

at intervals until peptization of ferric oxide was complete or until there was no further peptization. The results of a series of experiments after 4 days are given in Table VI.

TABLE VI  
Peptization of Mixtures of Hydrous Stannic Oxide and Hydrous Ferric Oxide with 0.01 N Ammonium Hydroxide

Mixed oxides prepared from N SnCl <sub>4</sub> + N FeCl <sub>3</sub>		Observations
cc	cc	
9.5	0.5	Clear, colorless colloidal solution
9.0	1.0	Clear colloidal solution with yellow tinge
8.5	1.5	Clear, light yellow colloidal solution
8.0	2.0	Clear, yellow colloidal solution
7.5	2.5	Clear, reddish yellow colloidal solution
7.0	3.0	Clear yellowish red colloidal solution
6.0	4.0	But little ferric oxide peptized; supernatant liquid cloudy.
5.0	5.0	No ferric oxide peptized; supernatant liquid clear and colorless.
2.0	8.0	No peptization of either hydrous oxide

The above results are quite conclusive. Hydrous stannic oxide is peptized by hydroxyl ion while hydrous ferric oxide is not. However, the colloidal stannic oxide adsorbs ferric oxide and carries it into colloidal solution as long as tin is present in excess. At the same time hydrous ferric oxide adsorbs stannic oxide and tends to take it out of colloidal solution so that when the former is present in large excess no tin remains peptized. This is quite analogous to the behavior of hydrous chromic oxide with the hydrous oxides of iron, manganese, cobalt, nickel, copper and magnesium.<sup>1</sup>

On account of the mutual adsorption of hydrous stannic oxide and hydrous ferric oxide, we should expect the precipitate obtained by mixing positive colloidal ferric oxide with negative colloidal stannic oxide to contain appreciable amounts of both oxides. I hope to determine whether the precipitate

<sup>1</sup> Northcote and Church: Jour. Chem. Soc., 6, 54 (1854); Nagel: Jour. Phys. Chem., 19, 331 (1915).

obtained by mixing yellow colloidal ferric oxide<sup>1</sup> with colloidal stannic oxide under suitable conditions, can be ignited without becoming red.<sup>2</sup>

*Peptization of Hydrous Stannic Oxide with Mixtures of Ferric Nitrate and Nitric Acid.*—Ten cubic centimeters of normal stannic chloride were mixed with an equal amount of normal alkali; 50 cc of water were added and the mixture centrifuged 2 minutes at 3000 r.p.m. After pouring off the supernatant liquid and rinsing the vessel, the precipitate was shaken with electrolyte. The details of a series of such experiments and the observations are given in Table VII. The colloidal solutions which were formed could be precipitated at once by the addition of a small amount of a sulphate solution.

TABLE VII  
Colloidal Stannic Oxide peptized by  $\text{Fe}(\text{NO}_3)_3$  and  $\text{HNO}_3$

0.38 g. $\text{SnO}_2 + x\text{H}_2\text{O}$ peptized by $\text{N HNO}_3 + \text{N Fe}(\text{NO}_3)_3 + \text{H}_2\text{O}$			Observations	
cc	cc	, cc	after 1 day	after 1 week
40	0	10	All precipitated	
39	1	10	Very cloudy; partly precipi- tated	All precipitated
38	2	10	Slightly cloudy	Very cloudy
37	3	10	Slightly opales- cent	Slightly cloudy
36	4	10	Clear	Slightly opales- cent
35	5	10	Clear	Slightly opales- cent
34	6	10	Clear	Clear
0	40	10	Cloudy	Clear

In addition to the above experiments an aged hydrous oxide that had stood several days was treated with a solution of ferric nitrate. Peptization resulted on standing.

<sup>1</sup> Weiser: Jour. Phys. Chem., 24, 322 (1920).

<sup>2</sup> Keane: Ibid., 20, 734 (1916); Scheetz: Ibid., 21, 570 (1917); Yoe: Ibid., 25, 196 (1921).

The explanation of these observations is now fairly simple. As previously noted, hydrous stannic oxide peptized by nitric acid coagulates spontaneously since the aged oxide is neither peptized nor dissolved by this acid. Ferric nitrate peptizes this oxide both when newly formed and when aged. Accordingly, if freshly prepared hydrous stannic oxide is peptized either by ferric nitrate or by a suitable mixture of ferric nitrate and nitric acid, coagulation does not take place on standing or boiling on account of the stabilizing action of the strongly adsorbed ferric ion; but if the concentration of ferric ion in the nitric acid solution is too low partial coagulation takes place as shown in the table.

#### Stannic Oxide Jellies

When a colloidal solution of hydrous stannic oxide is evaporated a transparent jelly is obtained; while precipitation with electrolytes is said always to give a gelatinous precipitate and not a jelly.<sup>1</sup> In a previous communication, I have pointed out that one should expect to get a jelly whenever a suitable amount of a highly hydrous substance is gotten into colloidal solution and precipitated under suitable conditions.<sup>2</sup> Since hydrous stannic oxide apparently possesses the desired properties, there seemed no reason why stannic oxide jellies could not be obtained by precipitation from colloidal solution. Accordingly the following experiments were carried out.

*Coagulation of Hydrous Stannic Oxide from Solution in Alkali.*—Chromic oxide jellies were obtained by the spontaneous coagulation of a colloidal solution formed by the rapid addition to a solution of  $\text{CrCl}_3$  of just enough alkali to cause complete peptization of the hydrous oxide first precipitated.<sup>3</sup> In a similar manner 10 cc portions of N  $\text{SnCl}_4$  were treated with varying amounts of N  $\text{NaOH}$  as given in Table VIII and the solutions allowed to stand. The results follow.

<sup>1</sup> Zsigmondy-Spear; *Chemistry of Colloids*, 1917, 155.

<sup>2</sup> Weiser; *Jour. Phys. Chem.*, 26, 429 (1922).

<sup>3</sup> *Ibid*: 26, 424 (1922).

TABLE VIII  
Peptization of Hydrous Stannic Oxide by Alkali

Solutions mixed		Observation	Nature of precipitate
N NaOH cc	N SnCl <sub>4</sub> cc		
12.0	10	Peptization incomplete	Granular
12.25	10	Peptization almost complete	Granular
12.50	10	Peptization complete	Granular
12.75	10	Peptization complete	Granular

The failure to get a jelly by the procedure described above was not unexpected. I have pointed out elsewhere that alkali hydroxides have not only a peptizing action on hydrous stannic oxide but also a solvent action which results in the formation of some stannate even in dilute solution. It is this solvent action which causes the precipitation of large particles instead of fine filaments or films that constitute a jelly structure. Chromic oxide jellies are formed under similar conditions since alkali hydroxides do not dissolve the oxide with the formation of chromite. In order to avoid the excess of alkali required to cause peptization of stannic oxide in the presence of an equivalent amount of chloride, the colloidal oxide was first prepared practically free from electrolytes and this colloid was then coagulated by the addition of electrolytes as described in the following paragraph.

*Coagulation of Colloidal Stannic Oxide with Electrolytes.*—Colloidal stannic oxide was prepared by Zsigmondy's method. 3.5 gm. of SnCl<sub>4</sub>·5 H<sub>2</sub>O was dissolved in 3 liters of water and allowed to stand 3 days. The resulting hydrous oxide was washed by the aid of the centrifuge until it was so free from chlorides that it started to go into colloidal solution. Several of these washed portions were combined, shaken up with water containing a small amount of ammonia and allowed to stand until peptization was complete. The excess of ammonia was removed by boiling which ages the colloidal oxide. The solution used in the subsequent experiments contained 28.3 g. SnO<sub>2</sub> per liter. This was determined by evaporating 10 cc portions to dryness and igniting the oxide.

The colloid was negatively charged and was readily coagulated by the addition of electrolytes. From the results obtained with hydrous chromic oxide it seemed altogether probable that jellies would be formed by the addition of sufficient electrolyte to cause slow coagulation. This conclusion was borne out by precipitation experiments with  $\text{BaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{NaCl}$  and  $\text{HCl}$ . The method of procedure was as follows: 5 cc portions of colloid were mixed with varying amounts of electrolytes diluted to 5 cc and the resulting mixture allowed to stand quietly. The colloid was measured with a 10 cc Mohr pipette and the electrolytes with a 2 cc Ostwald pipette graduated in 0.1 cc. The observations after allowing the mixtures to stand 2 days, are given in Table IX.

TABLE IX  
Precipitation of Colloidal Stannic Oxide by Electrolytes

Formula	Electrolyte		Observations
	Amount added	Concentration (millieq. per l.)	
$\text{BaCl}_2$	3.00 cc N/100	3.00	Clear, transparent jelly
$\text{BaCl}_2$	3.50 cc N/100	3.50	Clear, transparent jelly; very firm
$\text{BaCl}_2$	3.75 cc N/100	3.75	Jelly; somewhat cloudy and slightly synerized
$\text{BaCl}_2$	4.25 cc N/100	4.25	Gelatinous precipitate
$\text{SrCl}_2$	3.50 cc N/100	3.50	Clear solution; somewhat viscous
$\text{SrCl}_2$	4.00 cc N/100	4.00	Clear, transparent jelly
$\text{SrCl}_2$	4.50 cc N/100	4.50	Clear transparent jelly; very firm
$\text{SrCl}_2$	5.00 cc N/100	5.00	Cloudy jelly; synerized slightly
$\text{NaCl}$	2.00 cc N/10	20.00	Clear solution; viscous
$\text{NaCl}$	2.25 cc N/10	22.50	Soft, cloudy jelly
$\text{NaCl}$	2.50 cc N/10	25.00	Soft, cloudy jelly
$\text{NaCl}$	2.75 cc N/10	27.50	Gelatinous precipitate
$\text{HCl}$	1.50 cc N/50	3.00	Clear solution
$\text{HCl}$	1.75 cc N/50	3.50	Clear, transparent jelly
$\text{HCl}$	2.00 cc N/50	4.00	Clear, transparent jelly
$\text{HCl}$	2.25 cc N/50	4.50	Cloudy jelly; synerized slightly
$\text{HCl}$	2.50 cc N/50	5.00	Gelatinous precipitate



The results of the experiments described above confirm the conclusions reached from similar experiments with hydrous chromic oxide. To get a jelly all that is necessary is to precipitate a colloidal solution of the hydrous substance of suitable concentration at a suitable rate in the absence of electrolytes that may have an appreciable solvent action. The favorable concentration for different electrolytes is in the immediate region of their precipitation concentration. A little below this value, no precipitation or only a slight precipitation takes place; while a little above it a gelatinous precipitate and not a jelly is formed on account of the contraction resulting from too rapid precipitation. It will be noted that the hydrogen ion concentration within which jellies are formed can vary considerably. In the case of hydrous chromic oxide, jellies were obtained from strongly alkaline solution and from a colloidal solution stabilized by hydrogen ion; so with hydrous stannic oxide, jellies were obtained by precipitation of the colloid stabilized by hydroxyl ion both with neutral salts and with 0.004 N HCl which is approximately the precipitation concentration of the latter.

It is of interest to note that a greater concentration of aged stannic oxide than of chromic oxide is necessary to form a firm jelly. The best stannic oxide jellies prepared as above described contained approximately 1 mole  $\text{SnO}_2$  to 600 moles of  $\text{H}_2\text{O}$ ; while firmer chromic oxide jellies were formed containing 1 mole  $\text{Cr}_2\text{O}_3$  to 5000 moles of water.

#### Summary

The results of this investigation may be summarized briefly as follows:

(1) The so-called stannic and metastannic acids are not acids but are hydrous stannic oxides the composition and properties of which are determined by the conditions of formation.

(2) Stannic oxide, newly formed by precipitation from a solution of stannic salt at ordinary temperature, is a loose, highly hydrous mass that is readily peptized by dilute acids

and alkalis forming a colloidal solution and is dissolved by concentrated acids and alkalis forming salts. The oxide is more compact, less hydrous, less soluble and less easily peptized the higher the temperature of formation. The newly formed oxide undergoes this transformation on standing at ordinary temperatures.

(3) Experiments on the peptization by nitric acid of oxides prepared under different conditions disclose that the different products are not mixtures of varying amounts of a definite alpha oxide peptizable by nitric acid with a definite beta isomer not peptizable by nitric acid.

(4) Hydrous stannic oxides prepared at different temperatures or "aged" for varying lengths of time are chemical individuals which differ from each other in the size of the particles and the structure of the mass and hence in their adsorbability and mordanting action, their ease of peptization and their solubility.

(5) There are no definite hydrates of stannic oxide. Salts of the general formulas  $\text{SnR}_4$  and  $\text{M}_2\text{SnO}_3$  are formed by the action of concentrated acids and alkalis on newly formed hydrous stannic oxide. Numerous oxy-salts and complex stannates and metastannates have been prepared by the action of acids and alkalis on different hydrous stannic oxides. These are not definite compounds but are adsorption products, the composition of which is determined by the age of the hydrous oxides and the concentration of acid or base with which they were treated.

(6) Colloidal solutions of hydrous stannic oxide can be prepared by peptization of the newly formed oxide with dilute acids or alkalis. The colloid ages slowly on standing and rapidly on heating. Any number of colloidal solutions are possible each differing from the others in the size of the hydrous particles and hence in their reactivity, adsorbability and stability under given conditions.

(7) Hydrous stannic oxide adsorbs colloidal gold, silver and platinum forming "purples," the most common of which is the gold purple of Cassius. All of these purples are colloidal

in nature, the composition varying with the conditions of formation. Their colloid chemistry is chiefly that of hydrous stannic oxide. When freshly prepared they are readily peptized by dilute acids and alkalis but when "aged" by drying they are peptized but slightly even by concentrated reagents.

(8) A mixture of the hydrous oxides of iron and tin in certain proportions is soluble in dilute ammonia. Investigation of this phenomenon led to the following explanation: Hydrous stannic oxide is peptized by hydroxyl ion while hydrous ferric oxide is not. However, colloidal stannic oxide adsorbs ferric oxide and carries it into colloidal solution as long as tin is present in excess. At the same time hydrous ferric oxide adsorbs stannic oxide and tends to take it out of colloidal solution so that when the former is present in large excess none of the latter remains peptized.

(9) Stannic oxide does not precipitate in the usual way from a solution of tin in nitric acid containing a suitable amount of iron. An investigation of this behavior led to the following explanation: Hydrous stannic oxide peptized by nitric acid coagulates spontaneously since the aged oxide is neither peptized nor dissolved by this acid. Ferric nitrate peptizes the oxide both when newly formed and when aged. Accordingly, if freshly prepared stannic oxide is peptized either by ferric nitrate or by a suitable mixture of ferric nitrate and nitric acid, coagulation does not take place on standing or boiling on account of the stabilizing action of the strongly adsorbed ferric ion; but if the concentration of ferric ion in the nitric acid solution is too low, complete or partial coagulation takes place on standing or boiling.

(10) Stannic oxide jellies were prepared by coagulation of colloidal solutions of the oxide with suitable concentrations of electrolytes. The results of the investigations support the author's general theory of the formation of jellies.

*Department of Chemistry,  
The Rice Institute  
Houston, Texas*

## NEW BOOKS

**Proteins and the Theory of Colloidal Behavior.** By Jacques Loeb. 21 X 15 cm; pp. xi + 292. New York: McGraw-Hill Book Co., 1922. Price: \$3.00.—In the preface the author says that "colloid chemistry has been developed on the assumption that the ultimate unit in colloidal solutions is not the isolated molecule or ion but an aggregate of molecules or ions, the so-called micella of Naegeli. Since it seemed improbable that such aggregates could combine in stoichiometrical proportions with acids, alkalies, or salts, the conclusion was drawn that electrolytes were adsorbed on the surface of colloidal particles according to a purely empirical formula, Freundlich's adsorption formula."

From the reviewer's standpoint this brief paragraph contains at least three fundamental errors. Colloid chemistry has been developed on the assumption that colloidal solutions are suspensions and not solutions. Of course the suspended particles are not isolated molecules; but that is absolutely a side issue. It is perhaps because of this initial error that Loeb fails to grasp the important difference between a solution and a suspension. Adsorption was not postulated because of the improbability of aggregates combining in stoichiometric proportions with acids, alkalies, or salts, and it was not deduced from the behavior of colloidal solutions. The idea of adsorption came from the fact that a second phase, charcoal, silica, etc., took material out of solution in a manner which did not correspond to stoichiometric relations. The application of this to adsorption in a colloidal solution, by proteins for instance, was a secondary step and again had nothing to do with any question of improbability. Loeb has overlooked the fact that solid calcium sulphate presumably does not consist of isolated molecules and yet it will take up water in stoichiometric proportions. If one is not willing to accept water as typical, it would undoubtedly be a simple matter to find a sparingly soluble salt which would take another salt out of solution to form a double salt. Loeb is ascribing to the chemists' emotions and beliefs which are quite foreign to them. It is also a mistake to lay stress on Freundlich's adsorption formula. The important point is that the concentrations in the solution and in the adsorbent vary continuously. Whether the change of concentrations can be expressed quantitatively by any single formula is of no importance whatsoever. It is quite true that many articles are written in such a way as to imply that the quantitative agreement of the results with the formula is essential; but a man like Loeb cannot base his argument on carelessly expressed articles without throwing himself open to the charge of special pleading.

In the second paragraph of the preface Loeb says that "the writer's investigations have led to the result that this conclusion is based on a methodical error, as far as the proteins are concerned; namely to the failure to measure the hydrogen ion concentration of the protein solutions, which happens to be one of the main variables. When the hydrogen ion concentrations are duly measured and considered, it is found that proteins combine with acids and alkalies according to the stoichiometrical laws of classical chemistry and that the chemistry of proteins does not differ from the chemistry of colloids." This is the thesis which the book attempts to prove.

The volume is divided into two parts, the first giving the proof of the stoichiometrical character of the reactions of proteins in seven chapters, and the second outlining the author's theory of colloidal behavior based on Donnan's theory of membrane equilibria in nine chapters.

The first chapter is entitled historical introduction and takes up briefly: the alleged difference between the chemistry of colloids and of crystalloids; the isoelectric point of proteins; the adsorption theory and the precipitation of proteins; the Hofmeister ion series; the aggregation hypothesis; Pauli's hydration theory; Donnan's membrane equilibrium. The second chapter deals with the qualitative proof of the correctness of the chemical view-point and with the preparation of proteins free from ionogenic impurities. Here again we find the inaccuracy of statement, p. 27, which is too frequent in the book. "Those who believe in the adsorption theory assume that both ions of a salt are adsorbed by colloids and Pauli holds that both ions of a salt are adsorbed by the non-ionized molecules of protein." What Loeb should have said is that the protein may adsorb either ion and the undissociated salt, which is entirely different. Loeb's qualitative proof of the truth of the chemical theory consists in treating granulated gelatine with salt solutions and washing six times. He finds that at the iso-electric point,  $\text{pH} \approx 4.7$ , no salt is formed, while sodium gelatinate is obtained at higher values and gelatine chloride at lower values. He overlooks entirely that there is no proof of the formation of either and that the same results would be found if he postulates adsorption of hydroxyl and hydrogen ions instead of formation of sodium gelatinate and gelatine chloride.

In the third chapter are given the methods of determining the isoelectric point of protein solutions and in the fourth chapter the quantitative proof of the correctness of the chemical viewpoint. Loeb shows, p. 42, that some hydrogen ion disappears and no chlorine ion when hydrochloric acid is added to gelatine and water. He interprets this as showing that gelatine chloride has been formed: but of course it is what one would expect if hydrogen ion is adsorbed and chlorine ion is not. If Loeb had plotted hydrogen ion against adsorbed hydrogen ion he would have obtained a very nice curve. The truth of the matter is that experiments of this sort do not enable one to distinguish between the two hypotheses. On p. 44 Loeb gives data for the amounts of different acids necessary to bring crystalline egg albumin solutions to given pH values. He finds that "the curve is the same for  $N/10$  HCl and  $N/10$   $\text{H}_2\text{SO}_4$  since both are strong acids: or, in other words,  $\text{H}_2\text{SO}_4$  combines in equivalent proportions with egg albumin. The curve for  $\text{H}_3\text{PO}_4$  is the highest curve and if we compare the values for  $\text{H}_3\text{PO}_4$  with those for HCl (or  $\text{H}_2\text{SO}_4$ ) we notice that for each pH the ordinate for  $\text{H}_3\text{PO}_4$  is as nearly three times as high as that for HCl as the accuracy of our experiments permits. This means that phosphoric acid combines with albumin (inside the range of our experiment) in molecular proportions and that the anion of albumin phosphate is the monovalent anion  $\text{H}_2\text{PO}_4^-$ ." This is the natural way of accounting for the observations; but Loeb has overlooked the fact that the same results will follow if we postulate that we are dealing primarily with the adsorption of hydrogen ion.

In the fifth chapter the author deals with the valency rule—which he assumes to be absolute—and with the Hofmeister series. He puts a gelatine solution with additions in a collodion bag, which is immersed in water having

the same pH as the protein solution, p. 67, and measures what he calls the osmotic pressure. The reviewer would have welcomed a discussion whether this is really a measurement of osmotic pressure. From Loeb's point of view the collodion membrane is impermeable to dissolved gelatine or gelatine ion; but that begs the whole question because what we want to know is whether we have gelatine ion in solution: On the basis of his experiments, Loeb concludes, p. 70, that the Hofmeister series means nothing. This may be true; but potassium iodide solutions do liquefy gelatine in a way that potassium chloride solutions do not and this cannot be a question of hydrogen ion concentration alone, because the chlorine ions and the iodine ions would affect the hydrogen ion concentration equally if there were no specific disturbing factor. So far as we can see, the question of the purity of the gelatine is not essential under these circumstances. Unfortunately Loeb ignores the action of potassium iodide on gelatine, although this point seems to the reviewer a crucial one.

In chapter six we have the action of neutral salts on the physical properties of proteins and in the seventh chapter a discussion of the inadequacy of the present theories of colloidal behavior. On p. 112 Loeb says that "we have given a survey of the influence of electrolytes on the behavior of proteins and we may now single out those characteristics which are specifically colloidal, i. e., which do not seem to occur in crystalloids. These characteristics are:

1. The addition of little acid (or alkali) to an isoelectric protein (crystalline egg albumin, gelatin, and casein) increases, and the addition of more acid (or alkali) diminishes the osmotic pressure, the viscosity (and also, as will be seen, the potential differences) of solutions of these proteins; and the same is true for the swelling of gelatin.

2. This effect of acids and alkalies depends only on the sign and the valency of the ions in combination with the proteins; ions of the same sign and valency, e. g., Cl, NO<sub>3</sub>, CH<sub>3</sub>COO, H<sub>2</sub>PO<sub>4</sub>, HC<sub>2</sub>O<sub>4</sub>, etc., influence the properties in the same way, provided that the properties of the protein solutions are compared for the same pH and the same concentration of originally isoelectric protein, and provided that no constitutional changes occur in the protein molecule or ion.

3. When the ion in combination with a protein is bivalent (e. g., SO<sub>4</sub>, Ca, Ba) the osmotic pressure, viscosity, and swelling of the protein are considerably less than when the ion is monovalent (e. g., Cl, Br, NO<sub>3</sub>, H<sub>2</sub>PO<sub>4</sub>, HC<sub>2</sub>O<sub>4</sub>, Na, K, etc.).

4. The addition of a neutral salt to a protein solution (which is not at the isoelectric point) depresses the osmotic pressure, viscosity (and potential difference) of the solutions and the degree of swelling of gels, and this effect increases with the valency of that ion of the salt which has the opposite sign of charge to that of the protein ion.

"Any theory which claims to be able to explain colloidal behavior must account quantitatively for these four results. As a matter of fact the explanations offered in the colloidal literature do not even suffice as qualitative explanations since they are in contradiction with the facts.

"We have seen in the introduction how the original definition of colloids by Graham, based on the non-diffusion of colloids (through membranes), has of late been abandoned by colloid chemists in favor of the micella or aggregation theory of colloids, according to which the ultimate unit of colloidal matter in

solution or suspension is not the isolated molecule or ion, but an aggregate of the latter—the micella of Naegeli. Such aggregations occur and they play a rôle in gel formation, precipitation, and to some extent in the viscosity of protein solutions, but they cannot explain the influence of electrolytes on the properties of proteins mentioned, since they have only an indirect connection with colloidal behavior. It will be shown that the aggregates act like membranes blocking the diffusion of the ions constituting the aggregate and this prevention of diffusion is a source of colloidal behavior.

"The depressing effect of the addition of salts to protein solutions cannot be harmonized with the aggregation theory. Zsigmondy suggests that the depressing effect of a neutral salt on the osmotic pressure of a solution of a gelatin salt might find its explanation in the assumption that the addition of salt increases the degree of aggregation and hence diminishes the number of the particles in solution, the diminution in the number of particles leading to the lowering of osmotic pressure. It is undoubtedly true that salts precipitate proteins and that precipitation is due to an increase in aggregation, but the salting out of gelatin from its watery solution is not determined by the ion with the opposite sign of charge to that of the protein ion, while we have seen that the depressing effect of a salt on the osmotic pressure of gelatin solutions is determined by the ion with the opposite sign of charge to that of the protein ion. In other words, the salting out of gelatin from its watery solution is a process of an entirely different character from the lowering of the osmotic pressure of a protein solution by a neutral salt. It is, therefore, impossible to explain the latter process by the former.

"Moreover, the attempt to explain the depressing effect of the addition of salts on the basis of the micella theory fails completely in the case of the other properties of protein solutions which are equally depressed by them as the osmotic pressure, namely, the viscosity and the potential difference.

"We shall see in Chap. XIII that if the state of aggregation increases in a gelatin solution—i. e., if isolated protein molecules or ions unite to form a larger aggregate—the viscosity of the solution is thereby increased, for the reason that these aggregates occlude comparatively large quantities of water whereby the relative volume occupied by the gelatin in the solution is increased. This increase in the volume of the micellae at the expense of water leads, as will be seen, to an increase in viscosity. Hence, if we assume that the addition of a salt increases the degree of aggregation in protein solution, it would follow that this should result in an increase of viscosity: while the addition of salt depresses the viscosity. The attempt to explain the depressing influence of salts on the osmotic pressure and viscosity of protein solutions on the basis of the aggregation theory leads therefore to conclusions which are in contradiction with the actual facts."

Without going into the other points, the preceding paragraph may serve as a text for one remark. When a suspension agglomerates partially, the viscosity may increase or decrease, depending on the amount of water trapped in the aggregates. It is therefore possible, though not proved, that salts might increase the degree of aggregation of a protein solution and yet decrease the viscosity of the solution. Points like this are overlooked by Loeb throughout the book.



The final paragraph, p. 119, in this chapter summarizes Loeb's conclusions in regard to the first part of the book. "As long as chemists continue to believe in the applicability of the adsorption formula to the behavior of proteins, no scientific theory of colloidal behavior will be possible. We intend to show in the second part of the book that such a theory can be given on the basis of the stoichiometrical proof that proteins form true salts with acids and alkalies, and that these salts lead to the formation of protein ions. Colloidal behavior is due to the fact that these protein ions cannot diffuse through many membranes which are permeable to the majority of crystalloidal ions, or that protein ions form solid gels in which cohesive forces prevent their diffusion, while such gels are permeable to crystalloidal ions. The theory of the equilibrium conditions resulting from this difference in the diffusibility of the two opposite ions of an electrolyte was developed by Donnan. These equilibrium conditions give rise to forces, such as potential difference, osmotic pressure, etc., which are the only cause of colloidal behavior. It will be shown that Donnan's theory gives not only a qualitative but a quantitative and mathematical explanation of colloidal behavior."

In the second part of the book the chapters are entitled: membrane potentials; the origin of the electrical charges of micellae, and of living cells and tissues; osmotic pressure; swelling; viscosity; a reciprocal relation between the osmotic pressure and the viscosity of gelatine solutions; the stability of protein solutions; colloidal substances, colloidal state, and colloidal behavior. Loeb considers the case of a protein salt separated from distilled water by a collodion membrane as a case of a Donnan equilibrium; and he proceeds to calculate this type of potential difference under all sorts of varying conditions. It must be admitted that he does a good job, the agreement being quite remarkable. The Donnan equilibrium accounts, p. 177, "not only qualitatively, but almost quantitatively for the valency effect of the anion with which the gelatin is in combination and for the effect of the pH."

On p. 189 we read that "Procter (1914) and Procter and Wilson (1916) applied Donnan's equilibrium theory to the explanation of the swelling of gelatin in acid. According to these authors, the force which causes the entrance of water and hence the increase of volume in a solid block of gelatin in acid is osmotic, and the opposing force which limits the swelling is the force of cohesion between the gelatin molecules or ions constituting the framework inside of which the water is occluded. These cohesive forces thereby play the same rôle in the swelling equilibrium as does the hydrostatic pressure on the membrane in the experiments on osmotic pressure. The protein ions constituting a jelly of gelatin chloride cannot diffuse and hence, according to Procter and Wilson, can exercise no appreciable osmotic pressure, while the chlorine anions in combination with them are retained in the jelly by the electrostatic attraction of the gelatin ion but exert osmotic pressure. This difference in the diffusibility of the two opposite ions of the gelatine chloride gives rise to the condition leading to the establishment of Donnan's membrane equilibrium. It is immaterial for this equilibrium whether the diffusion of dissolved protein ions is prevented by a collodion membrane, or whether it is prevented by the forces of cohesion between the gelatine ions of a solid gel."

A solid framework of gelatin ions in which water is occluded is not the



classical physical chemistry which some of us studied. Some difficulties occur also with the study of viscosity, p. 195. After raising the question of how the Donnan equilibrium can be applied to the protein solutions, Loeb says that "the answer lies in the fact that although protein solutions may be and probably are as a rule true solutions, consisting of isolated protein ions and molecules distributed equally through the water, they contain under certain conditions submicroscopic solid particles of protein." Solid particles, even though submicroscopic, sound like a suspension and the admission is more significant because Loeb has never given any proof that protein solutions are ever true solutions.

On p. 284 Loeb says that "the problems of gel formation or of precipitation are not colloidal problems, they are a part of the more general problem of solubility. These problems enter only in a secondary way into the problem of colloidal behavior, since the phenomena of aggregation are only a means of preventing the diffusion of an ion, thereby creating the conditions for the establishment of a Donnan equilibrium." This may be true; but the reviewer would have been interested in some phase rule proof of the existence of gelatine chloride for instance. If the chemistry of protein solutions is merely the orthodox chemistry of hydrolyzed salts, it is a pity not to have shown the existence of these salts by the orthodox methods, merely as a guarantee of good faith.

Going back to the preface, p. vi, we read that "any rival theory which is intended to replace the Donnan theory must be able to accomplish at least as much as the Donnan theory, i. e., it must give a quantitative, mathematical, and rationalistic explanation of the curves expressing the influence of hydrogen ion concentration, valency of ions, and concentration of electrolytes on colloidal behavior and it must explain these curves not for one property alone but for all the properties, electrical charges, osmotic pressure, swelling, viscosity, and stability of solution, since all these properties are affected by electrolytes in a similar way."

Here Loeb is on firm ground. He has done a great deal of careful experimental work; he has developed a plausible theory for his results; and he has been able to calculate many of his results with what seems to be an entirely satisfactory degree of accuracy. Anybody who wishes to overthrow Loeb's theory must utilize Loeb's data at least as well as Loeb has done. Whether Loeb is right or wrong—and the reviewer believes him wrong—he has made out a good case and those of us who disagree with him have not made out any case as yet. Even in the moment of triumph, however, the other man's point of view is ignored. It has apparently never occurred to Loeb that undissolved gelatine with adsorbed hydrogen ion will also give rise to a Donnan equilibrium. Though Loeb's theory is based on the Donnan equilibrium the latter is independent of Loeb's theory. The attack will be on the latter and not on the former. This probably means that all of Loeb's tables will be taken over bodily by his adversary. Throughout the whole book Loeb has overlooked the fundamental principle of research that it is not sufficient to show that a given theory will account for the facts. It is also necessary to show that no other theory will account for the facts. Of course nobody ever really does this; but it will be rather pathetic if it turns out that Loeb has furnished most of the data necessary

to overthrow his own views. Until that time comes, however, Loeb's presentation will probably convince all those who are open to conviction.

*Wilder D. Bancroft*

**A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. II.** By J. W. Mellor. 24 × 16 cm; pp. vii + 894. New York and London: Longmans, Green and Co., 1922. Price: \$20.00.—There are only four chapters in the second volume; but they are rather important ones, being entitled: the halogens; the compounds of the halogens with hydrogen; the oxides and oxyacids of chlorine, bromine, and iodine; the alkali metals. The book is a reservoir of interesting facts. "Marine animals and plants assimilate iodine from sea water. It appears strange that the marine algae should select iodine from sea water and practically leave the bromine which is present in much larger proportions," p. 17. "According to Gautier, iodine must be a constituent of the chlorophyll or reserve protoplasm of plants because plants containing chlorophyll contain more than the algae and fungi which are free from chlorophyll," p. 18.

"Weldon's improved process is founded on the fact that the freshly precipitated manganese hydroxide, suspended in a solution of calcium chloride, is easily converted into the dioxide when an excess of lime is present. Many of the older processes recovered manganese dioxide by the action of a current of air upon the manganese hydroxide precipitated by lime; but the oxidation is so slow as to be useless in practice, and even then only about half is converted into the peroxide, for the oxidation seems to stop when the manganese is oxidized to the sesquioxide,  $Mn_2O_3$ . In Weldon's recovery process it is the excess of lime which led to commercial success, for there is a complete conversion to the dioxide in less than one-tenth of the time required for maximum conversion when there is no excess of lime," p. 28.

"The saturated vapour of iodine, in a layer 0.1 metre thick, is opaque to daylight or to candle-light; the vapour appears at the edges to be blue by transmitted light, black by reflected light, and, according to Schönbein, it appears to be the blacker the higher the temperature, owing to an increasing absorptive power for light. Sellak says that a thin layer of solid or molten iodine transmits only the rays in the extreme red. The fine purple colour of iodine vapour is due to its transmitting freely the blue and red rays of the spectrum, while it absorbs nearly all the green; but if the iodine vapour is in thick layers it absorbs the red rays, and the transmitted light is purely blue. A solution of iodine in carbon disulphide exhibits the same phenomena, since it appears blue or purple according to its density. The alcoholic solution does not show this phenomenon," p. 58.

"Faraday found that liquid iodine chloride can be electrolyzed, the iodine collecting at the cathode, the chlorine at the anode. According to the ionic hypothesis, this means that iodine chloride is partly ionized,  $ICl = I' + Cl'$ , that is, iodine monochloride is a compound of the action,  $I'$ ; with the anion,  $Cl'$ . This also corresponds with the chemical behavior of this compound and with Walden's experiments on the electrical conductivity of solutions of iodine monochloride in inorganic solvents—liquid sulphur dioxide, arsenic trichloride, and sulphuryl chloride," p. 119. The behavior of hydrofluoric acid is explained on the assumption, p. 133, that the molecule is  $HF$  and that the ions are, to some extent,  $H'$  and  $HF_2'$ . One would like to know why glass etches opaque and

dull with hydrofluoric acid gas, and shining and transparent with an aqueous solution, p. 135.

On p. 143 the author commits himself to the doctrine, that a catalytic agent cannot displace equilibrium; but, as usual, he is considering only the cases in which equilibrium is reached in finite time and in which the catalytic agent does not act as a solvent, two very important limitations. When discussing false equilibria, p. 161, no reference is made to a possible poisoning of the catalytic agent though that is the only case, so far as we now know, in which we really get false equilibria.

"Burgess and Chapman found that the presence of ammonia—even in very small traces—makes chlorine particularly inert towards hydrogen in light. It is assumed that the ammonia is converted into nitrogen chloride by the chlorine, and that it is nitrogen chloride which is the inhibiting agent. Chapman estimates that the presence of  $10^{-4}$  molecular parts of nitrogen chloride makes a sensitive mixture of hydrogen and chlorine a hundred times less sensitive than when the inhibiting agent is absent. He further found that oxygen, nitric oxide, chlorine peroxide, nitrosyl chloride, nitrogen peroxide, and ozone act as inhibitors. The mixture is indifferent to the presence of carbon dioxide, nitrogen, and reducing substances generally. Hence Chapman says that the so-called induction period is caused by the presence in the gas of a powerful inhibitive impurity—nitrogen chloride—which must be removed completely from the gases before the chlorine and hydrogen can interact. Further, Chapman and co-workers have made the interesting and important observation that if the chlorine gas be freed from traces of certain impurities, present in the ordinary distilled water of laboratories, there is virtually no period of induction. It is assumed that an exceedingly minute trace of some impurity suffices to retard or inhibit the reaction, and that the delay in the so-called period of induction is really due to the time required to destroy this impurity before the hydrogen and chlorine gases can unite directly. This conclusion was confirmed by Bodenstein and Dux," p. 151.

According to Luther and Goldberg, the photochlorination of hydrocarbons is inhibited by oxygen, and Goldberg suggests that oxygen acts as a specific poison to chlorine in photolytic changes. The desensitizing action of oxygen has also been noted in other photolytic reactions—e. g., mercuric chloride and oxalic acid, the silver halides, etc. In Bodenstein's first hypothesis the retarding effect of oxygen is explained by assuming that the electrons are partially consumed in activating the oxygen to form ozone which in turn reforms oxygen; in his second hypothesis the newly formed molecules of hydrogen chloride communicate part of their vibratory energy to oxygen molecules instead of to the reacting gases," p. 159.

"Bagster and Steele found that dry solutions of hydrogen bromide in liquid sulphur dioxide are practically non-conducting; but the addition of water gave conducting solutions which gave off hydrogen at the cathode and bromine at the anode, while water was carried from anode to cathode and deposited there. It was assumed that the water and hydrogen bromide form an oxonium compound which was electrolytic in character. It was shown that if a simple hydrate is formed, the deposit of water at the cathode must be due to the loss of hydrogen bromide holding it in solution. Bagster and Cooling have shown that

this hypothesis is untenable because no like deposit of water appears at the anode.

They further showed that the reaction is probably:  $\text{H}_2\text{O} + \text{HBr} = \begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{O} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{Br} \end{array}$

The oxonium compound then ionizes  $\text{H}_2\text{O} \text{ Br} = \text{H}_3\text{O}^+ + \text{Br}^-$  and the  $\text{H}_3\text{O}^+$  ion loses its charge at the cathode during electrolysis and forms hydrogen and water," p. 180. This raises the question whether we have the ion  $\text{H}_3\text{O}^+$  in aqueous solutions.

The work of Parsons on the solvent action of potassium iodide on iodine is mentioned, p. 233; the war work on the production of fluorine is given, p. 9; and Weiser's work on flame spectra is included, p. 464; but Liebreich's work on dead spaces is given, p. 312, as though it had not since been disproved. There is a very good discussion of the constitution of bleaching powder, pp. 258-265, which shows how unsatisfactory the state of our knowledge still is. The reviewer was interested in the paragraph on the interaction of sulphuric and hydrobromic acids, p. 204, because of its bearing on the preparation of ethyl bromide. The discussion of the colors of compounds, pp. 221-223, also appealed to the reviewer. Data for the colors of the alkali metals are given on p. 452, and it may be worth noting that solid ammonium bromiodide [?]  $\text{NH}_4\text{IBr}_2$ , is a lustrous green powder—blood-red in transmitted light and green in reflected light, p. 595. Since this compound can be formed by the interaction of an ethereal solution of iodine bromide on ammonium bromide, it seems probable that the formula should be written  $\text{NH}_4\text{Br} \cdot \text{IBr}$ .

When a fused mixture of sodium and potassium chlorides is powdered and kept at about  $200^\circ$  the properties of the mass become those of a mixture. If a molten mixture of the two salts is cooled rapidly, no eutectic can be found and the cooling curve gives a singularity between  $320^\circ$  and  $406^\circ$ . It is believed that the two chlorides form a continuous series of solid solutions which breaks down at about  $400^\circ$ , p. 537.

On p. 764 the author says that "the constancy of the vapor pressures of sodium hydrocarbonate noted by Lescoeur does not necessarily prove that no trona,  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ , is formed,  $5 \text{NaHCO}_3 = \text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{CO}_3 + 2\text{CO}_2$ , because, according to the phase rule, a system with four phases and three components is ternary [?], so that all combinations between  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ , must exercise the same pressure." There is a misprint here somewhere.

"The origin of the nitre beds is not known. It is generally agreed that the nitrogen is of organic origin—animal or vegetable. Since immense deposits of guano have been found on some of the islands off the coast of Peru—e. g., the Chincha Islands—it has been suggested that the nitrogen is derived from the guano. If so, it is not clear where the phosphates have gone, since there is practically no calcium phosphate in the nitre beds. Of course the soluble nitrates may have been leached from decayed guano in some other locality and deposited in their present form. The origin of the deposits has not been solved satisfactorily. The most generally accepted explanation is that the beds have resulted from the decay of enormous quantities of organic matter which probably accumulated in a narrow lagoon of water. This deposit was afterwards elevated by movements of the earth. The geologists claim to recognize the remains of seaweed in some of the nitre beds," p. 807.

In view of the discussion in regard to chemical warfare, it is interesting to note, p. 825, that in 1658 Glauber said: "Of the mischievous composition and diabolical abuse of gunpowder much might be written; but because the present world taketh delight only in shedding innocent blood, and cannot endure that unrighteous things should be reprov'd, and good things praised, therefore it is best to be silent."

*Wilder D. Bancroft*

**Laboratory Manual of Elementary Colloid Chemistry.** By *Emil Hatschek*. 19 × 13 cm; pp. 135. Philadelphia: P. Blakiston's Son and Co., 1920. Price: \$2.00.—"Although most of the existing text-books of Colloid Chemistry necessarily give, in more or less detail, descriptions of experimental procedure and instructions for making many of the classical preparations, no laboratory manual or collection of practical exercises, such as has been found indispensable in the teaching of other branches of chemistry, has so far appeared. The lack of such a work is all the more likely to check the spread of a practical knowledge of the discipline, as many of the methods and materials of colloid chemistry are peculiar, and strange even to students well trained in inorganic and organic chemistry.

"The present work is an attempt to fill this gap and to supply accurate and very detailed directions for carrying out the fundamental operations, for making a number of representative preparations, and for examining them by the standard methods. These are based throughout on personal experience of the processes described and of the difficulties experienced in teaching them. The examples chosen are, generally speaking, the simplest ones and, where alternatives are possible, those involving the smallest expenditure in apparatus and material. The task of selection has not been easy, and the attempt to delimit the elementary region of the whole domain may seem premature or arbitrary; the guiding principle has been to provide for the wants of those students of numerous branches of science who are finding some training in colloid chemistry an indispensable part of their equipment, and are able to devote a limited time only to acquiring its technique."

The chapters are entitled: general remarks on apparatus, materials, and procedure; dialysis; suspensoid sols; suspensions; organosols; emulsoid sols and gels; egg albumin sol; emulsions; ultra-filtration; optical methods of examination; cataphoresis; electrolyte precipitation of suspensoid sols; mutual precipitation of suspensoid sols; protection; viscosity measurements; adsorption (qualitative experiments); capillary analysis; determination of an adsorption isotherm; the Liesegang phenomenon.

This seems to be a helpful little book, though there are several points which might well be changed in subsequent editions. It is hardly the thing to speak of pure oil-water emulsions, p. 63, when one is adding alcohol or acetone. The reviewer does not believe that emulsions made with soap necessarily cream, p. 65; nor is it necessary to have the oil the same density as the dispersing phase in order to prevent separation. The author has been working with too coarse emulsions. There are no experiments to show the two types of emulsions. It is rather stretching the facts to say, p. 94, that "sols in which the disperse phases carry opposite charges precipitate each other when mixed in definite ratios, while no precipitation occurs if an excess of either sol is present."

The reviewer does not like to see the adsorption of positively charged

Night Blue or ferric oxide by silver sand described as adsorption due to neutralization of electric charges, p. 110; because the sand is not present as a sol. While the classification can be justified after a fashion, it is one that will bother the student and will do more harm than good. The reviewer would have liked to have seen some experiments on the effect of hydrogen ion on the adsorption of dyes. Experiments with wool would have been much better than the one with silver sand. It should have been possible to devise a much better experiment on selective adsorption than the one given on p. 110. A substantive and an acid dye with cotton would have been good and another type would have been either one of these with wool and cotton.

Wilder D. Bancroft

**The Theory of General Relativity and Gravitation.** By Ludwik Silberstein. 22 X 15 cm; 6 + 141. New York: D. Van Nostrand Company, 1922. Price: \$2.00.—This book is based on nine lectures given by the author in Toronto last year. The first chapter takes up special relativity and gives the foundations of general relativity and gravitation theory. In the second chapter we find the general relativity principle; minimal lines and geodesics; Newton's equations of motion as an approximation. The third chapter deals with the elements of tensor algebra and analysis. In the preface the author says that in this chapter "care has been taken to give the readers a systematic exposition of the calculus of generally covariant beings called Tensors. The exposition follows here mainly upon Einstein's own presentation of the subject with the difference, however, that due emphasis has been laid upon the distinction between metrical and non-metrical properties of tensors. But even in this chapter technicalities have been avoided, stress being laid upon the guiding principles of this new, or rather newly revived, and most powerful mathematical method. It seems hard to say whether Einstein's admirable theory has or has not a long life before it in the domain of Physics proper. But, independently of its fate, the time applied for studying the Tensor Calculus and acquiring some skill in handling it will be well spent."

The fourth chapter takes up the gravitational field-equations and the tensor of matter, while we find, in the fifth chapter, a discussion of radially symmetric fields, perihelion motion, bending of rays, and spectrum shift. The heading of the sixth chapter—omitted in the table of contents—is electromagnetic equations. In an appendix have been placed "such matter as seemed for the present too speculative and controversial; and also some points concerning the curvature properties of a manifold" as preparatory to Einstein's cosmological speculations. The subdivisions in the appendix are: manifolds of constant curvature; Einstein's new field-equations and elliptic space; space-time according to de Sitter; gravitational fields and electrons.

The lay reader will be interested in the paragraph on p. 99. "Einstein's formula for the secular motion of the perihelion of a planet, undisturbed by other planets, per period of revolution gives for Mercury, per century, 43" or 43.1", coinciding most remarkably with the famous excess of perihelion motion of that planet unaccounted for by the perturbations due to the other members of the solar family of celestial bodies. Although the rival explanation based on perturbing zodiacal matter, due to Seeliger—Newcomb (taken up more recently by Harold Jeffreys), cannot be considered as ultimately discarded, this is certainly a most conspicuous achievement, perhaps the greatest triumph of Einstein's theory,



yielding the required excess without the aid of any new empirical constant in addition to the light velocity and the gravitation constant. As to the remaining planets, Einstein's formula gives for them secular perihelion motions too small to be either contradicted or confirmed by observation in the present state of the astronomer's knowledge. In fact, the only other serious anomaly unaccounted for newtonian celestial mechanics (unless Seeliger's theory is accepted) is the excessive motion of the nodes of Venus: but with this Einstein's theory is essentially powerless to deal, since it yields for a radially symmetric centre of course, rigorously plane orbits. But even the outstanding node motion of Venus is generally felt to be much less important than Mercury's perihelion motion yielded so naturally by Einstein's theory of gravitation." In a foot-note the author adds that a more thorough analysis shows that the perihelion motion "is the only secular perturbation, the eccentricity, the period, and the remaining elements of planetary motion being unaffected by the deviation of Einstein's theory from that of classical celestial mechanics."

On p. 104 the author says that, from the experiments at Mount Wilson and elsewhere, "it would be premature to either assert or deny the existence of the gravitational spectrum shift.

"Einstein himself has, on more than one occasion, expressed the very radical opinion that, should the shift be absent, the whole theory should be abandoned. Yet, in view of the hypothetical nature of the sameness of atoms in the explained sense of the work, such an attitude, though personally intelligible, is by no means necessary. It is true that the invariability of an atomic  $s$ -period of vibration in a gravitational field can, with the aid of the equivalence hypothesis, be reduced to its invariability while the atom is being moved about,—a property of atoms as 'natural clocks' already utilised in special relativity. Yet we do not know whether the atoms actually possess even the latter property. Thus, Einstein's intransigent attitude proves only the strength of his belief that the atoms are or will turn out to be such natural, ideal clocks. But, after all, this is only a guess. A very reasonable one to be sure; for if not among the atoms, then there is indeed but little hope to find such clocks among other 'mechanisms,' natural or artificial.

"At any rate, a final astrophysical verification of Einstein's spectrum-shift formula, supported perhaps by repeated experiments on canal rays, would be an achievement of fundamental importance. Until then 'the natural clock' will remain a purely abstract concept."

There is something fascinating, though unintelligible to the reviewer, about the following sentences, pp. 20, 79, 80. "The physical significance of these world-lines is that the former represent propagation of light *in vacuo*, and the latter the motion of a free particle. "Notice that  $G$ , as defined by (63), is the invariant of the curvature tensor  $G_{\alpha\beta}$ . This invariant, or rather one-sixth of it is called the mean curvature of the world, at the world-point in question. . . . For a certain special world, to be treated later on,  $G$  will be proved explicitly to be six times the smallest value of the (constant and isotropic) curvature of three-space which it is possible to choose as a section of that four world." "The mean curvature of the world is thus proportional to the density of matter."

Wilder D. Bancroft

**Visual Illusions and their Applications.** By M. Luckiesh. 23 X 16 cm; pp. ix + 252. New York: D. Van Nostrand Company, 1922. Price: \$3.00.— The chapters are entitled: introduction; the eye; vision; some types of geometrical illusions; equivocal figures; the influence of angles; illusions of depth and of distance; irradiation and brightness-contrast; color; lighting; nature; painting and decoration; architecture; mirror magic; camouflage.

On p. 160 the author says that "when the beam of light from a powerful searchlight is directed into space, its path is visible owing to the scattering of some of the light by dust and moisture particles and the molecules of the air itself. While obviously the beam itself must go on indefinitely, its luminous path appears to end abruptly at no very great distance from the source." The reviewer does not see how the path of the beam can extend "practically to infinity" as the author assumes. Since light is being scattered at every point on the path, the beam must be getting fainter all the time. The reviewer is also sceptical about the statement that the beam "appears to be sharply cut off for the same reason that the boundary between earth and sky in a flat landscape is a sharp line." One important factor must be the angle at which the light is scattered.

On p. 178 the author says: "Arctic mirages are no less wonderful than those of the hot barren deserts. While traveling along over the ice and snow, distant peaks may assume the most fantastic shapes. At first they may appear flattened like a table-land and then suddenly they may stretch upward like spires. They may shrink then spread like huge mushrooms supported by the stalk-like bases and stretching out laterally. Suddenly they may shoot upward into another series of pinnacles as if another range had suddenly arisen. Such antics may go on for hours as one travels along a frozen valley."

On the same page is the interesting fact that the shadow cast by an aeroplane upon the clouds below may give color effects similar to those of the Spectre of the Brocken. This, of course, is not an illusion. While the range of brightness in a painter's palette is only about thirty to one, the range in a lantern slide may be a thousand to one, p. 186. Another interesting fact, though one for which the author gives no explanation, is that when a yellow cellulose nitrate solution is sprayed over a nickel surface in such a manner as to leave the medium rough or diffusing, the effect is no longer merely a yellow; but a remarkable lustre resembling gilt, p. 188. Quite extraordinary is the apparent distortion of a picture frame when the grain of the wood is conspicuously visible, p. 190.

While yellow and blue pigments give a green when mixed, yellow and blue patches blend to a neutral gray if properly balanced, p. 216. The author states that this will be simple to those who are familiar with the science of light and color though the artist would expect this blend to make green. The reviewer confesses to being one of the ignorant ones. The mixing of the blue and yellow pigments is usually said to give green because both pigments contain green; but it is not clear why the green should not be just as conspicuous when the same pigments are blended and not mixed. Incidentally the reviewer wishes that the author had explained why red and white blend to give gold.

On p. 240 the author tells us that there is an earth haze consisting chiefly of dust and smoke which usually extends to an altitude of about one mile. Its upper limit is very distinct, as seen by the "false" horizon. This horizon is used



more by the pilot when flying at certain altitudes than the true horizon. When above the earth haze, the sky is much less bright. In some extreme cases the sky was found to be only one-tenth as bright when observed at high altitudes of 15,000 to 20,000 feet as when seen from the earth's surface. At 20,000 feet the sky was found to contribute as little as four percent of the total light on a horizontal plane, p. 241.

While there are a great many interesting things in this book, it was rather a disappointment as a whole to the reviewer, perhaps because he had set his expectations too high. On p. 141, for instance, is the familiar statement that an effect of lustre is obtained if one combines two stereoscopic pictures in black and white with the black and white reversed in one of them. In a book on Illusions, one would rather like to find some suggestion as to the reason for this. The reviewer hoped also to find some statement why transparent oil films on an asphalt pavement look metallic. Although the author was Chairman of the Committee on Camouflage of the National Research Council during the war, p. 234, there is very little that is new in the chapter on camouflage. The original plan was apparently to have the whole book lead up to the chapter on camouflage; but somewhere something went wrong. The book is well worth reading, however, though it is distinctly not on the same plane as the author's other books.

*Wilder D. Bancroft*

**Chemical Reactions and their Equations.** By Ingo W. D. Hackh. 18 X 12 cm; pp. viii + 138. Philadelphia: P. Blakiston's Son and Co., 1921. Price \$1.75.—In the preface the author says that "the inability to balance a chemical equation is a most common difficulty of students of chemistry. The writer, when teaching a large university actually encountered graduate students of chemistry who were unable to balance an incomplete ionic equation that involved oxidation and reduction." This concise volume was written in order to supply students with necessary material and to expound the general principles of balancing equations.

Never having tried to balance "an incomplete ionic equation that involved oxidation and reduction," the reviewer does not know whether he could do it or not; but he remembers distinctly Lash Miller's balancing one reaction by a draft on the imagination. The reviewer fears that a graduate who cannot balance an equation may not be equal to understanding the book.

*Wilder D. Bancroft*

**L'équilibre des substances hétérogènes.** By J. Willard Gibbs. Translated by Georges Matisse. 19 X 12 cm; pp. viii + 100. Paris: Gauthier-Villars et Cie., 1919. Price: \$3.50 francs.—In 1878 Willard Gibbs published in the *American Journal of Science* what he called an abstract of his large paper which appeared the year before in the *Transactions of the Connecticut Academy*. This has now been translated into French by M. Matisse who has added fifty-eight pages of notes to the forty-one pages of text. Even with this help people will find the text hard reading. One is inclined to suspect that the translator felt the same way, because he has not dug out of the text anything new and yet one is quite certain that there must be treasures in the text which will be discovered independently.

*Wilder D. Bancroft*

## COAGULATION OF MANGANESE DIOXIDE SOL BY DIFFERENT ELECTROLYTES

BY PHANI BHUSAN GANGULY AND N. R. DHAR

### Introduction

The relations between the valency of ions and their coagulative powers, have formed the subject of a large number of investigations for a long time. Experiments on these lines led to the generalization known as the Schulze-Hardy Law, viz., the higher the valency of an ion, the greater is its precipitating action. The researches of Linder and Picton<sup>1</sup> on colloidal arsenious sulphide lent powerful corroboration to this law.

Later investigations in this direction show that the law is not followed by many colloidal solutions. Though the values obtained by Linder and Picton show a close agreement with the rule of valency, they are by no means completely free from discrepancies. Bancroft,<sup>2</sup> after a critical survey of the researches of various investigators, has come to the conclusion that the Schulze-Hardy Law is at best only a first approximation and should be used only as a guide. Wo. Ostwald<sup>3</sup> also does not believe in the Schulze-Hardy Law.

In the following experiments the coagulative powers of different electrolytes on manganese dioxide sol have been determined with a view to test the applicability of the rule of valency to this colloid. The variations of the coagulative powers with change of concentration of the sol are so marked that no conclusion can be drawn as to the applicability of the Schulze-Hardy Law by a comparison of the coagulative powers of electrolytes unless the concentration of the colloid is taken into consideration. If we neglect the influence of concentration of the colloid, there seems to be no common standard by

<sup>1</sup> Jour. Chem. Soc., 67, 63 (1895).

<sup>2</sup> Second Report on Colloid Chemistry, British Association, 1918, 8.

<sup>3</sup> See Zeit. Kolloidchemie, 26, 28, 69 (1920).

which to compare the precipitating powers of different electrolytes. The variations of the coagulative powers of different electrolytes with variation in the concentration of the sol, have also been studied and curves have been plotted showing the relations between the concentrations of the sol and the coagulative powers.

#### Preparation of the Sol

The preparation of a sol of manganese dioxide completely free from electrolytes is a matter of great difficulty. Gorgeu<sup>1</sup> and also Spring<sup>2</sup> and De Boeck<sup>3</sup> obtained colloidal manganese dioxide by washing a freshly precipitated sample with conductivity water. Although the above process might be capable of yielding a small quantity of the colloid, it can never be used for the preparation of any large amount, because manganese dioxide has been found to show quite a considerable percentage of adsorption of metallic ions and it has been found extremely difficult to wash away all traces of the adsorbed ions.

The most suitable means for the preparation of the colloid is the reduction of potassium permanganate by suitable reducing agents. Deiss<sup>3</sup> used sodium arsenite but a rapid and convenient method seems to be the reduction of potassium permanganate by an equivalent solution of manganous sulphate. The reaction takes place in the following manner:  $2\text{KMnO}_4 + 3\text{MnSO}_4 + 7\text{H}_2\text{O} = 2\text{KHSO}_4 + 5\text{MnO}_2 + \text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}$ . In dilute solutions the manganese dioxide separates out in a colloidal form, which, however, coagulates if kept for a long time. If, however, a stabilizer like gelatine be used, a fairly stable colloidal solution can be obtained which keeps unprecipitated for a sufficiently long time and is quite satisfactory for all practical purposes. It contains, however, sulphuric acid and potassium sulphate. Sulphuric acid has been found to have no marked coagulative effect. Attempts were made to remove the electrolytes by

<sup>1</sup> Ann. Chim. Phys., (3) 66, 155 (1862).

<sup>2</sup> Bull. Soc. chim. Paris, (2) 48, 170 (1887).

<sup>3</sup> Zeit. Kolloidchemie, 6, 69 (1910).

dialysis, but the sol was found to be precipitated on the parchment of the dialyzer and even when coagulation was checked by the addition of larger quantities of the stabilizer (gelatine solution) the sol after dialysis was rendered more unstable than before dialysis.

500 cc of a N/60 solution of potassium permanganate was taken in a beaker. 500 cc of a solution of manganous sulphate, containing 0.428 g of anhydrous manganous sulphate, (which is equivalent to the amount of permanganate used) was taken in another beaker. 6 cc of a 5% solution of gelatine were added to each of the two solutions, which were simultaneously poured in thin streams into a larger beaker. A reddish brown sol was obtained which contained 0.725 g of manganese dioxide per litre. The charge on the sol was found to be negative.

#### Experimental

2 N solutions of potassium nitrate, potassium iodide, potassium chlorate, potassium chloride, potassium hydroxide, sodium citrate, sodium chloride, sodium hydroxide, ammonium chloride, silver nitrate, copper chloride, copper sulphate calcium, strontium and barium chlorides, cadmium chloride, cadmium nitrate, nickel chloride, nickel nitrate, nickel sulphate, cobalt chloride, cobalt nitrate, cobalt sulphate, lead nitrate, zinc sulphate, aluminium sulphate, ferric chloride, potassium ferrocyanide, potassium ferricyanide, soda alum and N/3 solution of mercuric chloride were prepared. 25 cc of the colloidal solution were placed in clean boiling-tubes which were all labelled each for a particular electrolyte. 5 cc of each of the electrolytes were taken in clean test-tubes which were also labelled. The solutions of the electrolytes were added to the colloid, the two were rapidly but thoroughly mixed and the time taken for complete coagulation was noted in each case. These times give the order of the coagulative powers. The results are given in the following table:

TABLE I

Salt	Time, mins.	Salt	Time, mins.	Salt	Time, mins.
KNO <sub>3</sub>	30	CuSO <sub>4</sub>	95	CoSO <sub>4</sub>	>300
KI	20	CaCl <sub>2</sub>	73	Pb(NO <sub>3</sub> ) <sub>2</sub>	49
KClO <sub>3</sub>	33	SrCl <sub>2</sub>	105	ZnSO <sub>4</sub>	80
KCl	70	BaCl <sub>2</sub>	>300	HgCl <sub>2</sub>	>300
KOH	3	CdCl <sub>2</sub>	85	Soda alum	232
NaCit	28	Cd(NO <sub>3</sub> ) <sub>2</sub>	82	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	>300
NaCl	45	NiCl <sub>2</sub>	>300	FeCl <sub>3</sub>	>300
NaOH	3	Ni(NO <sub>3</sub> ) <sub>2</sub>	>300	K <sub>3</sub> Fe(CN) <sub>6</sub>	55
NH <sub>4</sub> Cl	108	NiSO <sub>4</sub>	150	K <sub>4</sub> Fe(CN) <sub>6</sub>	28
AgNO <sub>3</sub>	59	CoCl <sub>2</sub>	>300		
CuCl <sub>2</sub>	90	Co(NO <sub>3</sub> ) <sub>2</sub>	142		

From the above table the following order for coagulative powers is obtained:

KOH, NaOH > KI > K<sub>4</sub>Fe(CN)<sub>6</sub>, NaCit > KNO<sub>3</sub> > KClO<sub>3</sub> > NaCl > Pb(NO<sub>3</sub>)<sub>2</sub> > K<sub>3</sub>Fe(CN)<sub>6</sub> > AgNO<sub>3</sub> > KCl > CaCl<sub>2</sub> > ZnSO<sub>4</sub> > Cd(NO<sub>3</sub>)<sub>2</sub> > CdCl<sub>2</sub> > CuCl<sub>2</sub> > CuSO<sub>4</sub> > SrCl<sub>2</sub> > NH<sub>4</sub>Cl > Co(NO<sub>3</sub>)<sub>2</sub> > NiSO<sub>4</sub> > Soda Alum > BaCl<sub>2</sub>, HgCl<sub>2</sub>, NiCl<sub>2</sub>, CoCl<sub>2</sub>, FeCl<sub>3</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

The above procedure only gives in a qualitative way the order of the coagulative powers. To get the values of the coagulative powers, the minimal quantity of electrolyte necessary for complete coagulation of a fixed volume of the sol in two hours was determined in every case. The titration method for determination of the coagulative powers was not suitable in this case, because it was found that after the addition of a certain amount of electrolyte, the sol became so unstable that complete coagulation could always be brought about by mere shaking and consequently it was not possible to get a sharp end-point. The minimal quantity of electrolyte necessary for complete coagulation of 25 cc of the sol in two hours, was determined as the result of several trial experiments. We have taken the coagulative powers as the inverse of the number of gram-mols of electrolyte per litre of the mixture.

The following results were obtained.

TABLE II  
 Strength of sol = 0.725 g of MnO<sub>2</sub> per litre (A)  
 Weight of gelatine added = 0.36 g per litre  
 Temp. = 30° C

Salt	Vol. added, cc	Time for complete coagulation, mins.	Coagulative power
KOH	0.1	108	130
KNO <sub>3</sub>	1.8	112	7.5
KI	0.3	109	44
KClO <sub>3</sub>	2.8	114	5
KCl	2.8	112	5
K <sub>2</sub> SO <sub>4</sub> (N)	3.2	119	17.9
NaCit	2.7	115	5.2
NaCl	2.5	113	5.5
NaOH	0.08	87	170
NH <sub>4</sub> Cl	4.2	117	3.5
AgNO <sub>3</sub>	3.9	114	3.7
CuCl <sub>2</sub>	—	—	—
CuSO <sub>4</sub>	6.0	107	9.3
CaCl <sub>2</sub>	2.9	112	18.7
SrCl <sub>2</sub>	8.6	121	8
BaCl <sub>2</sub>	12.7	124	5.9
CdCl <sub>2</sub>	5.2	112	11.6
Cd(NO <sub>3</sub> ) <sub>2</sub>	5.0	115	12
NiSO <sub>4</sub>	12.0	116	6.1
Ni(NO <sub>3</sub> ) <sub>2</sub>	10.5	117	6.8
CoCl <sub>2</sub>	15.0	Insufficient	—
Co(NO <sub>3</sub> ) <sub>2</sub>	10.2	123	5
Pb(NO <sub>3</sub> ) <sub>2</sub>	2.9	125	19.2
ZnSO <sub>4</sub>	4.0	111	14.5
HgCl <sub>2</sub> (N/3)	14.0	127	16.7
Soda alum	6.5	130	14.6
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	10.0	133	10.5
FeCl <sub>3</sub>	15.0	Insufficient	—
K <sub>4</sub> Fe(CN) <sub>6</sub>	0.6	124	170.7
K <sub>3</sub> Fe(CN) <sub>6</sub>	2.2	116	37.2

### Discussion of Results

An examination of Table II gives the following order for the coagulative powers of different cations on manganese dioxide sol:

$K_4Fe(CN)_6$ , NaOH > KOH > KI >  $K_3Fe(CN)_6$  >  $Pb(NO_3)_2$  >  $CaCl_2$  >  $K_2SO_4$  >  $HgCl_2$  > Soda Alum,  $ZnSO_4$  >  $Cd(NO_3)_2$  >  $CdCl_2$  >  $Al_2(SO_4)_3$  >  $CuSO_4$  >  $SrCl_2$  >  $KNO_3$  >  $Ni(NO_3)_2$  >  $NiSO_4$  >  $BaCl_2$  > NaCl > NaCit > KCl,  $KClO_3$ ,  $Co(NO_3)_2$  >  $AgNO_3$  >  $NH_4Cl$ .

From the above results we see that monovalent potassium ions from potassium iodide and potassium sulphate, have greater coagulative powers than most of the divalent and trivalent ions. Potassium ion from potassium nitrate has also a coagulative power which is greater than those of divalent nickel, cobalt and barium ions. Again divalent lead, calcium and mercuric ions have greater coagulative powers than trivalent aluminium ion. Trivalent aluminium ion from aluminium sulphate comes in between divalent cadmium and copper while divalent cobalt occurs along with the monovalent ions. These results are quite opposed to the Schulze-Hardy Law.

The coagulative powers of divalent lead, calcium, zinc, mercury (mercuric), cadmium, and copper ions are greater than the coagulative powers of most of the monovalent ions; the trivalent aluminium ion from soda alum has a greater coagulative power than most of the divalent ions; and the greater part of the monovalent ions occur at about the end, and so far a tendency to follow the Schulze-Hardy Law is observable. But even in the above cases the differences in the values of the coagulative powers of trivalent and divalent ions is very small, trivalent aluminium ion having a value 14.6 and the majority of the divalent ions having values varying from 14 to 6.

From the experimental data of Table II, we also find that potassium ion from potassium nitrate has a coagulative power about 1.5 times greater than the coagulative powers of cobalt, nickel and barium ions, a result which it is difficult to reconcile with the Schulze-Hardy Law.

The coagulative power of potassium iodide has been found to be about eight times greater than that of either nickel or cobalt. We have observed that a solution of iodine has a marked coagulating effect on manganese dioxide sol and this behavior explains partly the abnormally high coagulative power of potassium iodide. Manganese dioxide easily oxidizes the potassium iodide liberating iodine, which then exerts its coagulating effects.

The chlorides of cobalt, nickel and iron (ferric) have been found to possess low coagulative powers, being less than one-third the coagulative power of lead nitrate. The exact coagulative powers of the above electrolytes were not determined as the conditions of the experiment were greatly altered by the large volumes of the electrolytes required for coagulation and the consequent dilution of the sol.

Manganese dioxide has been found to be a negatively charged colloid. Now on the addition of an electrolyte to it, the positive charge of the cations neutralizes the negative charge on the colloid particles. These discharged colloid particles, which previously owing to their similar charges, were prevented from coalescing, now do so and growing in size get precipitated. This coalescence of discharged colloid particles is clearly seen in the changes of colour during the gradual coagulation of a gold sol by electrolytes. So far, however, the effects of the cations only have been considered, the effects of the anions being altogether neglected; but in view of the marked differences in the coagulative powers of electrolytes having the same cation with manganese dioxide sol, the effects of anions cannot certainly be neglected. The anions tend to impart a portion of their negative charges to the discharged colloid particles before they have coalesced, and thus try to oppose the coagulative effects of the cation.

Linder and Picton<sup>1</sup> have found the ratio between the coagulative powers of mono-, di-, and trivalent ions to be as 1:35:1023, which values agree well with the geometric series of Whetham,<sup>2</sup>

<sup>1</sup> Loc. cit.

<sup>2</sup> Phil. Mag., (5) 48, 474 (1899).



viz., 1:x:x obtained from considerations based on the theory of probability. With manganese dioxide sol, taking the cases of potassium chloride, cadmium chloride and alum, the ratio between the coagulative powers of mono-, di-, and trivalent ions comes to about 1:2:3. It might be noted here that Whetham's law is not capable of extension to quadrivalent ions.

We have found the order of the coagulative powers of potassium, copper, aluminium, thorium and uranium ions on colloidal arsenious sulphide to be in the ratio of 1 : 16 : 600 : 60 : 11 which shows that quadrivalent ions do not follow Whetham's law. Freundlich and Schucht<sup>1</sup> have also found the coagulative power of uranyl ion to be of the same order as of divalent calcium or strontium ions in the coagulation of arsenious sulphide sol.

From our experimental results it will be observed that the change of concentration of the sol changes markedly the order of the coagulative powers of the electrolytes. The orders of the coagulative powers as obtained from Tables II, III and IV are all different from one another. Thus Table II gives the order:

$K_4Fe(CN)_6, NaOH > KOH > KI > K_3Fe(CN)_6 > Pb(NO_3)_2 > CaCl_2 > K_2SO_4 > HgCl_2 > Soda Alum > ZnSO_4 > Cd(NO_3)_2 > CdCl_2 > Al_2(SO_4)_3 > CuSO_4 > SrCl_2 > KNO_3 > Ni(NO_3)_2 > NiSO_4 > BaCl_2 > NaCl > NaCit > KCl, KClO_3, Co(NO_3)_2 > AgNO_3 > NH_4Cl,$

while Table III gives the order:

$NaOH > K_4Fe(CN)_6 > KOH > KI > K_3Fe(CN)_6 > CuSO_4 > HgCl_2 > Cd(NO_3)_2 > K_2SO_4 > CdCl_2 > Pb(NO_3)_2 > ZnSO_4 > CaCl_2, CuCl_2 > Co(NO_3)_2 > KNO_3 > NaCl, KClO_3 > NaCit > SrCl_2 > BaCl_2 > NH_4Cl > KCl > AgNO_3$

and Table IV gives yet another order:

$K_4Fe(CN)_6 > KOH > KI > K_3Fe(CN)_6, CaCl_2 > CdCl_2 > Cd(NO_3)_2 > CuSO_4 > KNO_3 > HgCl_2 > K_2SO_4 > CuCl_2 > Pb(NO_3)_2 > ZnSO_4 > Soda Alum > KClO_3, KCl > NaCl > Co(NO_3)_2 > SrCl_2 > NaCit, NH_4Cl > BaCl_2 > AgNO_3.$

<sup>1</sup> Zeit. phys. Chem., 80, 564 (1912).

From a comparison of the above three orders we see that while in Tables II and IV, calcium chloride occurs 7th and 5th, respectively, in Table III it occurs 13th, whereas lead nitrate which occurs 6th in Table II, occupies 11th and 13th positions, respectively, in Tables III and IV. Similar

TABLE III

Strength of sol = 1.450 g of MnO<sub>2</sub> per litre (2A)

Weight of gelatine added = 0.72 g per litre

Temp. = 32° C

Salt	Vol. added, cc	Time for complete coagulation, mins.	Coagulative power
KOH	0.1	127	120
KNO <sub>3</sub>	1.2	139	10.9
KI	0.16	107	88
KClO <sub>3</sub>	1.7	124	7.8
KCl	3.2	121	4.4
K <sub>2</sub> SO <sub>4</sub> (N)	1.5	130	17.7
NaCit	1.8	117	7.5
NaCl	1.7	115	7.8
NaOH	0.08	94	627
NH <sub>4</sub> Cl	2.5	127	5.5
AgNO <sub>3</sub>	4.4	121	3.3
CuCl <sub>2</sub>	4.2	123	14
CuSO <sub>4</sub>	2.5	115	22
CaCl <sub>2</sub>	4.2	131	14
SrCl <sub>2</sub>	10.0	127	7
BaCl <sub>2</sub>	13.0	124	5.8
CdCl <sub>2</sub>	3.2	118	17.6
Cd(NO <sub>3</sub> ) <sub>2</sub>	3.0	112	18.7
NiSO <sub>4</sub>	10.0	Insufficient	—
Ni(NO <sub>3</sub> ) <sub>2</sub>	10.0	Insufficient	—
CoCl <sub>2</sub>	10.0	Insufficient	—
Co(NO <sub>3</sub> ) <sub>2</sub>	4.5	120	13.1
Pb(NO <sub>3</sub> ) <sub>2</sub>	3.4	113	16.7
ZnSO <sub>4</sub>	3.7	119	15.5
HgCl <sub>2</sub> (N/3)	11.9	134	18.8
Soda alum	—	—	—
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	—	—	—
FeCl <sub>3</sub>	15.0	Insufficient	—
K <sub>4</sub> Fe(CN) <sub>6</sub>	0.3	117	337
K <sub>3</sub> Fe(CN) <sub>6</sub>	1.5	112	53

TABLE IV

Strength of sol = 0.3625 g of  $\text{MnO}_2$  per litre (A/2)  
 Weight of gelatine added = 0.18 g per litre  
 Temp. =  $31.4^\circ\text{C}$

Salt	Vol. added, cc	Time for complete coagulation, mins.	Coagulative power
KOH	0.095	132	125
$\text{KNO}_3$	0.4	111	32
KI	0.13	117	96
$\text{KClO}_3$	1.0	122	13
KCl	1.0	113	13
$\text{K}_2\text{SO}_4(\text{N})$	1.2	121	20.9
NaCit	1.5	123	8.8
NaCl	1.1	118	12
NaOH	—	—	—
$\text{NH}_4\text{Cl}$	1.5	126	8.8
$\text{AgNO}_3$	3.3	127	4.3
$\text{CuCl}_2$	2.9	125	19.2
$\text{CuSO}_4$	1.6	125	33.2
$\text{CaCl}_2$	1.0	113	52
$\text{SrCl}_2$	6.7	121	9.5
$\text{BaCl}_2$	10.5	121	6.7
$\text{CdCl}_2$	1.3	116	40.5
$\text{Cd}(\text{NO}_3)_2$	1.5	119	35.3
$\text{NiSO}_4$	—	—	—
$\text{Ni}(\text{NO}_3)_2$	10.0	Insufficient	—
$\text{CoCl}_2$	12.0	Insufficient	—
$\text{Co}(\text{NO}_3)_2$	5.5	131	11.1
$\text{Pb}(\text{NO}_3)_2$	2.8	126	19.1
$\text{ZnSO}_4$	3.0	117	18.9
$\text{HgCl}_2(\text{N}/3)$	9.5	124	21.5
Soda alum	6.5	137	14.5
$\text{Al}_2(\text{SO}_4)_3$	—	—	—
$\text{FeCl}_3$	15.0	Insufficient	—
$\text{K}_4\text{Fe}(\text{CN})_6$	0.5	121	204
$\text{K}_3\text{Fe}(\text{CN})_6$	1.2	123	65.5

fluctuations are also noticeable in the case of potassium chloride, etc. All these show clearly the importance of the concentration of the sol on the order of the coagulative powers of electrolytes.

The changes in the coagulative powers of ions with change of concentration of the sol is shown in Table V. An examina-

TABLE V  
Showing Variations of Coagulative Power with Changes of Concentration of the Sol

Salt	Concentration of sol = A/2 (0.3625 g of MnO <sub>2</sub> per litre) Coagulative powers	Concentration of sol = A (0.725 g of MnO <sub>2</sub> per litre) Coagulative powers	Concentration of sol = 2A (1.450 g of MnO <sub>2</sub> per litre) Coagulative powers
KOH	125	130	120
KNO <sub>3</sub>	32	7.5	10.9
KI	96	44	88
KClO <sub>3</sub>	13	5	7.8
KCl	13	5	4.4
K <sub>2</sub> SO <sub>4</sub> (N)	20.9	17.9	17.7
NaCit	8.8	5.2	7.5
NaCl	12	5.5	7.8
NaOH	—	170	627
NH <sub>4</sub> Cl	8.8	3.5	5.5
AgNO <sub>3</sub>	4.3	3.7	3.3
CuCl <sub>2</sub>	19.2	—	14
CuSO <sub>4</sub>	33.2	9.3	22
CaCl <sub>2</sub>	52	18.7	14
SrCl <sub>2</sub>	9.5	8	7
BaCl <sub>2</sub>	6.7	5.9	5.8
CdCl <sub>2</sub>	40.5	11.6	17.6
Cd(NO <sub>3</sub> ) <sub>2</sub>	35.3	12	18.7
Co(NO <sub>3</sub> ) <sub>2</sub>	11.1	5	13.1
Pb(NO <sub>3</sub> ) <sub>2</sub>	19.1	19.2	16.7
ZnSO <sub>4</sub>	18.9	14.5	15.5
HgCl <sub>2</sub> (N/3)	21.5	16.7	18.8
Soda alum	14.5	14.6	—
K <sub>4</sub> Fe(CN) <sub>6</sub>	204	170.7	337
K <sub>3</sub> Fe(CN) <sub>6</sub>	65.5	37.2	53

tion of the graphs plotted from this table reveals many interesting points.

It has been found that the coagulative powers of the monovalent ions, potassium, sodium and ammonium from potassium iodide, sodium chloride and ammonium chloride

with increase of the concentration of the sol first decrease and then increase. To take the case of potassium iodide when the concentration of the sol is  $A/2$  (i. e., contains 0.3625 g of  $MnO_2$  per litre), the coagulative power is 96, as the concentration is doubled and becomes  $A$ , the coagulative power falls to 44, but again rises to double this value, viz., 88, as the concentration of the sol becomes double, viz.,  $2A$ . Potassium iodide, sodium

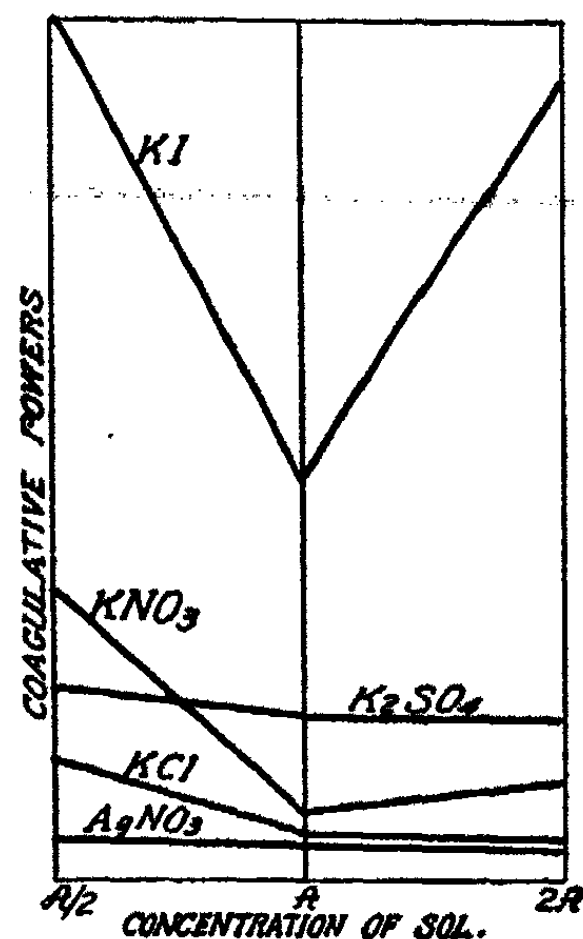


Fig. 1

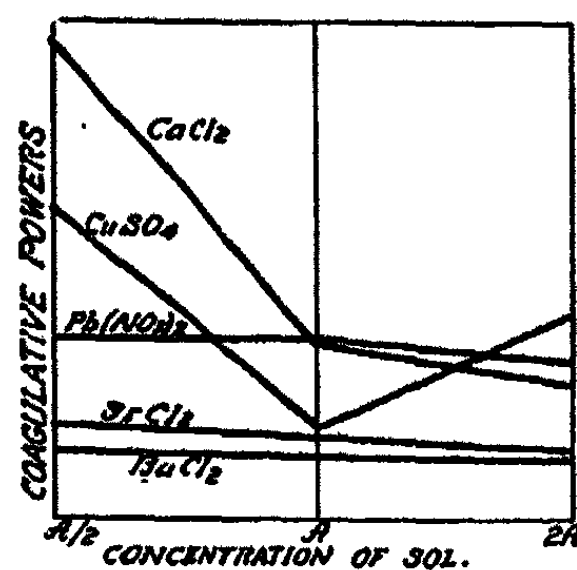


Fig. 2

chloride, ammonium chloride, and potassium nitrate, all behave in the same manner as potassium iodide, having a minimum coagulative power when the concentration of the sol is  $A$ . In the cases of potassium chloride, silver nitrate and potassium sulphate, with continual increase of the concentration of the sol, the coagulative power decreases gradually, Fig. 1.

Unkherji<sup>1</sup> found that the precipitation value of sodium chloride increased with decreasing concentration of arsenious

<sup>1</sup> Jour. Amer. Chem. Soc., 37, 2024 (1915).

sulphide sol; Kruyt<sup>1</sup> obtained the same relation in the case of potassium chloride as well. Burton<sup>2</sup> and his coworkers as a result of their investigations came to the generalization that for monovalent ions, the concentration of ion necessary for coagulation increases with decreasing concentration of the colloid.

In the light of our results obtained with manganese dioxide sol, the above generalization of Burton and his coworkers does not seem to be applicable in all cases. Thus in the cases of potassium iodide, sodium chloride, potassium nitrate, etc., the coagulative power first decreases and then increases with continual increase of concentration of the sol, a result which is not in agreement with the above generalization. In the cases of potassium chloride, silver nitrate, and potassium sulphate, however, the coagulative powers increase with decrease of concentration of the sol and these results agree with Burton's observations. But even in the above cases the difference in the coagulative powers is very small, the values of the coagulative powers in the case of silver nitrate might be looked upon as nearly constant with change of concentration of the sol.

Among the divalent ions with increase of concentration of the sol, the coagulative powers of mercury, cobalt, cadmium and copper ions first decrease and then increase. Thus in the case of copper sulphate, the coagulative power falls from 32 to 9.3 as the concentration of the sol increases from  $A/2$  to  $A$ , Fig. 2. On further increase of concentration of the sol from  $A$  to  $2A$ , the coagulative power increases from 9.3 to 22. In the cases of calcium, barium, strontium and lead ions, the coagulative powers decrease continually with increase of concentration of the sol. The range through which the coagulative powers of strontium, barium, lead, zinc and mercuric ions vary with change of concentration of the sol, is not very wide. In fact it may be taken as nearly constant in the cases of barium, strontium and lead ions. The difference in the highest

<sup>1</sup> Zeit. Kolloidchemie., 25, 3 (1919).

<sup>2</sup> Jour. Phys. Chem., 24, 701 (1920); 25, 517 (1921).

and lowest coagulative powers of barium ion is 0.9, of lead ion is 2.4, of strontium ion is 2.5, of zinc ion is 4.4 and mercuric ion is 5.2. In this respect barium and to a certain extent strontium and lead tend to follow the generalization of Burton and his coworkers, viz., the coagulative powers of divalent ions remain constant with change of concentration of the sol.

With trivalent aluminium ion as the concentration of the sol is doubled, there is a slight increase in the coagulative power of the ion. In the cases of potassium ferro- and ferricyanides, with increase of concentration of the sol, the coagulative power first decreases and then increases.

Sodium and potassium hydroxides have very great coagulating effects on manganese dioxide sol.

#### **Summary and Conclusion**

The determination of the coagulative powers of different electrolytes on manganese dioxide sol, shows that the Schulze-Hardy Law is only partially applicable to this sol.

Change of concentration of the sol markedly changes the order of the coagulative power of electrolytes on this sol. Our work on manganese dioxide sol thus leads us to the view that valency is by no means the chief criterion in determining the activity of ions in coagulating colloidal solutions. The coagulative power of the ions seems more a specific property of the ions, than purely a function of their valency.

The influences of the anions, the time allowed for coagulation, and the concentration of the colloidal solution have been found to be very marked on the coagulative powers of ions.

*Chemical Laboratory  
Muir Central College  
Allahabad, India  
May 4, 1922*

1-1768

## CATALYTIC ACTIVITY OF COPPER

BY O. W. BROWN AND C. O. HENKE

### Introduction

In a previous paper<sup>1</sup> we have given the results of some studies on the catalytic reduction of nitrobenzene to aniline by hydrogen in the presence of nickel and copper catalysts. The catalysts were prepared by ignition of the nitrate and reduction of the oxide by hydrogen. Sabatier states<sup>2</sup> that a copper catalyst prepared from an ignited nitrate is only moderately active. He also states that a catalyst prepared by precipitating the oxide from the nitrate by sodium hydroxide and reducing in hydrogen is an excellent catalyst. The latter he describes as being violet and the former red. In this paper we shall give the results of some studies with copper catalysts prepared by reduction of the precipitated oxide.

### Experimental Details

The apparatus used, method of work and analysis was the same as that described in a previous paper. In all the experiments a glass combustion tube was used instead of the iron pipe.

### Purification of Copper

Some preliminary experiments indicated that the purity of the copper nitrate had a very large influence upon the activity of a copper catalyst prepared from the ignited oxide. Small amounts of iron seemed to have a beneficial effect, by preventing the copper catalyst from losing its activity. In order to get a pure copper, c. p. copper sulphate was dissolved in water, some sulphuric acid added, and the solution electrolyzed using graphite anodes and thin sheets of copper for cathodes. This electrolytically precipitated copper was used as anode in a nitric acid electrolyte, the cathode being a sheet

<sup>1</sup> Brown and Henke: Jour. Phys. Chem., 26, 160 (1922).

<sup>2</sup> Sabatier: "La Catalyse," 106 (1913).



of copper covered with a thin film of vaseline. After the electrolysis the precipitated copper was broken off the original sheet of copper (the cleavage being possible because of the film of vaseline). The pure pieces of copper (140 grams) were then dissolved in nitric acid and the solution diluted to 500 cc. All the copper catalysts used in the experiments for this paper were prepared from this stock solution of pure copper nitrate.

#### Experimental Results

A 45-cc portion of this nitric acid solution of copper nitrate, containing 12.6 grams of copper, was diluted to 500 cc, heated to boiling and precipitated with a boiling hot solution of sodium hydroxide. To get a pure sodium hydroxide, metallic sodium was dissolved in water and the solution boiled and filtered. The hydroxide contained considerable carbonate. The precipitated copper hydroxide was filtered, washed and dried. Thirteen grams of the dry oxide was used as catalyst and placed in the same place in the catalyst tube as in our previous work. This was reduced at 260° by passing hydrogen over the catalyst at the rate of 10 liters per hour for 1<sup>3</sup>/<sub>4</sub> hours. The zone in which reduction was taking place became heated to a higher temperature due to the fact that the reduction is an exothermic reaction. When the zone of reduction reached the thermocouple (after a reduction of about a half hour) the temperature as indicated by the millivoltmeter rose in a few

TABLE I  
Temperature of catalyst—260° C.  
Rate of flow of nitrobenzene—3.9 grams per hour.

Hydrogen in liters per hour	Excess of hydrogen in % of theory	Material yield of aniline in % of theory
3.5	64	97.0
7	230	97.0
14	560	97.4
25	1070	92.6
35	1540	92.6
52	2340	86.3

minutes from 260° to 312° and after a short time dropped back again to 260°. This catalyst immediately gave constant results when used. The average deviation from the mean of the first five experiments was 0.4%. The results showing the effect of rate of flow of hydrogen with this catalyst are given in Table I.

The results of Table I are shown graphically in Curve Cu-A of Fig. 1. The results show that the slower the rate of flow of hydrogen the higher the aniline yield until very slow rates are reached. For purposes of comparison Curve Cu-B is redrawn from a previous paper in which the catalyst was prepared from an ignited nitrate. In the experiments represented by Curve Cu-B the rate of flow of nitrobenzene was the

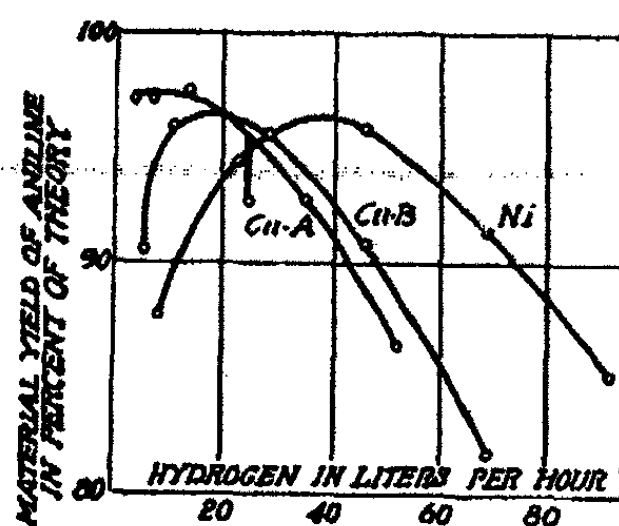


Fig. 1

same as in Cu-A. The curve for Ni is also redrawn from the same paper. The rates of flow of hydrogen as shown by curves Cu-B and Ni are probably a little too high since no glass-wool tube was used to remove the particles of sulphuric acid which were mechanically carried out of the sulphuric acid bottle. Above 20 liters of hydrogen per hour the two curves Cu-A and Cu-B are very similar but below this value they are different. Thus Cu-B gives a yield of only 90.5% at 5.7 liters per hour while Cu-A gives 97% material yields of aniline at 15 liters hydrogen per hour and does not drop even when the hydrogen flow is decreased to 3.5 liters per hour. The experiments of Curve Cu-B were carried out in the iron tube while those of Cu-A were carried out in a glass tube. However, experiments performed with a catalyst from an ignited nitrate in a glass tube show a similar decrease in yield with low rates of hydrogen flow as will be shown in Table II. This indicates that the best ratio of hydrogen to nitrobenzene for one copper catalyst

may not be the best for another copper catalyst prepared in a different way.

The decrease in yield with low hydrogen rates, with nickel as catalyst, is not due to incomplete reduction as in the case of the copper catalyst. At the lower hydrogen rates with the nickel as catalyst the product was colorless, a part of the nitrobenzene probably being reduced farther than the aniline stage, resulting in a low yield of aniline. It was impracticable with the apparatus employed to use lower hydrogen rates than 3.5 liters per hour. Even at this rate the nitrobenzene was not all carried into the furnace as soon as it was forced through the capillary into the catalyst tube, but it would drop onto the tube and then due to capillary action would tend to creep back between the capillary and the wall of the combustion tube toward the inlet end of the furnace. Pushing the capillary farther into the furnace overcomes this difficulty but then the nitrobenzene soon chars in the hot capillary and clogs it.

In our previous study of the catalytic activity of copper catalysts prepared from the ignited nitrate, ordinary c. p. copper nitrate was used, traces of iron, sulphates and chlorides being present. Also the catalysts were used in an iron tube instead of a glass tube. In Table II are given the results with two catalysts prepared from an ignited nitrate (produced from the double refined copper) and used in a glass tube. The nitrate (for both catalyst A22 and A25) was ignited in an electrically heated muffle, the temperature being allowed to rise to 420° C. About 26 grams of the ignited oxide were used for each catalyst and this was reduced with the rate of flow of hydrogen at about 4 liters per hour. In the first column are given the results with the catalyst from the pure nitrate (catalyst A22). The temperature during reduction of this catalyst rose to 295° C. In the second column are given the results with catalyst A25, which was prepared from the pure nitrate to which had been added an amount of ferric nitrate equivalent to 0.015% Fe in  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . This would make the iron content of the reduced copper catalyst equal to

0.069% Fe. The results with each catalyst are given in the order in which they were carried out.

TABLE II

Temperature of catalyst—260° C.  
Rate of flow of nitrobenzene—4 grams per hour.  
Rate of flow of hydrogen—14 liters per hour.  
Excess of hydrogen—540%.

Catalyst No. A22 (Pure)		Catalyst No. A25 (0.069% Fe)	
Material yield of aniline in % of theory		Material yield of aniline in % of theory	
94.3	60.8 <sup>1</sup>	95.3	93.2
93.6	37.8 <sup>2</sup>	93.6	92.9
87.3		94.3	64.9 <sup>2</sup>
		90.6	

<sup>1</sup> Rate of flow of hydrogen in this experiment was 9.3 liters per hour.

<sup>2</sup> Rate of flow of hydrogen in these two experiments was 4.6 liters per hour.

The results of Table II indicate that a catalyst prepared from the ignited oxide of a pure copper nitrate and used in a glass tube is not as good a catalyst for the reduction of nitrobenzene to aniline as a copper catalyst prepared from the precipitated hydroxide. Thus the highest yield with catalyst A22 was 94.3%, which decreased rapidly with use to 87.3% in the third experiment while the copper catalyst of Table I (which was prepared from the precipitated hydroxide) gave 97% yields of aniline when used under practically the same conditions. The addition of a small amount of iron seems to be very beneficial. Thus catalyst A25 (from nitrate containing 0.015% Fe) for the first six experiments averaged 93.3% aniline yields while catalyst A22 (from the pure nitrate) decreased to but 87.3% in the third experiment. Catalysts A22 and A25 both gave good yields in the first experiments. It will also be noted that with each of the catalysts from the ignited nitrate when the rate of flow of hydrogen was decreased to 4.6 liters per hour the yield of aniline decreased tremendously the yield with catalyst A25 decreasing from an average of 93.3% with the hydrogen flow at 14 liters per hour to 64.9%

with the hydrogen flow at 4.6 liters per hour. With catalyst A22 when the rate of flow of hydrogen was only decreased to 9.3 liters per hour the aniline yield dropped to 60.8%. This is similar to the results with the copper catalysts from ignited nitrates when used in iron tubes as was pointed out in the discussion under Fig. 1. However, the catalyst from the precipitated oxide gave 97.5% yields of aniline even when the hydrogen flow was decreased to as low as 3.5 liters per hour.

TABLE III  
Temperature of catalyst—200° C.  
Rate of flow of hydrogen—14 liters per hour.

Nitrobenzene in grams per hour	Excess of hydrogen in %	Material yield of aniline in % of theory
3.0	560	97.4
6.3	300	96.5
9.3	170	92.6
17.4	50	80.2

The effect of rate of flow of nitrobenzene with a copper catalyst from a precipitated oxide was studied with the same

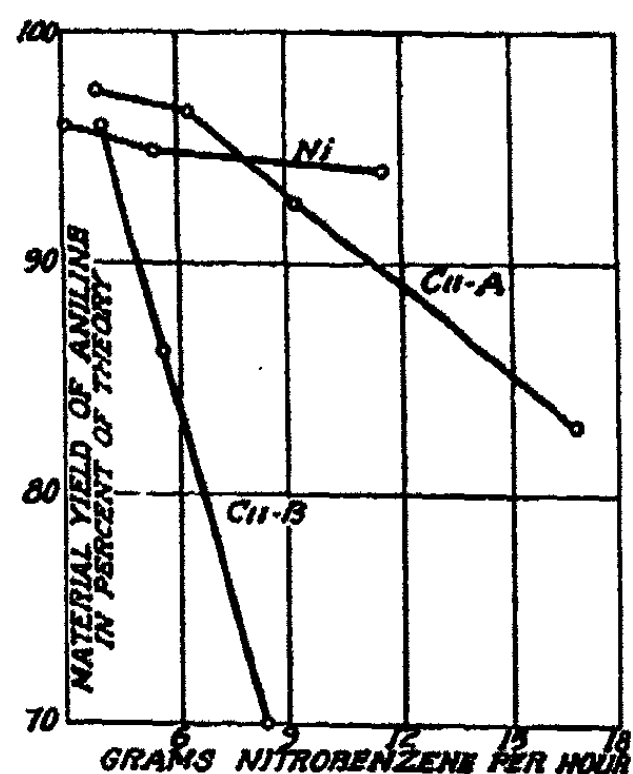


Fig. 2

the best rate for that catalyst. The curve for Ni is also redrawn from the same paper the hydrogen rate in this case being

catalyst that was used for the experiments of Table I. The results of several experiments at different rates of flow of nitrobenzene are given in Table III.

The results of Table III are plotted in curve Cu-A of Fig. 2. For purposes of comparison, curve Cu-B is redrawn from a previous paper in which the catalyst was prepared from an ignited nitrate. The rate of flow of hydrogen for the experiments of curve Cu-B was 11.4 liters per hour which was

17 liters per hour. The graph shows that the copper catalyst from the precipitated oxide is capable of carrying on the reduction of the nitrobenzene at a much greater rate than the copper catalyst from the ignited oxide. Up to 7.5 grams nitrobenzene per hour the catalyst from the precipitated copper oxide gives higher yields than the nickel catalyst.

The high rate at which the catalyst from the precipitated oxide is capable of carrying on the reduction and the high yields obtainable would make it superior to the catalyst from the ignited nitrate for commercial purposes. The higher yields obtainable would probably make it superior to the nickel catalyst up to about 8 grams nitrobenzene per hour, while with higher rates of nitrobenzene the nickel would be superior.

The copper catalyst from the precipitated oxide gave constant yields immediately when used as was noted above. After the first few experiments with this catalyst the aniline produced seemed to be perfectly colorless as not a trace of color could be detected. However, upon titration the yield was only 97 to 98%. After a few days' use of this catalyst the product became slightly colored, but upon titration the yield was found to still be practically the same.

After about three weeks' use during which time this catalyst was used at temperatures as high as 300° C it showed a slight decrease in activity, the yields of aniline being about 3% lower than at first. When this catalyst was taken out of the furnace it had a bluish black color while the catalyst from the ignited oxide was red and more compact. Upon examining this catalyst (from the precipitated oxide) it was found to contain bright pieces of hard massive copper. Upon examining these catalysts under the microscope (with a magnification of 100 diameters) the red copper catalyst looked as though it had been subjected to incipient fusion, the mass being made up of myriads of little spheres of copper. The catalyst from the precipitated oxide did not show this sintering to as great an extent as the red copper catalyst. When some of the hard

massive particles of copper (from the catalyst from the precipitated oxide) were broken up and examined under the microscope they showed a needle-like crystalline structure. From this and also from the slightly lower yields obtained after three weeks' use it appears that the catalyst slowly loses its activity probably due to a slow agglomeration or sintering of the small particles.

The catalyst from the precipitated oxide was also used in a rather extensive study of the effect of temperature upon the reduction. For this study a rather high rate of nitrobenzene, 9.7 grams per hour, was chosen. The results of experiments under different conditions are given in Table IV.

TABLE IV  
Rate of flow of nitrobenzene—9.7 grams per hour.

Temperature, degrees C	Hydrogen in liters per hour	Excess of hydrogen in %	Material yield of aniline in % of theory
260	3.5	-35 <sup>1</sup>	73.9
260	7.0	30	90.3
260	14	160	92.6
260	25	360	92.3
260	35	550	86.6
260	52	860	78.9
279	7	30	95.9
279	14	160	91.2
279	25	360	84.9
279	35	550	82.9
298	3.5	-35 <sup>1</sup>	81.2
298	7	30	93.6
298	14	160	91.2
298	25	360	86.9
298	35	550	80.2

<sup>1</sup> In these two experiments the rate of flow of hydrogen was 35% below the theoretical amount needed.

The percentage excess of hydrogen is calculated from the rates of flow of hydrogen and nitrobenzene. However, the furnace is full of hydrogen at the beginning of an experiment and hydrogen is passed for 20 minutes or more after all the nitrobenzene has been forced into the furnace in order to wash all the material out of the furnace into the condenser.

The results of Table IV are shown graphically in Fig. 3. From the curves it is seen that 260° C is the best temperature through the greater part of the range of variation of hydrogen flow. At the lower rates of hydrogen flow, however, a temperature of 279 is better. After using the catalyst at these higher temperatures it did not give as high yields of aniline at 260 as it did before being used at the higher temperatures. This indicates that for continuous use 260 is the best temperature.

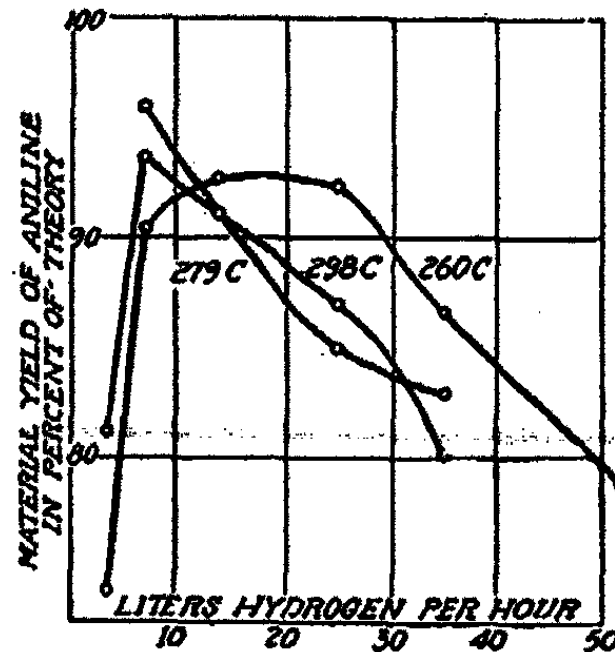


Fig. 3

An attempt was made to increase the rate at which the nitrobenzene could be reduced by precipitating the copper on a support. For this purpose some asbestos was thoroughly cleaned by boiling in  $\text{HNO}_3$ , washing and drying. This was soaked in 15 cc of the nitric acid solution of the pure copper nitrate containing 4.2 grams of copper. This was then dropped into 50 cc of boiling  $\text{NaOH}$  solution. The asbestos copper oxide was filtered, washed and dried. In this manner 4.6 grams  $\text{CuO}$  was added to 3 grams of asbestos. Five grams of this, containing 3 grams of copper oxide, was used as catalyst. Another catalyst was prepared with pumice as support. The pumice was broken up to pass a 10 mesh sieve and remain on a 20 mesh sieve. This was boiled in  $\text{HNO}_3$ , washed and dried. Ten grams of this pumice was soaked in 15 cc of the nitric acid solution of pure copper nitrate containing 4.2 grams copper. This was then dropped into 50 cc of a boiling  $\text{NaOH}$  solution. The pumice copper oxide was washed, filtered and dried. In this way 2 grams  $\text{CuO}$  was added to the pumice. Nine grams of this, containing 1.5 grams of  $\text{CuO}$ , was used as catalyst. The results with the copperized asbestos and pumice as catalyst are given in Table V.



TABLE V  
Temperature of catalyst—260° C.

Nitrobenzene in grams per hour	Hydrogen in li- ters per hour	Excess of hy- drogen in %	Material yield of aniline in % of theory (copper on asbestos)	Material yield of aniline in % of theory (copper on pumice)
3.9	9.5	350	97.0	—
3.9	14	560	98.3	99.0
3.9	25	1070	—	98.6
3.9	35	1540	95.9	—
3.9	52	2340	93.9	92.3
9.7	5	— <sup>1</sup>	70.9	—
9.7	9.5	80	97.0	—
9.7	14	160	97.9	—
9.7	35	560	92.6	—
20 <sup>2</sup>	25	120	96.3	—

<sup>1</sup> In this experiment the rate of flow of hydrogen was 6% below the theoretical amount needed.

<sup>2</sup> This was the fourth experiment with a new copper-asbestos catalyst.

The results of Table V (except the experiment in which the rate of nitrobenzene was 20 grams per hour) are shown graphically in Fig. 4. Curves Cu-3.9 and Cu-9.7 are redrawn from Figs. 1 and 3, respectively. The figures 3.9 and 9.7 refer to the rate of flow of nitrobenzene in grams per hour. Curves Cu-A-3.9 and Cu-A-9.7 refer to the copper on asbestos catalyst while Cu-P-3.9 refers to the copper on pumice. The experiments represented by the three curves, Cu-P-3.9, Cu-A-3.9 and Cu-3.9, were all carried out under the same conditions. The copper on pumice shows the highest yields with the copper on asbestos a close second while the curve for copper alone falls below both of these. Upon increasing the nitrobenzene flow to 9.7 the results with the copper catalyst are considerably below those for the copper on asbestos catalyst as is shown by the curves. From these curves it would appear that copper on pumice is the best catalyst with copper on asbestos a close second. However, this is not necessarily true because the copper in pumice catalyst quickly lost its activity. Thus after one day's use an experiment with 3.9 grams nitrobenzene

per hour and 52 liters hydrogen per hour gave only a 75.2% yield of aniline instead of a 92.3% yield on the first day. This bad feature places the copper on asbestos catalyst as superior to the copper on pumice when the volumes of the two are approximately the same. However, there were 3 grams CuO on the asbestos and only 1.5 grams on the pumice. When

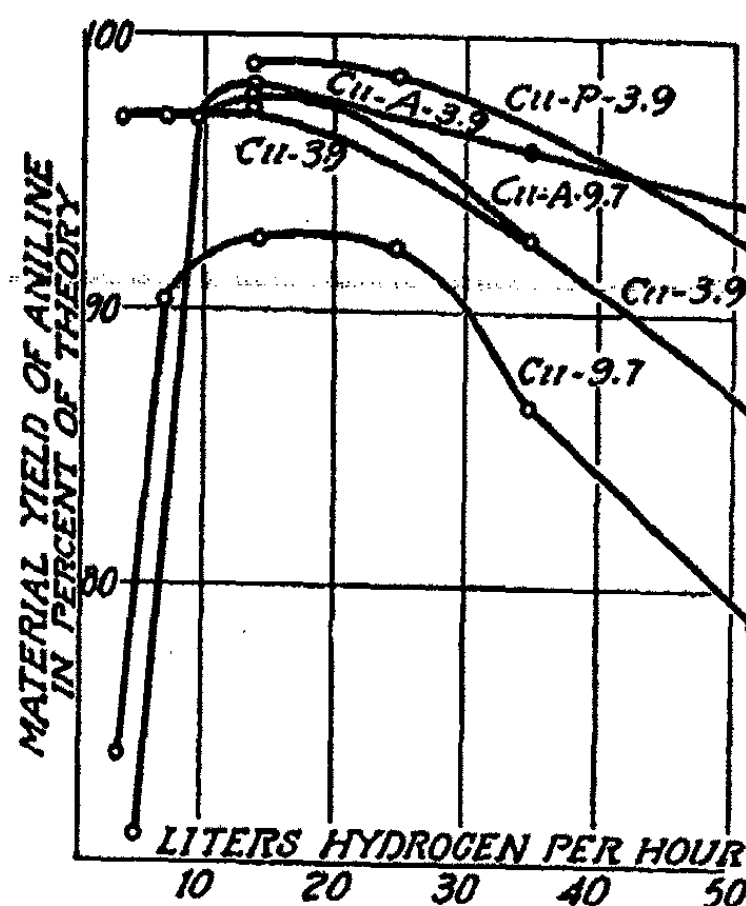


Fig. 4

copper was used without a support 13 grams of the precipitated CuO was used while 27 grams of the ignited CuO are required to fill the same approximate volume. The same volume of catalyst was used each time.

The copper asbestos catalyst may be used with a very high rate of nitrobenzene as is shown by the experiment with 20 grams nitrobenzene per hour in which the yield of aniline was 96.3% of the theoretical yield. However, at these rapid rates of nitrobenzene the catalyst quickly loses its activity. This loss in activity is probably due to a heating effect. Thus in one experiment with 17 grams nitrobenzene per hour the temperature as indicated by the thermocouple rose 20° C in

about 8 minutes. It would be reasonable to suppose that the temperature became much higher at the surface of the catalyst where the reaction took place than that indicated by the thermocouple, and that this heating causes the diminution in activity.

The yield obtained with the rate of nitrobenzene at 20 grams per hour is much higher than that obtained with nickel, which indicates that this copper with an asbestos support has an even greater speed of reduction than nickel without a support.

The higher yield with the copper on asbestos catalyst does not necessarily mean that copper on asbestos is "more active" than copper alone. Probably a greater surface of copper is exposed to the gaseous mixture when the copper is precipitated on the asbestos fibers than when it lies in the tube in the form of a powder. When it is remembered that only 3 grams CuO were used on the asbestos catalyst while 13 grams of the copper oxide were used for the copper catalyst, it is seen that the difference in rates per gram of copper is very great.

#### Summary

1. Sabatier's statement that a copper catalyst prepared from a precipitated oxide is a better catalyst than one prepared from an ignited nitrate has been confirmed.
2. Much lower rates of hydrogen may be used without loss in yield of aniline with a copper catalyst from a precipitated oxide than with one from an ignited nitrate.
3. The copper catalyst from the precipitated oxide is capable of carrying out the reduction of the nitrobenzene at a much greater rate than the one from the ignited nitrate.
4. The difference in physical appearance of the catalysts from the precipitated oxide and ignited nitrate has been pointed out.
5. The best temperature for carrying out the reduction was found to be near 260° C—about the same as in our previous work with catalysts from the ignited nitrate.

6. Copper on asbestos was found to be capable of reducing the nitrobenzene at a much greater rate per gram of copper than copper alone.

7. When the copper on asbestos catalyst is used at high rates of nitrobenzene it quickly loses its activity.

8. Copper on asbestos is a better catalyst than an equal volume of copper on pumice, although the latter only contained half as much copper as the copper on asbestos catalyst.

9. A small amount of iron in a copper catalyst prepared from an ignited oxide prevents the rapid decrease in the activity of the catalyst.

*Laboratory of Physical Chemistry  
Indiana University  
Bloomington*

2  
957-

## ON THE PREPARATION OF COLLOIDAL SOLUTIONS OF NICKEL AND COBALT HYDROXIDES AND SOME OTHER COMPOUNDS OF THESE METALS

BY O. F. TOWER AND MARTHA C. COOKE

Some years ago one of us, while investigating the tartrates of nickel and cobalt,<sup>1</sup> encountered a number of solutions of these substances which were evidently of a colloidal nature. In this paper the results of further investigations of these same substances are described together with some new methods for preparing colloidal solutions of the hydroxides of nickel and cobalt. The former paper should be consulted for a description of the nature and properties of the simple tartrates of these metals and of their double tartrates with potassium. The methods of analysis employed in this work are the same as those there set forth. Dialyzing was carried out either in parchment or collodion bags, which insures rapid diffusion. These were hung in distilled water, which was frequently changed. Parchment seemed to work the best, as the collodion apparently allowed larger particles to pass through, especially in the strongly alkaline solutions.

Simple nickel and cobalt tartrates, when prepared by dissolving the freshly precipitated hydroxides in tartaric acid are not colloids. These solutions are in a state of supersaturation and on standing deposit the crystalline salts. When, however, to these solutions sodium or potassium hydroxide is added a colloidal solution results, and in case solutions as concentrated as "normal" are employed the nickel solution forms a green transparent gel. If fifth-normal solutions are used no gel is obtained. The solution is, however, colloidal as examination by means of the ultramicroscope shows. The gel obtained with the more concentrated solutions after standing several days deposits a light green precipitate of nickel tartrate mixed with variable amounts of potassium tartrate.

<sup>1</sup> Tower: Jour. Am. Chem. Soc., 22, 501 (1900).

Whatever may be the nature of the substance in solution,<sup>1</sup> the precipitate in every case is simply nickel tartrate with more or less potassium tartrate adsorbed in it. The dilute solutions which did not gel were subjected to dialysis. In most cases all of the potassium and tartrate radical passed through the membrane leaving colloidal nickel hydroxide inside. Solutions containing at the most 3.2 grams of nickel hydroxide per liter were prepared in this way. The results just described were best obtained when tartaric acid and potassium hydroxide were in molecular proportions, that is, one molecule of the acid (not as free acid, but as nickel tartrate) to one molecule of the hydroxide. If the quantity of hydroxide exceeded this to any great extent, either all of the nickel would diffuse through the membrane also, or some nickel tartrate would precipitate inside the parchment bag as the potassium tartrate diffused out.

Similar solutions containing cobalt acted quite differently; for one reason because cobalt has a tendency to become oxidized to the cobaltic condition in a strongly alkaline solution. If the amount of potassium hydroxide employed was the least possible required to hold cobalt hydroxide in solution,<sup>2</sup> no oxidation seemed to take place. When such a solution was dialyzed one of two results occurred: either light pink cobalt tartrate was precipitated after a day or two inside the bag, or no precipitation at all took place and after dialyzing several days the contents of the bag consisted of a currant-red gel. Analysis of this gel showed it to be for the most part cobalt tartrate with small quantities of potassium tartrate adsorbed in it. Prolonged shaking of this gel with distilled water failed to peptize it.

In case a greater excess of potassium hydroxide was used in forming these solutions, oxidation would begin at once and the color would change from pink to purple, to green, and after many days to brown. If solutions as concentrated as "normal"

---

<sup>1</sup> See loc. cit., p. 510.

<sup>2</sup> See loc. cit., p. 517.

were used the solutions would set to a gel in about 24 hours (not at once as in the case of the nickel solutions), or about the time the color began to change. This gel lasted about two weeks, or about the time the color change was completed, when it gradually passed over into an ordinary solution containing a slimy brown precipitate. More dilute solutions passed through the same changes except that no gel was formed. No attempt was made to dialyze any of the solutions in which cobalt had obviously become oxidized, as methods of obtaining colloidal solutions of cobaltous hydroxide were being sought.

The literature, as far as we have been able to find, contains but one reference to the preparation of colloidal cobalt hydroxide without the employment of a protective colloid. A. Müller,<sup>1</sup> in 1908, peptized a number of freshly precipitated metallic hydroxides by means of hydrochloric acid or hydrolyzed salts of the same metals. In the case of cobalt he used the freshly precipitated hydroxide and hydrochloric acid and obtained a colloidal solution, which, however, began to deposit a precipitate within 24 hours. Nickel hydroxide is not mentioned.

In addition to the experiments, which have been described to try to obtain colloidal solutions of nickel and cobalt hydroxide by dialyzing solutions of their double tartrates and which resulted successfully only in the case of the former, other methods were also undertaken as follows. Nickel and cobalt hydroxides dissolve in excess of both ammonium hydroxide and carbonate, but as in these cases they form well defined double salts or complex molecules, it was scarcely expected that any colloidal solutions would be produced by subjecting them to dialysis; and such was found to be true. On dialyzing, either the whole of the substance in solution passed through the membrane, or sometimes only the ammoniacal portion, in which latter case the metallic hydroxide or carbonate, as the case might be, was precipitated inside the bag.

<sup>1</sup> *Zeit. anorg. Chem.*, 57, 311.

One of the best ways of preparing a colloidal solution of nickel hydroxide was discovered accidentally while preparing the hydroxide for conversion into the tartrate. For this purpose a solution of nickel chloride was treated with a little more than the equivalent quantity of a solution of potassium hydroxide, the precipitated nickel hydroxide allowed to settle, the supernatant liquid siphoned off, more water added, and the process repeated several times. It was found that the original concentration of the two solutions mixed was the principal factor in determining how rapidly the nickel hydroxide would settle. If normal solutions were mixed and then diluted afterwards, settling occurred fairly rapidly (say 20 minutes) and all traces of alkali can be washed out in three or four hours. If tenth-normal solutions are mixed, settling takes place much more slowly; and if hundredth-normal solutions are mixed, all day is required for the nickel hydroxide to settle sufficiently so that the supernatant liquid can be drawn off. For the purpose in hand solutions of a concentration about tenth-normal gave the best result. About 500 cc of each solution were poured together in a tall beaker, thoroughly mixed and set aside to settle. This took about one hour the first time. After siphoning off the solution about 900 cc of distilled water was added and thoroughly mixed with the precipitate by pouring back and forth from one beaker to another. Settling took longer this time, and the time increased with each successive washing. After about six such washings during one day, the precipitate was allowed to stand over night with the same quantity of water to settle again, but in the morning the precipitate had vanished and a colloidal solution of nickel hydroxide remained. The solution was somewhat opalescent, exhibited the Tyndall effect and showed distinct particles under the ultramicroscope.

On different trials the amount of nickel hydroxide thus going into solution varied considerably, for this depends so much on the nature of the precipitate formed when the two original solutions are mixed. If too dilute solutions are



employed the precipitate first formed is so finely divided that it is almost impossible to wash it by this method as it settles too slowly; and unless the potassium chloride is for the most part removed colloidal nickel hydroxide will not form, or at least the sol will not be sufficiently stable to last any length of time. To strike just the right conditions is a matter of some difficulty. In the most successful experiments one liter of solution contained about 1.5 grams of nickel hydroxide.

When such solutions were subjected to dialysis, nickel hydroxide would begin to precipitate within 24 hours and traces of chloride ions would be found in the dialysate, although the original colloid solution gave a practically negative test for these ions. By estimating the quantity of chloride ions removed by dialyzing,<sup>1</sup> it was calculated that the solutions contained an equivalent of about 1 cc tenth-normal potassium chloride in one liter. This seems to show that in order to hold nickel hydroxide in colloidal solution there must be approximately 1 molecule of potassium chloride to 200 molecules of nickel hydroxide. Experiments showed that nickel hydroxide, like other metallic hydroxides, is a positive colloid and gradually drifts toward the negative pole under the influence of a sufficient potential difference. These experiments were carried out in U tubes using a potential difference of 110 volts. The nickel hydroxide is probably stabilized by the potassium ions adsorbed by it. It is well known that other similar colloids adsorb positive ions in this way; but, so far as we know, no colloid is so sensitive to a small change of concentration of these ions as is the nickel hydroxide prepared in the manner just described; for it is precipitated by a slight increase in the concentration of potassium chloride as well as by its removal. Aggregation of the particles in these solutions goes on slowly

<sup>1</sup> This was accomplished by comparing the cloudiness obtained by adding tenth-normal silver nitrate to 500 cc of the dialysate with that obtained from standards prepared by treating 500 cc of solutions containing known amounts of potassium chloride with tenth-normal silver nitrate. This method could not be used with the original colloidal solution because of its greenish color and slight opalescence.

but continuously, for in the course of six or eight weeks all of the nickel hydroxide precipitates and the solutions become optically empty. The colloidal solutions of nickel hydroxide prepared by dialyzing the double tartrate are more stable, as most of them are perfectly transparent now after standing four months.

Cobalt hydroxide does not pass as readily into colloidal solution when prepared in this manner as does nickel hydroxide, that is, by precipitating from dilute solutions and washing by repeated siphoning off of the supernatant liquid. However, very dilute solutions of a brownish color can be obtained in this manner. They exhibit the Tyndall effect and show particles under the ultramicroscope, although their concentration in no case exceeded 0.05 gram of cobalt hydroxide per liter. They are also not very stable, for after standing a few days all of the hydroxide coagulates and precipitates.

Since tartaric acid holds nickel hydroxide in solution, one would expect that glycerine would act similarly. In fact, Chatterji and Dhar<sup>1</sup> state that this is the case, provided the glycerine is added to the solution of the metallic salt before adding sodium hydroxide. We have, however, been unable to confirm this for nickel salts, although we have found it to be true for cobalt salts and the others mentioned by these investigators. Four salts of nickel, the chloride, nitrate, sulfate and acetate, were tried in varying concentrations and with varying quantities of glycerine with both sodium and potassium hydroxides, but with negative results. In a few cases precipitation of nickel hydroxide would be delayed for four or five minutes but not longer. Nickel acetate dissolves directly in glycerine. If to such a solution an aqueous solution of sodium or potassium hydroxide was added, a precipitate resulted at once. If, however, an alcoholic solution of potassium hydroxide was employed, no precipitation occurred and in a few minutes the whole mixture set to a gel. These were the only conditions under which we found that glycerine would hold

---

<sup>1</sup> Trans. Faraday Society, Vol. 16, appendix to Part 3.

nickel hydroxide in solution. If this gel was diluted with water or with 90% alcohol, nickel hydroxide was thrown down immediately by the water and after a few minutes delay by the alcohol. On standing this gel underwent some interesting changes. After standing about 24 hours it clouded up and became opaque. It continued in this state for 10 or 12 days, after which syneresis began. The liquid portion rapidly increased in amount and in a few days entirely peptized the solid portion, so that a limpid green solution remained. Dilution with water now caused no precipitation, although the solution was distinctly alkaline. A portion of this dilute solution was then placed in a collodion tube and dialyzed. In three or four days the contents of the tube had gelled. The gel consisted of nickel hydroxide with some organic matter in it. The excess of alkali had dialyzed out. A second portion of the diluted solution standing without dialyzing for the same length of time did not gel. It of course still contained excess of potassium hydroxide.

It might be stated in closing that both colloidal nickel and cobalt hydroxides are reported to have been prepared by Paal's method,<sup>1</sup> that is, by employing certain protein decomposition products as protective colloids. Our experiments have, however, been limited to attempts to prepare such solutions without the aid of protective colloids.

It is well known that nickel sulfide is readily held in colloidal solution in the presence of a large excess of alkali, especially if an organic substance like tartaric acid or glycerine is present.<sup>2</sup> We have found that if such solutions are dialyzed the nickel sulfide is completely precipitated and the remaining liquid is optically empty. The tartrates, glycerine and excess of alkali pass through the dialyzing membrane, and their stabilizing effect is evidently required to keep nickel sulfide in the colloidal state.

The conclusions of this paper may be thus summarized:

<sup>1</sup> German patent (1906), described in Svedberg's "Herstellung kolloider Lösungen," p. 327.

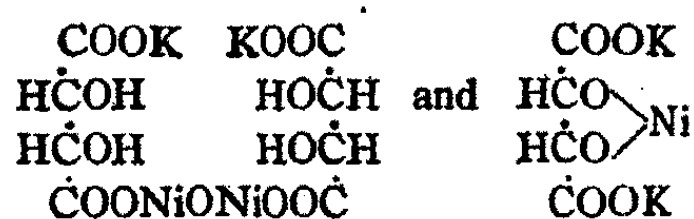
<sup>2</sup> Loc. cit., p. 518.

1. Two methods are described for preparing colloidal solutions of nickel hydroxide, one by dialyzing a solution of nickel tartrate in the presence of an alkaline solution of potassium tartrate, and the other by a special method of precipitating and washing the hydroxide itself.

2. Cobalt(ous) hydroxide does not pass readily into colloidal solution by these methods; only very dilute solutions of it could be obtained.

3. The tartrates of nickel and cobalt in the presence of an excess of alkali exist in the colloidal state.

4. In a former paper evidence was presented for the existence in solution of such salts as,



but since we have here to deal with solutions of colloids that evidence is of little value. Any solids obtained from such solutions appear to be only nickel tartrate with more or less potassium tartrate adsorbed in it.

5. Glycerine does not prevent the precipitation of nickel hydroxide from aqueous solutions. In alcoholic solution interesting transformations occur, and a solution is eventually obtained from which nickel hydroxide cannot be precipitated by diluting with water.

6. Colloidal solutions of nickel sulfide, which are readily formed in the presence of an alkaline solution of a tartrate, immediately decompose with precipitation of the sulfide on dialyzing out the tartrate.

*The Morley Chemical Laboratory  
Western Reserve University  
June, 1922*

31 10/19

## MORDANTS. III

BY WILDER D. BANCROFT

### CHROME

#### Wool and Bichromate

Although the use of chromic oxide as a mordant with dyes other than logwood only goes back about seventy years, Liechti and Hummel<sup>1</sup> stated in 1893 that "the most important mordants in wool dyeing are certainly the chromium mordants—indeed they have been called the mordants of the future." Only ten years later, Ganswindt<sup>2</sup> said that ninety-eight percent of all the mordanting of wool is done with chromic oxide. Matthews<sup>3</sup> says that "chromium mordant is used for dyeing practically all of the alizarin, mordant, and acid-mordant or after-chromed dyes; it is also the principal mordant used in conjunction with the natural dyewoods."

Instead of starting with the chromic salt, as would naturally have been expected, chromic acid in the form of bichromates of potassium and sodium is the most important and most generally used wool mordant.<sup>4</sup> Matthews<sup>5</sup> says that "formerly potassium bichromate was used almost entirely; but, during the recent war, potassium salts were very scarce, and even before the war sodium bichromate was coming into vogue as a mordant, as the sodium salt was cheaper than the potassium salt. In former times the potassium salt was preferred owing to the fact that it crystallized nicely and could thus be prepared very pure and free from iron (which is very essential in its use as a mordant for most colors), whereas the sodium salt was difficult to obtain in a crystalline condition, and, furthermore, it deliquesced on exposure to the air and be-

<sup>1</sup> Jour. Soc. Chem. Ind., 12, 241 (1893).

<sup>2</sup> "Theorie und Praxis der modernen Färberei," II, 69 (1903).

<sup>3</sup> "Application of Dyestuffs," 344 (1920).

<sup>4</sup> Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 255 (1910).

<sup>5</sup> "Application of Dyestuffs," 344 (1920).

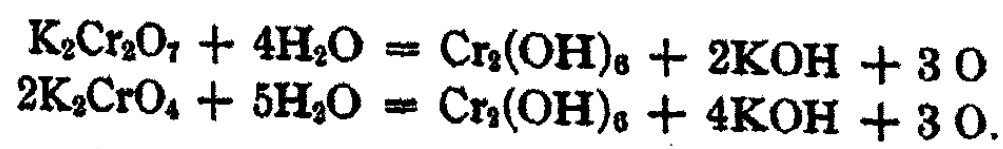
came pasty and hard to handle. Modern and improved methods of manufacture, however, developed a crystalline form of sodium bichromate in a highly purified state and it rapidly displaced the sodium salt."

In a bichromate solution wool, of course, becomes yellow; but neither bichromate or chromic acid is really a mordant in itself. Liechti and Hummel<sup>1</sup> say that "the [wool] fibre itself is incapable of really fixing chromic acid as such, as some maintain, and during washing, especially in hot water, a larger or small quantity is dissolved from the fibre. So much, indeed, is this the case that some have been led to declare that the mordanting of wool with bichromate of potash is of a purely physical nature, since by washing nearly the whole of the chromium may be removed." Whitely<sup>2</sup> did not succeed in washing out all the chromic acid; but recent experiments at Cornell are quite conclusive to the effect that there is no very strong adsorption of chromic acid by wool. Since chromic oxide is the real mordant, mordanting with bichromate involves a reduction. The chromic acid may react with the wool fiber, with the dye, or with reducing agents added to the bath. There seems to be no question but that chromic acid reacts with wool under suitable conditions. In the light the color of the wool changes from yellow to green and, in the dark, reduction always takes place<sup>3</sup> if the wool is kept in the bath at 100° for an hour and a half, the wool becoming a brownish yellow or pale olive color. In another experiment "wool was saturated with solutions of potassium chromate and bichromate of such a strength that the amount of mordant absorbed was equivalent to the use of three percent bichromate of potash [on the wool] in the ordinary manner. After drying, the fents were steamed, and in this way not only was the bichromate, but even the chromate of potash almost entirely reduced, particularly the former, presumably according to the following equations:

<sup>1</sup> Jour. Soc. Chem. Ind., 12, 244 (1893); Ganswindt: 14, 654 (1895).

<sup>2</sup> Ibid., 6, 131 (1887).

<sup>3</sup> Liechti and Hummel: Jour. Soc. Chem. Ind., 12, 244 (1893).



This experiment demonstrates conclusively the fact that reduction may be effected by the wool fibre itself, and one need not necessarily therefore adopt Nietski's view, that, owing to the amido-acid character of the wool fibre, both  $\text{K}_2\text{O}$  and  $\text{CrO}_3$  are fixed simultaneously."

When the reduction takes place at the expense of the wool fibre the latter may easily be weakened thereby. There has been a good deal of discussion over this and von Kapff has urged the substitution of vat dyes for mordant dyes<sup>1</sup> on the ground that in Germany alone the annual damage to wool from chrome mordanting amounts to 250 million marks. Others claimed that the damage is relatively small. The truth of the matter is that a reducing agent is usually added, either by itself or in the form of dye as in the case of logwood. The amount of oxidation of the wool is small at most because one usually adds three percent of potassium bichromate on the weight of the wool and only about one-third of this is adsorbed. Liechti and Hummel<sup>2</sup> estimate that this means, in round numbers, about one hundred grams of available oxygen to one hundred and fifty kilograms of wool, in case the chromium is fixed, as they assume, in the form of a chromic chromate,  $\text{Cr}_2(\text{CrO}_4)_3$ , from which the chromate is afterwards washed out.

If an oxidizable dye is used, the dye will reduce the chromic acid, which will therefore not attack the wool. Matthews<sup>3</sup> says that potassium bichromate and sulphuric acid "in connection with logwood oxidize the hematoxylin to hematine and thus utilize the coloring matter completely. If the ordinary chrome and tartar mordant is employed, a green reduced chromium oxide is obtained on the fibre which has no oxidizing properties; consequently, on dyeing with logwood, the color obtained is chiefly due to hematine and the hematoxylin is

<sup>1</sup> Schwalbe: Zeit. Kolloidchemie, 5, 130 (1909).

<sup>2</sup> Jour. Soc. Chem. Ind., 12, 242 (1893).

<sup>3</sup> "Application of Dyestuffs," 477 (1920).



not utilized completely. This accounts for the fact that different dyers may obtain entirely different results with the same lot of logwood extract."

Liechti and Hummel<sup>1</sup> have proved that alizarin alone, in the absence of wool, is capable of reducing alizarin. "With the presence of wool the reaction proceeded even more favorably. Along with one gram alizarin (20 percent paste) the theoretical amount of bichromate of potash was employed, viz., 0.082 g; also the following amounts: 0.123, 0.164, 0.205, 0.246, 0.328 grams. The wool was entered into the bath at 40° C and then boiled for two hours. All the baths contained lake, which gradually increased in quantity from baths one to six. All had a neutral reaction and were totally free from alizarin. No. 1 contained the merest traces, No. 2 slightly more, and the rest gradually increasing amounts of chromate of potash. Notwithstanding the absence of lime salts, the dyed wool stood soaping very well, and all the colours were bright claret reds, very similar to each other in shade. It must not be forgotten, however, that the wool itself contained a little lime. Cotton submitted to the same process merely acquired a pale peach colour, while the bath contained a good deal of lake."

"If a filtered aqueous solution of Coerulein S, made in the cold, is heated with not too much bichromate of potash, a fine colour lake is obtained. If there is a deficiency of readily oxidisable substances present, then the wool itself continues and completes the reduction. This fact can be established experimentally, for in no single case did we ever succeed in detecting chromic acid in the dye-bath.

"In most cases of dyeing an oxidising action on the part of the mordant is undesirable, and in some cases it is absolutely injurious, hence many attempts have been made to reduce the chromic acid entirely before dyeing. The method proposed some time ago by Knecht, namely, by the use of sodium bisulphite, effects this in the simplest manner; but

<sup>1</sup> Jour. Soc. Chem. Ind., 12, 244, 246 (1893).



this method has long been known, for already in 1853 C. Koechlin mordanted wool with bichromate of potash, and after washing, effected reduction by means of sodium bisulphite, repeating the operations four or five times. Witt, too, has long adopted the same method. In 1881 one of us used the method with silk. Further, in 1866, Chaudet recommended the treatment with a variety of reducing solutions after mordanting—e. g., sulphurous acid, alkali sulphides, organic acids, alcohol, sugar, etc. Grison too, who recommends 1.5 percent  $K_2Cr_2O_7$  + 8 percent  $H_2SO_4$ , effected reduction by means of sodium bisulphite, or by using a solution of arsenious acid (10 grams per litre), treating the mordanted material with this until it acquired a green colour, and repeating the operations if necessary. Then again, in 1857 Francillon padded wool or silk in bichromate of potash or chromic acid, and effected reduction after a few hours, by hanging the materials in the sulphur stove or by means of a solution of sulphurous acid."

"Nietzki suggests that the ultimate dyed colour produced is due to a triple combination of wool, colouring matter, and chromic acid. There is, however, no fact which can be advanced in favor of this supposition, and we have always been inclined to adopt the view, shared also by Herzfeld and by Witt, namely, that in the dyed colour the chromium exists as a chromic oxide lake, reduction taking place chiefly by means of the foreign organic substances which almost always accompany the colouring matter employed, sometimes by the impurities contained in the water (Cochenhausen), frequently by the colouring matter itself, as in the case of logwood, and lastly by the sulphurous acid of those colouring matters which have been rendered soluble by combination with sodium bisulphite."

Chromic acid mordants wool more strongly than either potassium bichromate or chromate. Knecht states<sup>1</sup> that with neutral potassium chromate only thirty-six percent and with potassium bichromate only forty-eight percent of the

<sup>1</sup> Liechti and Hummel: Jour. Soc. Chem. Ind., 12, 242, 246 (1893).

amount of chromium is fixed as when wool is boiled in a bath of chromic acid itself. Liechti and Hummel say that "most authors agree with us that chromic acid mordants better, that is stronger, than bichromate of potash. Most recommend 3 percent  $K_2Cr_2O_7$  + 1 percent  $H_2SO_4$ ; Lodge gives 2 percent  $H_2SO_4$ ; and Kertesz, 3 percent  $H_2SO_4$ . Nietzki observed on using excess of sulphuric acid, e. g., 3 molecules, that the chromic acid is taken up rapidly and almost completely by the wool. This observation agrees with ours; but it is difficult to understand why his samples appeared yellow after washing, since ours had invariably a greenish-brown or olive colour, sometimes the green (chromic oxide), sometimes the brown (chromium chromate) predominating. Leaving out differences of intensity the colour varied from a pale reseda colour to pale olive."

In a later paper Hummel and Gardner<sup>1</sup> modify this statement somewhat, because they find a maximum mordanting with about 1.5 mols sulphuric acid. "A series of six wool patterns was mordanted with three percent  $K_2Cr_2O_7$  (1 mol) with the addition of 0, 0.5, 1, 1.5, 2, 3 mols of  $H_2SO_4$ . The mordanted patterns varied in colour from a drab-white in No. 1 to a pale olive-yellow in No. 4, after which from No. 4 to No. 6 the colour became distinctly greener. The mordant liquor of No. 1 had a pale greenish-yellow which gradually became slightly paler up to No. 6. The addition of sulphuric acid up to 1.5 mols results therefore in an increased fixation of mordant, from which point with larger proportions of acid the amount of reduction increases." In a second set of experiments "larger variations in the amount of sulphuric acid were employed, three percent  $K_2Cr_2O_7$  being used with 1.5, 3, 4.5, 6, 7.5, 9 mols  $H_2SO_4$ . No further information was obtained, the addition of 1.5 mols  $H_2SO_4$  again giving the maximum fixation, while with 3 mols partial reduction of the chromic acid occurred and with increased amounts of acid the reduction was somewhat greater."

<sup>1</sup> Jour. Soc. Chem. Ind., 14, 452 (1895).

This statement is typical of what one encounters when reading papers on dyeing. The conclusion may be right; but it is in direct contradiction with the facts as stated. Hummel and Gardner say that the waste mordant liquor in the first set of experiments becomes increasingly paler, with increasing amount of acid. If this is true, there is less chromium in the bath and consequently more has been taken up. They are really talking about the adsorption of chromic acid as such, though they speak of the fixation of the mordant. The fact that the wool becomes greener shows that there is less free chromic acid but not that there is less chromium.

Experiments were also made with three percent  $K_2Cr_2O_7$  (1 mol) and 0, 1, 2, 3, 4, 6 mols of hydrochloric acid. The appearance of patterns Nos. 1, 2, and 3 was similar to the corresponding ones in the series with sulphuric acid. "A very remarkable difference, however, was shown in patterns Nos. 4, 5, and 6, which here had a pronounced olive-yellow colour. In accordance with this gradual increase in colour of the mordanted patterns, there was a corresponding decrease in the colour of the waste mordant liquors, in which, from No. 4 to 6, the colour was much paler than in the corresponding waste liquors of the previous experiment; indeed Nos. 5 and 6 mordant baths with 4.5 [4.0?] and 6 mols HCl were almost entirely exhausted. A continuation of this experiment, using larger amounts of hydrochloric acid (6-16 mols), showed that 6 mols sufficed for the fixation of the chromium chromate, and that larger amounts merely caused a further slight reduction; but even with 16 mols the reduction was far from complete when three percent bichromate was used.

"The corresponding experiments with nitric acid indicated that the use of this acid gives a result very similar to that obtained with hydrochloric acid; the mordanted patterns showed the same deep olive-yellow colour and the waste liquors were equally well exhausted. The amount of nitric acid necessary to give the maximum amount of fixation of mordant was indeed somewhat less than in the case of hydrochloric acid,

4-5 mols only being required. Excess of nitric acid appeared also to induce a somewhat greater degree of reduction of the chromium chromate than excess of hydrochloric acid."

Here again there is no evidence of any maximum fixation of chromium mordant. The only two things which the experiments prove—and that only qualitatively—are that hydrochloric and nitric acids exhaust the bath more completely than does sulphuric acid, and that reduction of chromic acid by wool takes place more readily with sulphuric acid than with hydrochloric or nitric acid.

We can now consider what one can predict in regard to these matters. It seems probable that wool first adsorbs chromic acid, which is not held strongly enough to be a real mordant and which is reduced under certain circumstances to chromic oxide which constitutes the real mordant. It is of no special importance whether there is an intermediate formation of a chromium chromate or what that chromium chromate is. It is of interest only in accounting for the intermediate color because everybody admits that the chromate part of the hypothetical chromium chromate can be washed out of the wool and that this substance is not the mordant. It is clear that wool will take up less chromic acid from a potassium chromate solution than one containing free chromic acid. Other things being equal, more chromic acid will be taken up the more acid we make the solution; but other things are not equal because we cannot add hydrogen ions without adding anions to correspond. If we add an acid which is adsorbed strongly in itself, it will tend to displace the chromic acid. This is probably the reason why sulphuric acid does not exhaust the bath of chromic acid so rapidly as does nitric or hydrochloric acid. In line with this is the fact that a mixture of sodium chloride and sulphuric acid behaves like so much sulphuric acid and not at all like hydrochloric acid. The sulphate ion is apparently an important factor. With increasing acid content there will come a point where the chromic oxide formed will be peptized or converted into a soluble acid.

It is hard to tell whether this is a factor or not. Hummel and Gardner<sup>1</sup> say that "a careful examination of the waste mordant liquors showed that although the exhaustion of the bath appeared complete when using 4 mols H<sub>2</sub>SO<sub>4</sub>, it really contained a notable amount of chromium in the reduced condition."

We have now accounted tentatively for all the facts except the difference in the reduction of the chromic acid when sulphuric and hydrochloric acids are used. It seems better to admit frankly that my knowledge of chemistry is not sufficient to enable me to give a decisive answer on this point. We do know that chromic acid is a stronger oxidizing agent the more acid the solution. When the reduction is done by the wool, the acidity in or at the wool surface is the more important thing. If the sulphuric acid is adsorbed more strongly under these conditions than the hydrochloric acid, the acidity, and therefore the oxidizing power, may well be greater in the sulphuric acid solutions than in the ones containing an equivalent quantity of hydrochloric acid. This is only a suggestion, however, and there are no data.

Since percentage adsorption of chromic acid will decrease with increasing concentration, we should expect any acid to exhaust the bath more completely the lower the initial concentration of the bichromate. This is exactly what happens. Hummel and Gardner<sup>2</sup> found that with one or two percent potassium bichromate a small addition of hydrochloric acid was sufficient to exhaust the bath, while the four percent bath could not be exhausted completely by any acid concentration that was tried.

Knecht<sup>3</sup> points out that "if a large excess of bichromate is used, especially in conjunction with sulphuric acid, it exerts an injurious effect on some colouring matters by oxidising them and destroying their colouring principles, while at the same time the fibre is injured. Wool so treated is said to be "over-

<sup>1</sup> Jour. Soc. Chem. Ind., 14, 454 (1895).

<sup>2</sup> Ibid., 14, 453 (1895).

<sup>3</sup> Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 256 (1910).

chromed." Small amounts of bichromate do not exert this influence to so large an extent, but the products of oxidation diminish the brilliancy of the ultimate colour more or less, and the excess of mordant bleeds out and precipitates the colouring matter in the dye-bath, and this being taken up more or less mechanically by the wool gives rise to colours which rub off. The reduction of the bichromate previously to dyeing not only prevents this loss from overchroming, but also, by checking the decomposition of the colouring matter, allows of more brilliant shades being obtained."

Reference has already been made to the possibility of reducing the chromic acid with sulphurous acid or bisulphite but the more customary thing is to use an organic acid instead of sulphuric or hydrochloric acid.<sup>1</sup> "When sulphuric acid is used as the assistant along with the bichrome, then there is formed on the wool a deposit of chromic acid and chromium oxide, and this exerts an oxidizing effect on the colouring matter or dye-stuff, which in some cases, as the Alizarine Blue, Alizarine Yellow, etc. leads to a destructive effect, and, therefore, the production of weak shades, so that it is not possible always to use an oxidising mordant. When tartar, argol, oxalic acid, lactic acid, and other assistants of an organic nature are used, then a different effect is obtained, the bichromate is decomposed completely and a deposit of chromium oxide formed on the wool. This does not exert any action on the colouring matter and hence this mordant is known as the non-oxidising mordant. It may be pointed out that, when wool is mordanted with potassium or sodium bichromate and sulphuric acid (oxidizing mordant), it has a deep yellow color, while it has a green color when mordanted with bichromate or other chrome salt and the assistants enumerated above. One sign of a well-mordanted wool is when it has a good bright tone, free from yellowness.

"Of the organic assistants, tartar is undoubtedly the best in general use, and, although slow in its action, leaves a good

---

<sup>1</sup> Beech: "The Principles and Practice of Wool Dyeing," 116 (1902).

deposit of oxide of chrome on the wool in a suitable condition to develop the best results on dyeing. Argols are only an impure tartar. They can only be used when dark shades are to be dyed. Oxalic acid does not work as well as tartar, and there is not so much chrome oxide deposited on the wool, while there is a slight tendency for a small proportion of this to be in the form of chromic acid. Of late years lactic acid and lignorosin have been added to the list of assistant mordants; both these give excellent results, they lead to a more complete and more uniform decomposition of the bichromate, and therefore the mordanting baths are exhausted more completely so that rather less bichromate is required; the shades which are obtained are in general fuller and brighter."

Knecht<sup>1</sup> says much the same thing. "More brilliant colours are obtained when organic acids or acid salts (for example, formic or oxalic acid or tartar) are used along with the bichromate. The latter is partly reduced, and chromic hydroxide formed on the fibre. In this case the wool has a greenish colour, like that of the chromium salts and chromium hydroxide. The quantity, however, of organic substances usually employed is not always sufficient to reduce the whole amount of bichromate that is extracted from the bath by the fibre. Up to a few years ago tartar was employed most generally as an assistant for mordanting with bichromates, three percent of bichrome and 2.5 percent of tartar being the usual quantities, or, for very dark shades, four percent of bichrome and three percent of tartar. Sometimes the oxalic acid was used on account of its lower price, although its action as regards even mordanting and good reduction of the bichromate is inferior; for 3-4 percent of bichrome about 1-2 percent of oxalic acid was employed. During the last few years lactic acid, lactoline, and lignorosine have come very generally into use; they exert a very good reducing effect, and the mordant is satisfactorily and fairly evenly fixed. The proportions recommended are 2-3 percent of bichrome and 3-5 percent of lactic

<sup>1</sup> Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 256 (1910).



acid, with or without the gradual addition of 1-1.5 percent of sulphuric acid; or 1.5 percent of bichrome and 3 percent lactoline; or 2.7 percent bichrome, 4-5 percent lignorosine, and 1.8 percent of sulphuric acid for dark shades; and for light ones, 1.3 percent of bichrome, 2.7 percent lignorosine, and 0.8 percent sulphuric acid. Recently formic acid has been introduced by S. Kapff<sup>1</sup> as a very effective assistant which exhausts the chrome bath entirely, and makes it possible to mordant even the deepest shades with only 1.5-2 percent of bichrome and the same quantity of formic acid."

Matthews<sup>2</sup> is a good deal worried over the chemistry of the process. "Chromium hydrate is a greenish blue body, and if this substance were precipitated in the fibre by the usual methods of mordanting, the wool should have a greenish blue appearance; but as a matter of fact it has a yellow color, which is a certain indication that chromium hydrate has not been precipitated in the fibre. Indeed, it would be difficult to explain, in a chemical manner, just how chromium hydrate could be formed by boiling wool in a solution of potassium bichromate and tartar or lactic acid, and more so as it is well known that certain organic bodies such as sugar, glycerol, organic acids, etc, prevent by their presence the precipitation of chromium salts. . . . Furthermore if wool is mordanted with chrome and lactic acid, the bath at first is yellow, then green, and finally colorless, while the wool becomes colored only slightly, in spite of the fact that all the chrome has been taken up by the fibre. If chromium hydrate were in the fibre, the color of the latter should be bluish green, and if a salt of chromium oxide as such were in the fibre, the latter would be green."

Everybody seems to be against Matthews on the question of color. Beech's statement has already been quoted. Nearly thirty years ago Liechti and Hummel<sup>3</sup> reported on the same subject. "Now, when wool is mordanted with three percent

<sup>1</sup> Jour. Soc. Dyers and Colourists, 1905, 75.

<sup>2</sup> "Applications of Dyestuffs, 502 (1920).

<sup>3</sup> Jour. Soc. Chem. Ind., 12, 234 (1893).



bichromate of potash and 2.5 percent cream of tartar, the following appearances are observed. At first the tartar merely acts as an acid and liberates chromic acid, which as usual is immediately attracted by the wool. If then the temperature is raised to about 60° C, the reductions begin, and in fact upon the wool fibre itself, which thus acquires a greenish colour; the mordant solution remains of a yellow colour, due to potassium chromate, and only towards the end of the mordanting process does it become pale greenish-yellow and show a faint turbidity and an alkaline reaction. The presence of chromic hydrate can be detected in the solution by adding clear lime water, and a relatively larger proportion of potassium chromate is also discernible therein."

Since everybody but Matthews knows that chromic acid will oxidize tartaric and lactic acids, it is difficult to see what he had in mind. It is possible that Matthews meant that chromic acid does not have much oxidizing power in such dilute solutions. Liechti and Hummel<sup>1</sup> worked ordinarily with ten grams of wool in 600 cc of water. If now a solution of three percent bichromate and 2.5 percent tartar, referred to wool (molecular ratio 1 : 1.3), and as dilute as is usual in mordanting (0.5 g and 0.4 g per liter) be boiled for an hour and a half, no reduction whatever takes place. "If the solution is evaporated to dryness on the water-bath and the residue is then re-dissolved and the solution again evaporated, or if the two dry substances mixed together are moistened with a very little water and then allowed to act upon each other, being heated on a sand-bath, reduction certainly occurs; but it is for the most part incomplete. Most remarkable is the fact that the liquid, which is of a fine, dark, pure green or olive green colour according to the amount of reduction, shows a strongly alkaline reaction and deposits a dirty white powder." In the presence of the wool, however, reduction takes place readily and, for the most part, in and on the fiber. This has been shown particularly well in the case of oxalic acid. "If wool is impregnated

<sup>1</sup> Jour. Soc. Chem. Ind., 12, 242, 334 (1893).

with solutions containing oxalic acid and bichromate of potash and is steamed, then even one mol oxalic acid produces considerable reduction and with two mols it is complete. Here too, it is evident that the wool itself has assisted materially in the reduction for if a solution of one mol bichromate of potash with two mols oxalic acid is boiled, one obtained partial reduction only, namely, to chromium chromate and not to chromic oxide." "Whenever wool is mordanted with bichromate of potash with additions of oxalic and tartaric acid, the reduction with oxalic acid is invariably less than that with tartaric acid."

Liechti and Hummel<sup>1</sup> duplicated their experiments with oxalic acid, using tartaric acid as an assistant. "The chief difference noticed is that here total reduction, i. e., green mordanted wool is obtained with ease, and that even large amounts of tartaric acid have comparatively less injurious effects than oxalic acid. Bichromate of potash with 1-2 mols tartaric acid gives somewhat darker colours in dyeing than when bichromate alone is employed; with increasing amounts of tartaric acid the dyed colour becomes somewhat greener and paler (quercitron bark). The mordanted fents have a dull green colour, the intensity of which increases with the use of 1-4 mols tartaric acid. Although the waste mordant solution with bichromate of potash and four mols tartaric acid had only a pale yellowish-green colour and the mordanted wool appeared to be the best of the series, the quercitron-dyed colour appears the palest and most greenish in tint.

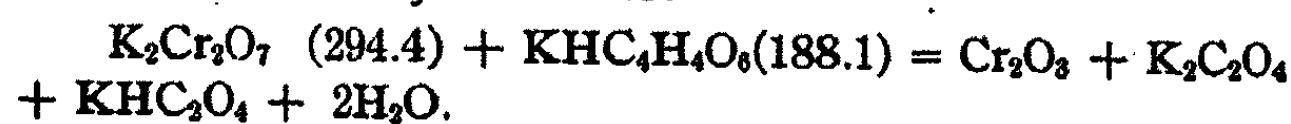
"If wool is padded in a solution of one mol bichromate of potash, one mol of tartaric acid and is then steamed, total reduction takes place; on washing with water an alkaline chromic oxide salt solution is obtained; with two mols tartaric acid the colour of the wool is grass-green, and the wash-water only very slightly alkaline; with three mols tartaric acid and wool showed a violet-grey colour and water extracted chromic oxide salt solution having an acid reaction.

"If a solution of bichromate of potash with the addition

<sup>1</sup> Jour. Soc. Chem. Ind., 12, 333 (1893).

of only two mols tartaric acid is boiled, unlike the case with oxalic acid, reduction does occur here, although only on evaporating. With larger amounts of tartaric acid the reduction is increased correspondingly, but apparently six mols tartaric acid are required to effect complete reduction when boiling 2-3 hours."

These experiments of Liechti and Hummel furnish the explanation for the later experiments of Ganswindt.<sup>1</sup> He claims that ten parts of tartar are necessary to effect the complete reduction of one part of potassium bichromate. This may perfectly well be true under the conditions of his experiments for Liechti and Hummel needed six mols (four parts) when boiling two to three hours; but that does not justify Ganswindt in saying that the use of two and a half parts of tartar to three of bichromate is utterly foolish and not based on chemical knowledge. One can have complete reduction if the reduction runs to an end even on the assumption that the tartrate is oxidized only to oxalate:



Nobody claims that the bath is exhausted under these circumstances. Liechti and Hummel<sup>2</sup> say, for instance, that "it is quite certain that wool mordanted with bichromate of potash and cream of tartar contains both chromic oxide and chromic acid, for by boiling with sodium carbonate one obtains a solution of sodium chromate and green coloured wool." The serious mistake that Ganswindt has made is in assuming that the amount of reduction would be the same with and without wool.

Liechti and Hummel made some interesting experiments on the reduction of the bichromate before the wool is added. "If wool is boiled with three percent bichromate of potash, one percent sulphuric acid, and 2.5 percent cream of tartar, the

<sup>1</sup> Jour. Soc. Dyers and Colourists, 1895, 152; "Theorie und Praxis der modernen Färberei," II, 73 (1903).

<sup>2</sup> Jour. Soc. Chem. Ind., 12, 335 (1895).

wool is decidedly better mordanted; it has a purer and darker green colour, and acquires a deeper colour in an alizarin dye-bath. If the above-mentioned liquors are previously reduced, i. e., apart from the fibre and only then employed for mordanting wool (instead of adding the several ingredients at once to the mordant-bath) one obtains, curiously enough, very poor results; the baths contain potassium chromate and a quantity of precipitated chromic hydrate, and exhibit an alkaline reaction. When the mordanted patterns are dyed with quercitron bark, the depth of the colour is less than one-third of that obtained with the fresh unreduced mordant.

"Our attention was first drawn to this point by noticing that poor shades were obtained whenever, in pursuing the ordinary course of dye trials, a student had allowed the mixed mordant in concentrated solution to stand over night or longer before use. A satisfactory, non-oxidizing, chromic oxide mordant, ready for immediate use by the dyer, cannot therefore be prepared in this manner. The unfavorable result is mainly to be attributed to the alkaline state of the solution since tolerably fair results are obtained by adding to the reduced mordant solution the requisite amount of acid, for example, sulphuric acid. This experiment indicates that wool must never be mordanted in alkaline baths, a fact afterwards substantiated invariably whenever alkaline baths were employed incidentally."

This last conclusion does not seem to me to be justified by the facts. While an alkaline solution may be bad, the real difficulty in this case was that the chromic oxide was not peptized sufficiently and consequently was not taken up satisfactorily.

Liechti and Hummel<sup>1</sup> have made experiments, starting with the so-called chromium chromate. "In recent years three chromium chromate mordants have been recommended for cotton and silk by von Gallois and introduced to the trade as chrome mordants, HA I, GA II, GA III, by Messrs. Meister,

<sup>1</sup> Jour. Soc. Chem. Ind., 13, 363 (1894).

Lucius, and Brüning of Hoechst. It seemed desirable, therefore, to try similar compounds for wool. Experiments were made with mixtures of chrome alum and bichromate of potash.

The simplest method to obtain a chromium chromate seemed to be to follow the equation:



On mordanting wool with the above mixture, equivalent to three percent  $\text{K}_2\text{Cr}_2\text{O}_7$ , the bath quickly became turbid and the experiment was not continued. Another experiment in which the proportions were in accordance with the equation:



showed this mixture also to be of no use."

Experiments were made with varying amounts of different acids and the conclusion was that "the use of solutions of chromium chromates as mordants for wool seems unpromising. Useful results are obtained only when fairly large amounts of organic acid are used as well, in which case there is no advantage over bichromate of potash. It is well to note that wool mordanted in the manner described always seemed to have a pleasant soft feel.

"In a subsidiary experiment a piece of wool was padded with a solution containing one mol chrome alum, one mol  $\text{K}_2\text{Cr}_2\text{O}_7$ , and two mols oxalic acid, dried and steamed; it thus acquired a dull olive-grey colour, so that here too the reduction was incomplete. Total reduction occurred, however, if two mols of tartaric acid were used instead of oxalic acid, and the wool acquired a violet-greenish-grey colour rather than green, indicating that a chromic oxide salt was present in the fibre rather than chromic hydrate.

"In comparing the two methods of fixing the mordant by steaming and by boiling, it is generally found that in the former the presence of less acid was needed than in the latter, evidently because of the greater concentration of the mordant solution in the former case. If in the last-mentioned experiment the acid was omitted entirely, the fent acquired a brownish-green

colour, pointing to the presence of both  $\text{Cr}_2\text{O}_3$  and  $\text{CrO}_3$ , and there was apparently total fixation of the mordant."

Though it is outside the scope of this article, one cannot help wondering whether the violet color obtained twice by Liechti and Hummel may not be the same form of chromic oxide which gives the red color to the ruby and to the chrome pink glazes. Ganswindt<sup>1</sup> appears to have got something similar, using oxalic acid. "Wool was boiled for an hour and a half with three percent potassium bichromate and three percent oxalic acid. The violet and not the green modification of the chromium salts is formed under these conditions. The mordanted wool shows a characteristic dichroism. In thin layers it is green by transmitted light. In thicker layers, or by reflected light, it is violet."

Ganswindt<sup>2</sup> holds forth in a characteristic manner on the addition of lactic acid to bichromate. "The process came to us originally from America, where lactic acid was first prepared and used technically. The use of lactic acid as a reducing agent when mordanting with bichromate was advertised in such a typically American manner that lactic acid was not taken seriously at first. The American technical press told so many good things about the process that it seemed worth while to test it. It turned out that lactic acid was really a first-class reducing agent for bichromate, better than tartar or oxalic acid. In 1896 the firm of C. H. Boehringer and Sons began the manufacture of lactic acid technically and assigned to the author of this book [Ganswindt] the task of working out the details of its commercial application. The fundamental experiments were made with a 70 percent lactic acid and the original formula was three percent bichromate of potash and two and a half percent lactic acid. When fifty percent lactic acid was put on the market later, the formula was changed to three parts bichromate to three of lactic acid. Reduction takes place much more rapidly and at

<sup>1</sup> "Theorie und Praxis der modernen Färberei," II, 75 (1903).

<sup>2</sup> "Theorie und Praxis der modernen Färberei," II, 76 (1903).

a distinctly lower temperature when lactic acid is used instead of tartar or oxalic acid and more chromium is taken up by the fiber. Dreher changed the original formula to 2.75% bichromate, 2.5% lactic acid and 25% sulphuric acid; and still later to 1.5% bichromate, 3% lactic acid (50% pure), and one percent sulphuric acid. The idea evidently was that lactic acid would reduce free chromic acid more easily than a potassium salt of it. This did actually give an admirable mordant; but the addition of sulphuric acid is not absolutely necessary. The author [Ganswindt] has usually had his students work with two percent bichromate and three percent lactic acid, which forces the whole of the chromium on the fiber in a relatively short time. One can also use 1.5-3.0 parts of bichromate of potash or soda, 3-5 parts of fifty percent lactic acid and three parts of thirty percent acetic acid (6° Baumé). Dreher assumes that the chemical reaction in the mordant bath is the oxidation of lactic acid by chromic acid to acetic and carbonic acids; but, in that case, the solution should become violet through formation of chromic acetate. This does not happen. The originally yellow color of the solution disappears in about ten minutes but the solution does not become either green or violet, which shows that some other chemical reaction takes place. Wool is almost colorless after mordanting with bichromate and lactic acid and shows no sign of yellow, thus differing from wool mordanted with tartar or oxalic acid. When the mordanting is done properly, the bath is almost colorless and chromium cannot be detected in it. The chief advantage of the lactic acid mordant is that it forces the chromium quantitatively on the fiber." Somebody will of course have to find out why chromic oxide does not color wool under these conditions; but, beyond that, this paragraph is interesting chiefly for its psychological bearing. Lactolin is a mixture in equivalent parts of potassium lactate and lactic acid, thus being superficially analogous to acid potassium tartrate.

A German patent<sup>1</sup> claims that formic acid is the cheapest

<sup>1</sup> Zeit. Farben-Industrie, 4, 159 (1905).



and best organic acid to use because it requires no sulphuric acid, reduces the chromate so slowly that there is no danger of uneven mordanting, and yet fixes the chromium quantitatively on the fiber. This optimistic view is not confirmed entirely by Whittaker<sup>1</sup> who recommends using 1-2 percent bichromate and an equal amount of 85 percent formic acid. "Since the reduction of the bichrome with this assistant takes place rapidly, uneven dyeings result, unless the mordanting is carried out carefully. The wool should therefore be entered at 140° F (60° C), and the wool worked whilst the bath is brought gradually to the boil, then boiling continued 1-1.5 hours. The bath will be exhausted of chrome.

"When bichrome and formic acid are used, it will be noticed that much less bichrome is used, the whole being precipitated on the fibre. The bath is so well exhausted of chrome that the same liquor may be used for dyeing as was used for mordanting. In no case must the bichrome and assistant be dissolved together in a small quantity of water. The assistant should be added to the bath just before the wool is going to be entered."

#### Wool and Chromic Salts

Liechti and Suida<sup>2</sup> have studied the visible decomposition of various chromium salts on boiling or dilution, starting with chrome alum and with the sulphates, sulphocyanates, and acetates of chromium. As was to be expected, the hydrolysis is greater the more basic the solutions. Only those basic chromium acetates which contain sulphates are hydrolyzed visibly by dilution alone. This is the result of the coagulating action of the sulphate ion. Freshly prepared chromium acetates resist the action of precipitating agents more strongly than do solutions which have aged. This merely means that there is a time factor in the hydrolysis.

Liechti and Hummel<sup>3</sup> have studied the behavior of chrome

<sup>1</sup> "Dyeing with Coal Tar Dyestuffs," 52 (1919).

<sup>2</sup> Jour. Soc. Chem. Ind., 4, 586 (1885).

<sup>3</sup> Ibid., 13, 222, 256 (1894).



alum and of other chromium salts with wool. "Among the various chromic oxide salts the first to be considered is chrome alum,  $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ . Although seldom or never used by woolen dyers, this salt has long been employed by calico printers, who already, more than forty years ago, recognized the necessity of applying chromium in some other form than that of potassium bichromate, wherever, indeed, the oxidising property of the latter was found to be injurious, or was not beneficial. At one time a very expensive chemical, and consequently excluded from use in practice, it has now for many years been the custom of the calico printer's colourist to prepare chrome alum by reducing potassium bichromate in the presence of sulphuric acid, with glucose, starch, glycerin, etc.

"As early as 1851 C. Koechlin made experiments with chrome alum, not only as a mordant for cotton, but also for wool. His results appear to have been very unsatisfactory, for he says that chrome alum is the least satisfactory of the salts from which to obtain the oxide; the nitrate gives better results. For wool (probably woolen printing is meant) he recommends the use of chromium acetate with the addition of one equivalent of oxalic acid; he finds the oxalate and the nitrate to be the best mordants for wool.

"Gehe recommends chrome alum in place of bichromate, because, he says it is cheap, does not make the wool hard and brittle, and it gives level colours which do not rub off so much. Peissert also prefers chrome alum to bichromate of potash because he finds it to yield more level colours, and he recommends it to be used with the addition of a little sulphuric acid. Joclet, too, recommends chrome alum for wool, and states that the fibre absorbs the salt as such, not as a basic salt or as a hydrate. He considers that the salt is decomposed in the dye bath only, for although the chrome alum is not washed out by cold water it can be removed by hot water. The addition of cream of tartar he deems to be unnecessary, although it is absorbed by wool to the extent of one-fourth the weight of the chrome

1  
1  
1  
1

alum employed. Curiously enough Joclet says that chrome colours are not very fast to light. Ganswindt and Kertesz recommend the use of cream of tartar as an assistant. Dé-pierre considers all chromic oxide salts to be inferior mordants to bichromate of potash. According to Herzfeld green solutions of chrome alum give up more oxide to the fibre than violet solutions, and he finds it desirable to employ large amounts of cream of tartar. Kay and Bastow find, on comparing bichromate of potash with chrome alum as mordants, using equivalent amounts, that the latter gives up to the fibre twice as much  $\text{Cr}_2\text{O}_3$  as the former; they also observe that by employing larger amounts of chrome alum, e. g., twenty per cent instead of ten per cent, less chromium is fixed, e. g., 53.07 per cent instead of 63.87 per cent; and with the use of three per cent of tartaric acid the amount fixed is reduced as low as 30.7 per cent. Koepp enumerates the following advantages in connection with the use of chromic oxide mordants (referring no doubt to the use of chromium fluoride): the wool preserves a soft handle and is readily wetted out and there is no fear of over-chroming. Knecht, Rawson and Loewenthal consider that part of the chromium sulphate is probably simply absorbed by the wool fibre and is not fixed in a permanent manner, and thus account for the poor results obtained in dyeing. Cochenhausen recommends the use of four mols cream of tartar; Witt also recommends tartar, but does not find chrome alum to be an advantageous mordant. Previous experiments in the Yorkshire College dyehouse have shown that cream of tartar, tartaric and oxalic acids are all useful assistants with chrome alum."

"The differences in the opinions expressed regarding the value of chrome alum as a wool mordant are due no doubt to two causes:—first, the different percentages, reckoned on the weight of wool, employed; second, the concentration of the mordanting bath and the quality of the water. Here too, as in the case of the bichromate of potash mordant, little or no attention has been paid to the ratio which ought to subsist be-

tween the amounts of colouring matter and mordant employed."

Unless otherwise specified the experiments of Liechti and Hummel were made with ten grams of wool in 600 cc Leeds water. Usually ten percent of chrome alum (referred to wool) was taken which is about equivalent to three percent bichromate of potash. When this solution was heated and cooled without any wool, there was no turbidity. In presence of wool the bath began to become turbid at about 80°-82°, the turbidity increasing rapidly so that the solution became quite opaque. "The precipitate was excessively fine and had by no means the ordinary flocculent character of chromic hydrate. Now it has long been known that wool has the property of absorbing or attracting in a mechanical manner very finely divided insoluble matter in suspension, and this feature was shown strikingly in the present instance. Before the appearance of the turbidity the wool scarcely showed even traces of any green tint; but from this point it rapidly acquired a yellowish-green colour. At a temperature of about 95° the solution became clear again and, after boiling a little, it was perfectly limpid and almost colourless, the wool having mechanically fixed nearly the whole of the precipitate. When the bath was allowed to cool, it contained only a small quantity of a pale green precipitate, and if the wool was kneaded and pressed in the liquor with the fingers a little of the adhering precipitate could be removed from it; still even with vigorous washing the major portion still remained attached to the wool, colouring it a pleasing shade of yellowish-green." The water contained 14.3 percent of the original chromic oxide content, so that about 86 percent was partly fixed on the wool and partly in the precipitate. "On repeating the experiment with the addition of ten percent sodium chloride to the bath, the decomposition was quite complete, for the waste liquor proved to be entirely free from chromium. Another experiment in which only five percent chrome alum was employed, also showed mere traces of chromium in the filtered liquor. A certain re-

relationship seems therefore to exist between the amounts of wool and of chrome alum, so that, as already stated, when using five percent of the latter total decomposition is produced, while with ten percent it is affected only to the extent of 85.7 percent."

Analyses of the precipitate gave ratios of 0.836, 0.819, 0.538, and 0.360  $\text{SO}_3$  to one of  $\text{Cr}_2\text{O}_3$ . Liechti and Hummel consider that "the varying composition here shown is not surprising, and it is no doubt caused by the different lengths of time taken to heat the bath up to the point of initial turbidity. Moreover, the last portions of chrome alum may also become insoluble by long-continued heating at the boiling point. Liechti and Hummel average these data and consider that the precipitate is a definite compound having the formula  $2\text{Cr}_2(\text{SO}_4)_3(\text{OH})_4 \cdot \text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$  or  $\text{Cr}_2\text{O}_3 \cdot 0.66\text{SO}_3$ . Analyses of the solution showed less sulphate percent than there should be. Liechti and Hummel therefore conclude that the wool contains both a basic sulphate and free sulphuric acid. They say that it seems difficult to imagine the presence of basic chromic sulphate and of free sulphuric acid in the wool at the same time; but the corrections of this view will be established by experiments to be cited later on. It may, however, be already stated here that long boiling of the wool with excess of hydrochloric acid did not dissolve off the basic sulphate." In different runs the wool contained 1.9, 2.3 and 1.7  $\text{SO}_3$  to one  $\text{Cr}_2\text{O}_3$ .

Experiments with potassium sulphate alone showed no adsorption by wool, and chromic sulphate apparently gave the same results as chrome alum. When sodium carbonate was added to a chrome alum solution, the solution decomposed badly and the wool was not well mordanted, although it took on a fine sea-green color. Presumably the particles of the chromium compound were too coarse to adhere well to the wool.

"In all cases of mordanting wool with acid salts, as was already observed long ago by Havrez, and referred to more recently by Knecht, the presence of ammonia could be detected in the waste liquors, and this too was observed with

certainty, even in the case of the wool mordanted in the cold. The ammonia, however, was not estimated quantitatively. It is well to point out here that in all the analyses of waste liquors given, a portion of the sulphuric acid reckoned as in combination with chromium is really combined with ammonia. It is not unnatural, therefore, to consider that the ammonia which is given off from the wool combines with some of the  $\text{SO}_4$  groups of the chrome alum and so effects its decomposition. This occurs undoubtedly; but only to a limited extent, and cannot be accepted as a full explanation of the reaction which takes place, otherwise the analyses would not show any disappearance of sulphuric acid from the waste liquor. To avoid any misconception on this point, consider the following typical case a little more in detail. When wool is boiled with five percent chrome alum in solution, the decomposition of the salt is practically complete, as we have seen. A small amount (equal to  $\frac{2}{3}$  mol  $\text{H}_2\text{SO}_4$ ) is combined with the precipitated  $\text{Cr}_2\text{O}_3$ , so that the waste liquor should contain  $\frac{10}{3}$  mols  $\text{H}_2\text{SO}_4$  capable of being estimated as barium sulphate. Such is, however, never the case, as numerous analyses have shown; invariably a large proportion of the sulphuric acid is wanting, and must, therefore, have been taken up by the wool."

In order to check up on the results obtained, "an experiment was made in which chrome alum was titrated with normal sodium hydroxide, and it was observed that a first change of colour really occurred when one-sixth of the  $\text{SO}_3$  was neutralized, and a second change to a decided yellowish-green colour was noticed when one-third of the  $\text{SO}_3$  was saturated. These observations correspond exactly with the appearance noticed during the mordanting process, so that the decomposition of the wool can scarcely be explained in any other manner than by considering that the wool gradually absorbs the sulphuric acid from the dissociated green solution with the formation of a more and more basic salt, and that this process continues until the wool becomes saturated under the existing

conditions. As above shown, this point occurs when about 85.7 percent of the 10 percent chrome alum presented to the fibre is decomposed, and it has already been shown that five percent chrome alum is decomposed completely by the wool."

In order to determine the effect of increasing concentration "wool was mordanted with 10, 15, 20, 25, 30, 35, and 40 percent chrome alum in the ordinary manner. With increase of concentration of the baths their decomposition was diminished, as indeed was to be expected on physical grounds, so that the solutions containing the largest amounts remained perfectly clear. With the increase in the amounts of mordant used, the separation and fixing of insoluble basic sulphate disappeared gradually; the samples had the appearance of being better mordanted, showing signs of having fixed large amounts of chromium. Instead of the yellowish-green colour observed before, they had now a violet-greenish grey tint, and they gave one the impression that chrome alum as such was in a state of solution within the wool fibre. The samples were dyed with logwood, alizarin, and Persian berries, and the colours obtained became darker and darker, corresponding to the increasing amounts of chrome alum employed. When examined more carefully, however, the colours were seen to have an irregular, speckled, or seedy appearance, since separate wool fibres had evidently taken up different amounts of mordant, and therefore of colouring matter as well. A microscopic examination showed this peculiarity extremely well, and fibres of every degree of intensity of colour were to be seen, some being colourless, others very dark; indeed, similar differences were noticed even in one and the same fibre. . . . Why different fibres should behave so differently, as is here shown, is a moot point; whether it is due to a mixture of wool or whether the mature fibres behave differently to those of more recent growth, with respect to their power of absorption of the mordant constituents, is not yet determined. It always appeared, however, as if the coarser fibres had deeper colours than the thinner ones. In any case it is very striking that simi-

lar marked differences are never met with in wool mordanted with bichromate of potash, and explains to some extent the preference of practical dyers for this mordant."

"With chromic acid, i. e., bichromate of potash, it is easy to mordant the wool evenly, so that, when examined microscopically, the individual fibres scarcely differ from each other in depth of colour. With the chromic oxide mordants, however, such regularity is difficult to attain and is only met with in the very best of this class. No doubt this difficulty has to some extent caused practical wool dyers to discard chrome alum. With the dyestuffs above alluded to (logwood, alizarin and Persian berries) and with the increasing amounts of chrome alum, the colors varied respectively from pale grey to deep bluish-black, from pale yellowish-claret to a dark dull-purple, and from straw-yellow to a brownish-orange."

In order to determine the effect of free acid, "wool was mordanted with ten percent chrome alum plus 0, 1, 2, 3, 4 mols sulphuric acid. In baths Nos. 1 and 2 strong dissociation occurred, in No. 3 there was much less, but in Nos. 4 and 5 the solutions remained perfectly clear; the waste liquor of No. 1 appeared almost colourless, but the rest showed a green colouration, which became gradually more intense towards No. 5. Nevertheless the dyed patterns showed that from Nos. 2-5 the amount of chromium increased gradually, Nos. 4 and 5 giving especially dark colours. Here too, however, a microscopic examination showed very unequal dyeing of the different fibres, and the patterns themselves had a 'seedy' appearance, just as when large percentages of chrome alum were employed. In individual fibres the tips always appeared darker than the roots, i. e., the younger parts of the fibre. The same observations were made in the case of unspun lamb's wool scoured in the laboratory, which was tried perchance the woolen cashmere employed contained more than one quality of wool. Here, too, the use of bichromate of potash gave level colours, the irregularities appearing only with the employment of the chromic oxide salt."



"Parallel experiments boiling wool with one gram chrome alum and 6 cc normal  $H_2SO_4$ , respectively, i. e., equal amounts of  $SO_3$ ," showed that practically equal amounts of sulphate are adsorbed in the two cases, thus showing "that the decomposition of the chrome alum by the wool is really due to the adsorption of the acid by the fibre."

Liechti and Hummel do not explain how, with the constant amount of chrome alum, both the solution and the wool can become richer in chromium with increasing addition of sulphuric acid; but it is probable that it is at the expense of the precipitate which was not fixed on the wool. This makes these results practically worthless.

They "are inclined to share Knecht's view as expressed in his conclusions, viz., that the acid is not combined permanently with the wool, although it is certainly very difficult to remove the last traces of acid from the fibre. A sample of wool boiled with a solution (600 cc) containing 10 cc normal  $H_2SO_4$ , absorbed 0.314 g. When the squeezed wool was extracted as completely as possible with water, and this was neutralised with normal NaOH, the wool still lying in the liquid, the latter invariably became acid again after some time; but by neutralising again and again after similar rests, it was possible to show the presence in the liquid of the full amount of acid originally employed. In another repetition experiment, the wool, having absorbed 0.317 g  $H_2SO_4$ , was boiled with water for two hours; the liquid was then neutralised with normal NaOH, and the operations were repeated till no further quantity of sulphuric acid could be extracted: here all the sulphuric acid absorbed could be accounted for. Indeed, in both cases a little more than 10 cc normal NaOH was required, it is namely very difficult to titrate with exactitude in protracted and intermittent operations such as those above, and during the intervening time the indicators may have altered slightly."

It will now be profitable to consider what all this really means. It is apparently clear that with bichromate of potash we have chromic acid adsorbed at first but not strongly and



that this is then reduced to a hydrous chromic oxide which is the true mordant. Addition of sulphuric acid cuts down the adsorption of chromic acid because of the adsorption of the sulphuric acid and increases it because of the increasing acidity. What actually happens is the resultant of these two factors. With hydrochloric and nitric acids, the effect due to increasing acidity is the important one. With chromic sulphate or chrome alum, the conditions are quite different because of the high sulphate concentration. It seems quite reasonable that the wool should adsorb sulphuric acid first, setting free a basic sulphate, apparently  $\text{Cr}_2\text{O}_3 \cdot 0.66 \text{SO}_3$ , which is adsorbed by the wool but which is not the actual mordant. The fact that some of this salt appears in the bath shows that the heating schedule is wrong. It is probable that faulty rate of heating is responsible for the uneven dyeing, because alum is used for mordanting wool and the sulphate problem is the same in the two cases. The salt that is precipitated first with alum is said to be  $\text{Al}_2\text{O}_3 \cdot 0.5 \text{SO}_3$ , and of course it is possible that part of the difference in behavior is due to the difference in the properties of the basic aluminum and chromium salts. Speaking as one who has no practical knowledge of dyeing whatsoever, it seems to me that rinsing with a dilute soda solution would be desirable, so as to convert the basic sulphate into the oxide. We know that the statement is not generally true that alizarin will only dye alumina in presence of lime salts. It is true only when the alumina contains sulphate. If a mistake like that can persist for years, it is quite probable that there are still a good many things about mordanting with chrome alum which have been overlooked. Of course the increased mordanting with increasing concentration of chrome alum is just what one would expect. On the other hand I do not see at all why increasing the acid content of a chrome alum bath should increase the amount of chromium taken up. It cannot be true if the heating is conducted so that there is no precipitate formed in the bath because Liechti and Hummel admit that the bath is exhausted less completely when more

sulphuric acid is added, which is just as it should be. This is a striking instance of faulty experimentation and this should have been pointed out years ago.

Liechti and Hummel<sup>1</sup> find that chromium chloride and chromium nitrate solutions behave quite differently from chromium sulphate solutions. "It seemed desirable to determine carefully the behaviour of chromium chloride and nitrate towards wool. These salts were prepared from chrome alum in the same manner as the chromium sulphate [by precipitating with caustic soda and dissolving in acid], in order to be quite certain that exactly the same amount of  $\text{Cr}_2\text{O}_3$  was used in each case. The chromium chloride bath became yellowish-green on heating, but remained perfectly clear throughout. The wool acquired a peculiar greenish-yellow tint and had not the appearance of being mordanted at all. Analysis showed that 86.5 percent of the chromium remained in the waste liquor, so that only 13.5 percent was fixed on the wool. The waste liquor contained  $\text{Cr}_2(\text{OH})_2\text{Cl}_4$ , hence the wool must have contained the compound  $(\text{Cr}_2 + 18.3 \text{ Cl})$ . This corresponds to  $(\text{Cr}_2\text{O}_3 + 9.15 \text{ SO}_3)$ , hence in this case a very acid salt is fixed on the wool. The circumstance that here none of the chromium was precipitated, as was the case with chrome alum, is quite in accordance with the fact that both chromium chloride and nitrate in solution bear the addition of a large proportion of sodium carbonate (up to 2 mols) without a precipitate being formed. With chromium nitrate too, a very indifferent mordanting of the wool was effected, the material acquiring even a paler greenish-yellow tint. The waste liquor contained 0.1339 g  $\text{Cr}_2\text{O}_3$ , i. e., 87.5 percent of the original amount, so that the wool contained only 12.5 percent."

We can, of course, account for the relatively slight mordanting from chloride and nitrate solutions in the same way that Liechti and Hummel have done by referring to the marked peptizing power of these solutions for chromic oxide and that seems the most plausible explanation. In that case, however,

<sup>1</sup> Jour. Soc. Chem. Ind., 13, 224 (1894).

addition of a moderate amount of soda should have increased the mordanting. Doubtless that would have happened; but Liechti and Hummel did not try it, which they should have done in view of the fact that they report that adding sulphuric acid increases the mordanting with chrome alum. It is rather curious that they did not try this, because, in a later paper,<sup>1</sup> they account for the beneficial action of adding suitable amounts of organic acids to chrome alum by assuming that these acids prevent the precipitation of the basic salt, which is their way of saying that the organic acids peptize the possible precipitate. On that basis the objection to the chromic chloride solution is that it overdoes the peptization. It is quite evident that Liechti and Hummel did not see this and I am inclined to think that, with our present knowledge, there is danger of reading into their papers a good deal more than they knew was there.

“At a very early period dyers must have noticed that when wool is mordanted with alum alone poor colours are obtained in dyeing, and in order to avoid this defect they began to add, along with it, organic acid, in the form of cream of tartar. No doubt its employment in preference to other acids was the result of pure empiricism, and who the discoverer was is altogether unknown. At the present time one endeavours, wherever possible, to economise by replacing it with the much cheaper oxalic acid.”

“In the course of the following experiments it was noticed that when organic acids were employed along with chrome alum for mordanting wool, the green solutions became more and more violet according to the amount employed, from which it would appear that their addition retards or prevents dissociation of the chrome alum. Comparing the effect of equivalent amounts of oxalic and tartaric acids the latter gives greener solutions, and such as show less tendency to become turbid. Closely connected with this is the fact that an addition of oxalic acid to the chrome alum solution only

<sup>1</sup> Liechti and Hummel: *Jour. Soc. Chem. Ind.*, 13, 356 (1894).

partially prevents its precipitation by caustic soda, whereas an addition of tartaric acid prevents it entirely. Altogether the behavior of these two acids towards chrome alum is somewhat different."

"Six fents of wool were mordanted with ten percent chrome alum plus 0, 1, 2, 3, 4, 5 cc normal oxalic acid (=0, 0.5, 1.0, 1.5, 2.0, 2.5 mols). With increasing amounts of acid the dissociation apparent in No. 1 liquor diminishes gradually, No. 3 is still fairly turbid, Nos. 4, 5, and 6 are quite clear. The dried mordanted fents appear as follows: No. 1 yellowish-green, No. 2 similar to No. 1 but less yellow, Nos. 3 and 4 are still less yellow, No. 5 has the deepest colour, a greyish-green, No. 6 is slightly paler than No. 5. It is interesting to note that in gas light the mordanted fents exhibit a peculiar reddish tint, and one is tempted to entertain the opinion that the chromium is on the fibre in some peculiar soluble condition. The liquors too, with increase of oxalic acid, acquire a reddish tint, which may possibly be explained by supposing that a part of the chromium has been taken up by the fibre as  $\text{Cr}_2(\text{SO}_4)_3$  in addition to free sulphuric acid, and that in the bath there remains  $\text{Cr}_2(\text{C}_2\text{O}_4)_3$  as well as  $\text{Cr}_2(\text{SO}_4)_3$ . This change of colour occurs only during the mordanting process. Notwithstanding the presence of the oxalic acid the hot liquor is first green; but, while the wool gradually acquires a greyish-green colour, the bath becomes more and more violet, appearing distinctly red when cold, quite like the colour of pure chromium oxalate. On heating chrome alum solution with three mols  $\text{Na}_2\text{C}_2\text{O}_4$  without the presence of wool, a violet solution is also obtained, showing therefore that interaction occurs at least partially; here the sulphuric acid would be taken up by the NaOH in place of the wool."

"The six fents of the present experiment were dyed with twelve percent alizarin, with the result that No. 5, i. e., the mordant  $\text{Cr}_2(\text{SO}_4)_3 + 2 \text{H}_2\text{C}_2\text{O}_4$  gave the best colour. Under the microscope No. 1 showed dull red and almost colourless fibres, differences which became less apparent from Nos. 2 to 4,

and almost disappeared in Nos. 5 and 6. It may be added that a much deeper claret colour was obtained if the wool mordanted with chrome alum and 2 mols oxalic acid and washed was passed, previous to dyeing, through a very dilute sodium carbonate solution; for 600 cc water 0.53 g  $\text{Na}_2\text{CO}_3$  (0.005 mols)."

"A further observation may be here cited. The appearance of the waste dye liquor of No. 5 indicated that it contained excess of alizarin and possibly chromium mordant as well, and this proved indeed to be the case, since on boiling in it a small piece of wool (1.66 g) it acquired a pink colour. Wool mordanted with chrome alum and two mols tartaric acid exhausted the dye-bath somewhat more and the waste dye-liquor dyed a piece of fresh wool a paler pink than the foregoing in consequence. Altogether wool mordanted with the addition of tartaric acid seemed to be better mordanted, the yellowish-green tint being replaced by one of a pure greyish-green."

Since oxalic acid and tartaric acid acted so well as additions to chrome alum, Liechti and Hummel tried chromium oxalate and chromium tartrate as mordants. "Chromium oxalate gave much better results than chrome alum and two mols oxalic acid, or than chromium fluoride, and since this mordant is comparatively cheap it may be strongly recommended for use on the large scale. To correct the temporary hardness of the water employed, a little sulphuric acid would require to be added to the bath. A microscopic examination of the fibres supported this favourable view, and it may be added that of all the chromium oxide salt mordant baths that of chromium oxalate was the best exhausted, and the dye-bath following it, in the case of alizarin, was almost entirely exhausted."

Further experiments convinced Liechti and Hummel that "the best of all chromic oxide salts as a mordant hitherto examined is chromium tartrate; chromium oxalate is almost as good, and to be preferred in practice because cheaper. . . . The difference in action between chromium sulphate and chro-

mium tartrate is truly remarkable, for whereas the former is decomposed almost entirely and scarcely mordants the wool at all, the latter mordants it in the best possible manner. So far as our present knowledge of the wool fibre goes, it seems to us that the cause of this difference lies, first, in the greater affinity of the wool for sulphuric acid, and secondly, that the organic acids are capable of forming much more basic and at the same time soluble compounds than is the case with sulphuric acid."

"Chromium acetate gave an unlevel yellowish-green colour and the dyed colour was very bad. The microscope revealed the greatest differences in colour in the different fibres, although chromium acetate is not dissociated, a fact which shows clearly that wool can only be mordanted properly by chromic salts in acid solution. In the case of chrome alum alone the differences in colour of the individual fibres were very great indeed even in the different parts of the same fibre, but by the addition of oxalic acid these differences became less marked; no colourless fibres were seen, at most such as were greyish blue and bluish-black."

"Chromium fluoride gave an uneven yellowish-green colour; the dyed colour was somewhat better than that given by chrome alum; blue as well as black fibres were noticed under the microscope."

"One point worth noting in connection with wool mordanting in the ordinary manner is, that the less acid the mordanted wool is, the lower the temperature at which it begins to dye. Wool mordanted with chromium oxalate was strongly acid, and began to dye with alizarin only at a temperature of 70° C. As soon, however, as the calculated amount of calcium acetate was added to the bath, the wool began at once to acquire a deep colour and the bath was soon entirely exhausted, although it still had an acid reaction at the end of the dyeing process, having previously passed through a neutral if not even a slightly alkaline condition. It is here plainly evident that the acid previously absorbed is slowly bleeding out of the dye bath."

### Adsorption of Chromic Oxide by Silk

Silk does not take up chromic oxide as well as wool does.<sup>1</sup> Liechti and Hummel<sup>2</sup> mordanted wool with chrome alum and obtained a good claret color on dyeing with alizarin; but the green color of the mordanted silk was not as intense as in the check experiment with wool. Knecht, Rawson and Lowenthal<sup>3</sup> say that "for the mordanting of silk with chromium compounds normal or basic chromium salts are used. Bichromate does not serve as a mordant proper, although it is used as an oxidising agent in the developing of cutch browns."

Whittaker<sup>4</sup> says that "in order to preserve the lustre of silk, it is not mordanted in the same way as wool, but in the following way: Mordant the silk overnight in a cold bath of chromium chloride 32° Tw., work half an hour in a cold bath of sodium silicate 3/4° Tw., and wash thoroughly. By this means basic chromium salts are precipitated on the fibre." This is presumably a case of fixing a mordant with silica and will therefore be referred to more in detail in a later paper. The main thing for the moment is that the general principles apply to silk exactly as to wool; but the adsorption by silk is less strong.

### Adsorption of Chromic Oxide by Cotton

Cotton takes up chromic oxide very much less readily than silk does. Liechti and Hummel<sup>5</sup> heated cotton with a ten percent chrome alum solution (referred to the cotton) and obtained no mordanting at all. Knecht, Rawson and Loewenthal<sup>6</sup> say that "it is difficult to impregnate the vegetable fibres with an amount of chromium salt sufficient to obtain a full shade. The sulphates, nitrates, acetates, nitrate-acetates, etc., have been employed with good results in calico printing; but the demand for a good chromium mordant for the dyeing

<sup>1</sup> Ganswindt: "Theorie und Praxis der modernen Färberei," II, 19 (1903).

<sup>2</sup> Jour. Soc. Chem. Ind., 13, 223 (1894).

<sup>3</sup> "A Manual of Dyeing," 258 (1910).

<sup>4</sup> "Dyeing with Coal Tar Dyestuffs," 50 (1919).

<sup>5</sup> Jour. Soc. Chem. Ind., 13, 223 (1894).

<sup>6</sup> "A Manual of Dyeing," 252 (1910).



of cotton, especially of cotton yarns, has not been completely satisfied as yet." The Hoechst Color Works recommend the use of the so-called chromium chromate, dissolved in or peptized by hydrochloric or acetic acid, and followed by a dilute soda bath. Koechlin<sup>1</sup> has recommended the so-called alkaline chromite solution, which is really chromic oxide peptized by alkali. Knecht, Rawson and Loewenthal say that "Koechlin's alkaline mordant is one of the best chromium mordants for cotton which has been proposed. Unfortunately, it cannot well be used for yarns on account of its caustic action on the hands of the workmen. Another disadvantage is that it cannot be used on oiled material, since the oil would be stripped from the fibre. Cotton piece goods are saturated with the cold liquor on the padding machine, rolled up and left for twelve hours, then washed, if possible in running water. . . . The precipitation takes place by mere contact, and fixing agents are useless."

The general conclusions of this paper are:

1. From bichromate solutions wool first adsorbs chromic acid and this is then reduced to chromic oxide, which latter forms the true mordant.
2. Within limits, increasing the acid concentration increases the amount of chromic acid taken up. This is less marked with sulphuric acid than with hydrochloric or nitric acid, presumably owing to the adsorption of sulphuric acid by wool.
3. Chromic acid oxidizes organic compounds more readily in presence of wool than when the wool is not there. Sulphuric acid is more effective than hydrochloric or nitric acid in causing the oxidation of wool by chromic acid, possibly because of higher acidity at the surface of the wool.
4. When tartar, oxalic acid, lactic acid, or formic acid is used as an assistant it is possible that there is no appreciable oxidation of the wool.
5. When wool is mordanted with chrome alum, a basic

<sup>1</sup> Dingler's Polytech. Jour., 254, 132 (1884).



sulphate is apparently adsorbed first. This is said to have the composition  $\text{Cr}_2\text{O}_3 \cdot 0.66 \text{SO}_3 \cdot x\text{H}_2\text{O}$ . It changes later to chromic oxide, which is the true mordant.

6. Liechti and Hummel found that addition of sulphuric acid increases the amount of chromium taken up; but this is unquestionably faulty experimentation. Increasing alkalinity favors adsorption until the oxide or basic salt becomes too coarse.

7. Liechti and Hummel obtained almost no mordanting with chromium chloride solutions; but this result could undoubtedly have been changed had they added soda.

8. Chrome alum gave uneven mordanting on wool. Since one can get even mordanting with alum, this difference can not have been due to sulphate and must therefore have been due to faulty experimentation.

9. Silk adsorbs chromic oxide less strongly than wool does.

10. Cotton takes up scarcely any chromic oxide from chrome alum; but adsorbs it from an alkaline solution.

11. It is not known why chromic oxide colors wool gray under certain conditions.

12. There is no evidence of any definite compound being formed when wool is mordanted with chromic oxide. It is a plain case of adsorption.

*Cornell University*

THE SOLUBILITY OF LIQUIDS IN LIQUIDS. THE PARTITION OF THE LOWER ACIDS, PARTICULARLY FORMIC, BETWEEN WATER AND VARIOUS ORGANIC SOLVENTS<sup>1</sup>

BY NEIL E. GORDON<sup>2</sup> AND E. EMMET REID

That some substances dissolve when brought into contact with various liquids must have been one of the first observations that can be classed as chemical. In the last three decades the study of solutions has been the chief occupation of chemists. Yet our knowledge of solutions is still far from adequate and some of our conceptions are still not clear.

If we shake a portion of water with oxygen, another portion with ether, and a third with sugar, assuming constant temperature, equilibria are reached and we call the three solutions saturated, speaking of the concentrations of the three solutes in the water as their solubilities. The words "saturated and solubility" are used for all, but actually have quite different meanings in the three cases.

The solubility of the sugar is definite, since in that case the solid phase is pure sugar, unchanged in composition and concentration by its contact with the water. In the case of the oxygen and water, the only thing that we can determine is the ratio of the concentrations of oxygen in the two phases. Since the water vapor does not affect the partial pressure of the oxygen, this ratio is definite and independent of the water vapor present in the gas phase. As previously pointed out<sup>3</sup> while the solubility of the ether is definite, yet the solubility that we find is not the true solubility, i. e., the amount of ether taken up by water in contact with anhydrous ether. We can no more determine the solubility of ether in water than we can

<sup>1</sup> Contribution from the Chemical Laboratory of the Johns Hopkins University.

<sup>2</sup> From dissertation of Neil E. Gordon.

<sup>3</sup> Wroth and Reid: Jour. Am. Chem. Soc., 38, 2316 (1916).

that of formic acid, since we cannot have a solution of either ether or formic acid in contact with the anhydrous liquid. We may hope that sometime a method, or formula, may be devised for finding the true, or ideal, solubility of ether in water, perhaps from the observed equilibrium of the solution of ether in water with one of water in ether, perhaps from some other data.

In the case of solid iodine, where the solubilities are true solubilities, Jakowkin<sup>1</sup> found the ratio of the solubilities in two solvents,  $S_a/S_b$ , remarkably near to the partition ratio,  $C_a/C_b$ , or  $r$ , measured with the same two solvents. He further found that  $r$  changes progressively, approaching more and more nearly the value  $S_a/S_b$  as the concentrations of iodine in the two solvents increase, i. e., as  $C_a/C_b$  approaches  $S_a/S_b$  as  $C_a$  and  $C_b$  approach  $S_a$  and  $S_b$ .

As is well known, the partition ratio,  $r$ , remains constant with changing concentrations, only when the substance partitioned dissolves in both solvents in the same form. Furthermore, it is stipulated that the two solvents must be absolutely insoluble in each other, even when both contain large amounts of the common solute. This condition is, of course, never more than approximately fulfilled, the disturbing influences becoming greater, the higher the concentrations of the solute.

In the present investigation formic acid has been partitioned between water and the following solvents: cottonseed oil, kerosene, benzene, toluene, xylene, carbon tetrachloride, carbon disulphide and bromoform. The so-called solubilities of formic acid in these eight solvents and the solubilities of these liquids in formic acid have been determined.

If the solubility figure found for formic acid in benzene, say, were the ideal solubility and the partition ratio found were correct, then the product of these two should give the ideal solubility of formic acid in water which we cannot find directly. The ideal solubility from the data obtained from these eight solvents should be the same, or, since the several

<sup>1</sup> Zeit. phys. Chem., 18, 590 (1895).

partition ratios vary with the concentrations, the values found should tend to approach some one limit, as the concentrations of formic acid in the non-aqueous solvents approach the solubilities of formic acid in these solvents.

In the case of carbon disulphide and water, and in that only, the partition ratio remained practically constant with changing concentration, being 1606 when the acid in the water layer was 8.4% and 1616 when this had increased to 54.8%. When carbon disulphide and formic acid are shaken together there is 1.28 g of the acid to 100 g carbon disulphide in the one layer and 4.66 g carbon disulphide to 100 g formic acid in the other. Even in this case 1.28 is not the ideal solubility of formic acid since the solution was in contact with a mixture of 95.55% formic acid and 4.45% carbon disulphide and not with the pure acid, but as in this case the mutual "solubilities" are the lowest and the partition ratio is the most nearly constant, this appears to be, by far, the most favorable case. Multiplying 1.28, the "solubility" of formic acid in carbon disulphide, by the partition ratio, 1616, we have 2068 as the ideal solubility of formic acid in water, i. e., 2068 g of the acid should be taken up by 100 g of water in contact with *anhydrous* formic acid, a condition which can, of course, never be realized. With the other seven solvents the products of the several solubilities by the respective partition ratios should approach 2068 as the concentrations increase. That is the figures in the last columns of Tables 1 and 7-12 should approach 2068 as we read down. The results are represented graphically in Fig. 1 in which these hypothetical ideal solubilities are plotted against the percentage of saturation of the non-aqueous layer. The curves as drawn extend only to 8%, not far enough to include all the points on the kerosene, cottonseed oil and bromoform curves. For very dilute solutions the figures obtained are more or less erratic on account of the difficulties involved in determining the small amounts of acid present in even large amounts of the oil layers, e. g., in the most dilute solution with carbon tetrachloride the amount of formic acid per 100 g of oil was only 0.0038 g.

Most of the series were terminated at 55% to 60% of formic acid in the water layer as it was thought that results with greater concentrations could not be trusted on account of mutual solubilities of the two solvents in presence of so much of the solute. But with cottonseed oil the concentration was carried up to 87.2% of formic acid in the water layer when there was 5.026 g of acid per 100 g of the oil layer while the solubility of the anhydrous acid in the oil is 8.68 g per 100 g. This gives us a point in the cottonseed oil curve at 58% for which the ordinate is 1179 which is well on the way to the figure indicated by the carbon disulphide curve.

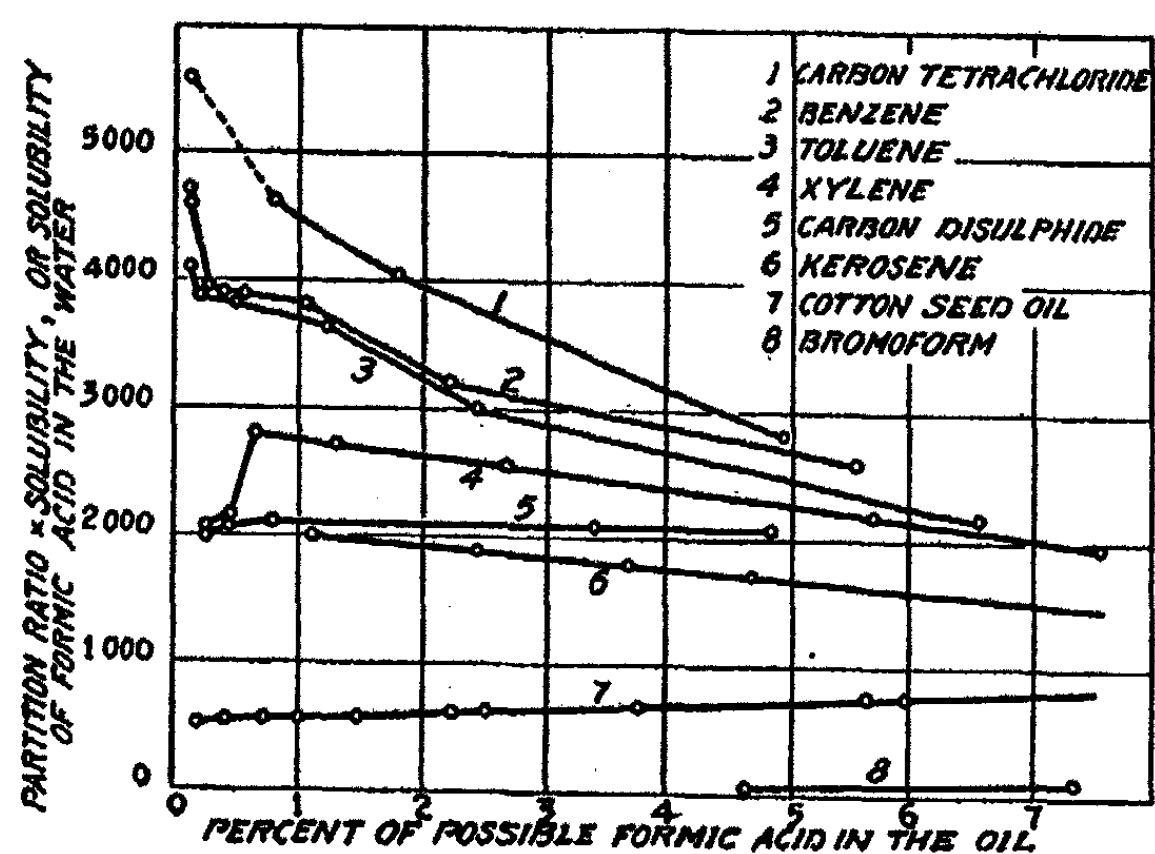


Fig. 1

It is interesting to note that cottonseed oil takes up only 58% as much formic acid from an 87% acid as from the 100% acid. On a molecular basis 73% of the molecules are formic acid, so it appears that the water in the acid is more than a diluent: it restrains the formic acid molecules from passing into the oil layer. A similar inference may be drawn from other experiments. In most cases where the water layer con-

tains over 50% of formic acid the oil layer takes up only 5% to 7% as much acid as from 100% formic acid.

The results with kerosene are regarded as unreliable as the oil layer was much colored at the higher concentrations indicating some sort of reaction.

Looking at the figure, there appears to be a tendency for the various curves to converge on the carbon disulphide line indicating an ideal solubility around 2000, though the bromoform curve is very low down and the one for cottonseed oil has a considerable distance to go. The xylene curve appears to cross the 2000 line. It is certainly hazardous to extrapolate from 6 or 8% to 100%.

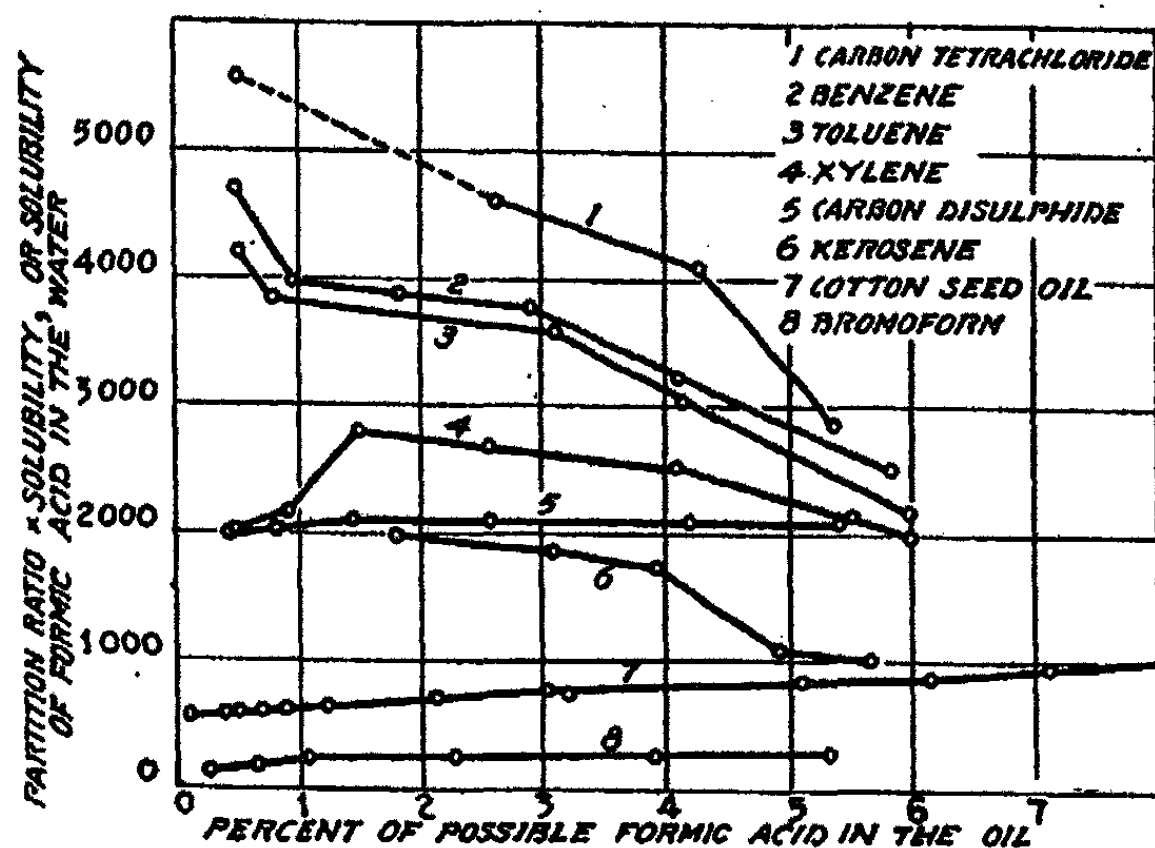


Fig. 2

In Fig. 2 the same data are presented on a different basis; the ordinates are the same but the abscissae are the percentage of formic acid in water layer at equilibrium. On this basis the curves are steeper and do not show as much tendency to converge though we have the advantage of having to extrapolate over a much shorter distance, as all of the curves go as far as 55% and one even to 87%.

The results obtained do not settle the question but it is hoped they do open it. One method of approach has been tried: better ones may be found. Even by this method more measurements are desirable at higher concentrations, with other solvents, and with other solutes. The results so far obtained have value as partition and solubility measurements. The degrees of association of formic acid in the various solvents can be calculated from the variation of the partition ratios.

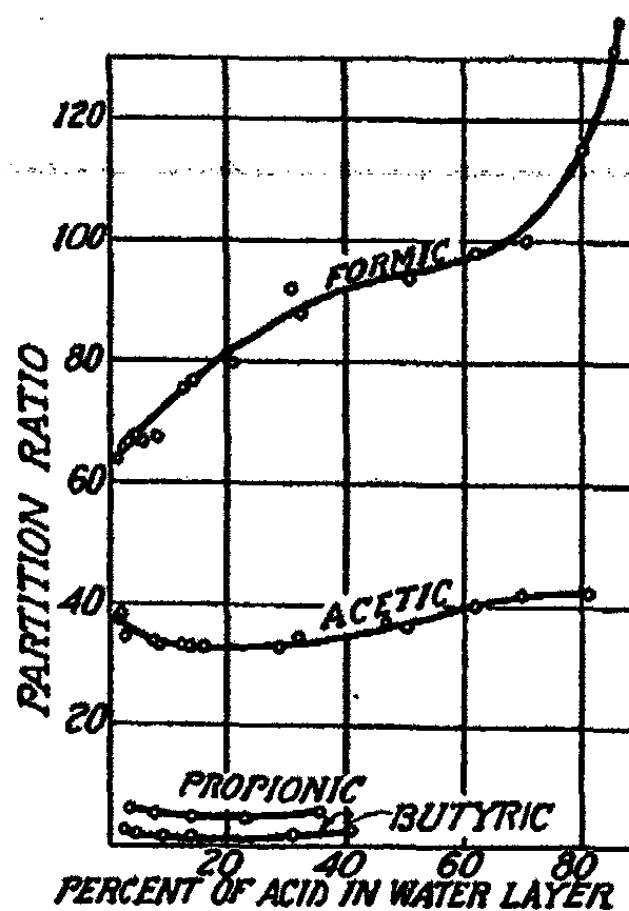


Fig. 3

As formic acid is a strong acid, its dissociation in the water layer influences the partition ratios, but as its lowest concentration was 0.24 N, at which it is only moderately dissociated and, as it turned out, the high concentrations are the ones which are of most interest from the present point of view, the dissociation may be disregarded. It is interesting to note that formic acid shows a real partition ratio in all cases even in dilute solution, which is in marked contrast to the behavior of silver perchlorate as found by Hill.<sup>1</sup>

<sup>1</sup> Jour. Am. Chem. Soc., 43, 254 (1921).

Georgievics<sup>1</sup> partitioned formic acid between benzene and water. Calculating his results according to our method we obtain the following partition ratios:

% Acid	4.4	5.8	6.7	7.8	8.6	8.7	13.3	13.3	18.9	23.9
Ratio	370	261	400	302	264	562	304	347	269	298

Disregarding the sixth, the average of these is 316 which is not far from 292 the average of our results over the same range.

In addition to the experiments with formic acid, acetic, propionic and butyric were partitioned between cottonseed oil and water and acetic acid between kerosene and water. The partition ratios are plotted in Fig. 3. The proportion of the organic acid taken by the water layer increases rapidly as we go from formic to butyric. The formic acid curve bends sharply upward at about 70% of acid in the water layer. Acetic acid has a definite solubility in the oil but propionic and butyric have not. Formic is the only one of these that shows limited solubility in the other solvents.

#### Materials

*Cottonseed Oil:* The Wesson oil used was found to have an acid reaction. In order to eliminate this the oil was shaken with a dilute solution of barium hydroxide for an hour. It was then centrifuged and filtered, when it gave a perfectly neutral reaction.

*Formic Acid:* This was distilled under reduced pressure over anhydrous copper sulphate as suggested by Garner, Saxton and Parker. The pressure used was 120 mm, when the acid distilled over at 50°. This method was found to be a very satisfactory one. Beginning with an acid 89.2 percent pure, the first distillation resulted in an acid 96.5 percent, the second 98.2 percent, and the third distillation gave an acid 99.99 percent pure. This acid melted at 8.35° and had density 1.2170<sub>25</sub>.<sup>2</sup> This anhydrous acid was used for the solubility work only. For the partition work, commercial acid was used

<sup>1</sup> Zeit. phys. Chem., 84, 359 (1913).

<sup>2</sup> Am. Chem. Jour., 46, 236 (1911); J., 1886, 216.



since it was found to contain only water. The water it contained was calculated and added to the weight of water taken.

*Acetic Acid:* Like formic acid the commercial acid was used for the partition work. For the solubility the acid was purified by freezing. It was found that the number of freezings necessary to render it anhydrous could be cut down by introducing a crystal of the acid to prevent too great undercooling. It melted at  $16.7^{\circ}$ , and titrated 99.9 percent pure. Its density was  $1.0445_{25}^{25}$ .

*Propionic and Butyric Acids:* These acids mixed in all proportions with both oil and water and thus it was not necessary to make them anhydrous. As their densities and titrations showed they contained only water as an impurity, they were used without further purification.

*Organic Solvents:* First class commercial grades of benzene, toluene, xylene, carbon tetrachloride, carbon disulphide, and bromoform were used. To insure purity, the boiling points and densities were taken and found to agree well with those given in the literature.

Waddell<sup>1</sup> found in his investigation that the same partition coefficient was given with purified benzene as with commercial benzene.

*Standard Solutions:* Standard solutions of approximately N/10 were prepared, and frequently standardized. The solutions were kept in large stock bottles from which they were siphoned into the burettes. The barium hydroxide bottle and burettes were protected from the air by tubes containing soda lime.

*Water:* Freshly distilled water was used.

*Kerosene Oil:* Commercial kerosene oil was distilled and the portion obtained between  $180^{\circ}$  and  $260^{\circ}$  was used in the partition work. It had a density of  $0.798_{25}^{25}$ .

<sup>1</sup> Jour. Phys. Chem., 2, 233 (1895).

### Procedure

The filling, shaking and centrifuging of the bottles containing cottonseed oil, water and the respective acids was carried out approximately as the former work where the alcohols were used instead of the acids. It seemed necessary to shake the acids longer than the alcohols to obtain concordant results. The centrifuge was used only with the cottonseed oil and water.

*Estimation of Acids in Non-aqueous Solvent Layers.*—The oil layer containing the acid was drawn off by means of a special pipet, shaped similar to the Ostwald pycnometer. An amount of oil was taken out with the pipet sufficient to require about 10 cc of the barium hydroxide for neutralization. The oil was put into a 180-cc beaker containing about 80 cc of distilled water for titration. The oil, with ordinary stirring failed to give up its acid promptly, making the titration slow and uncertain. A mechanical stirrer was used and this accelerated the speed with which the acid passed from the oil into the water. Even under these conditions the end-point was not as accurate as it was in the water. In spite of all efforts the acid seemed to have a slight tendency to cling to the oil. The other organic solvents were handled similarly.

*Estimation of Acid in Water Layer.*—A small thin-walled glass bulb was weighed, partly filled from the water layer, sealed and reweighed. The bulb was then broken under water to avoid evaporation, and the amount of acid, which it contained was determined by titration.

The absolute solubilities of formic and acetic acids in cottonseed oil were found by shaking the oil and anhydrous acids in the constant temperature bath for four hours, and then estimating the amount of acid in the oil layer and the amount of oil in the acid layer by the titration method as just described. The absolute solubility of formic acid in the other organic solvents used and the solubility of the solvents in the formic acid were carried out in a similar manner.

## Solubilities at 25°

Formic Acid in Cottonseed Oil			Cottonseed Oil in Formic Acid		
Sample	Found	In 100 g	Sample	Found	In 100 g
0.3154	0.0251	8.65	0.1656	0.0013	0.78
0.1656	0.0416	8.72	0.1141	0.0009	0.79
0.4437	0.0360	8.84	0.1086	0.0008	0.74
0.5019	0.0393	8.50	0.1142	0.0009	0.79
Av. 8.68			Av. 0.77		

Acetic Acid in Cottonseed Oil			Cottonseed Oil in Acetic Acid		
Sample	Found	In 100 g	Sample	Found	In 100 g
0.1421	0.0508	55.4	0.1016	0.0058	5.8
0.0858	0.0309	56.3	0.0996	0.0055	5.5
0.0831	0.0299	56.3	0.0616	0.0036	5.7
0.0684	0.0245	55.96	0.1373	0.0073	5.6
0.1008	0.0345	54.3	0.0894	0.0050	5.6
Av. 55.7			Av. 5.6		

Formic Acid in Benzene			Benzene in Formic Acid		
Sample	Found	In 100 g	Sample	Found	In 100 g
0.2718	0.0341	14.3	0.1825	0.0238	15.0
0.3300	0.0416	14.4	0.0992	0.01312	15.2
0.3950	0.0502	14.5	0.1455	0.0189	14.9
0.4277	0.0537	14.3	0.0030	0.0122	15.4
0.4197	0.0527	14.40			
Av. 14.40			Av. 15.14		

Formic Acid in Toluene			Toluene in Formic Acid		
Sample	Found	In 100 g	Sample	Found	In 100 g
0.2815	0.0284	11.20	0.1793	0.0149	9.08
0.3795	0.0376	10.98	0.1323	0.0110	9.06
0.2986	0.0295	10.96	0.0851	0.0071	9.10
0.3565	0.0358	11.17			
Av. 11.08			Av. 9.08		

Formic Acid in Xylene			Xylene in Formic Acid		
Sample	Found	In 100 g	Sample	Found	In 100 g
0.5440	0.0442	8.83	0.1009	0.0063	6.81
0.3535	0.0251	8.70	0.0790	0.0057	7.77
0.4480	0.0357	8.70			
Av. 8.74			Av. 7.29		

Solubilities at 25°

Formic Acid in Carbon Tetrachloride			Carbon Tetrachloride in Formic Acid		
0.1910	0.0069	(3.76)	0.0484	0.0030	6.60
0.3434	0.0115	3.45	0.0934	0.0062	6.95
0.3623	0.0119	3.40	0.0918	0.0063	7.31
0.3158	0.0105	3.44			
Av. 3.43			Av. 6.95		

Formic Acid in Carbon Disulphide			Carbon Disulphide in Formic Acid		
2.4628	0.0313	1.29	0.0631	0.0604	4.47
1.9878	0.0240	1.28	0.1429	0.1398	4.85
2.6070	0.0311	(1.21)			
4.7033	0.0549	(1.18)			
4.9431	0.0569	(1.16)			
7.461	0.0959	1.29			
Av. 1.28			Av. 4.66		

Formic Acid in Bromoform			Bromoform in Formic Acid		
1.9684	0.0475	2.47	0.1301	0.0362	25.2
1.2830	0.0310	2.47	0.1085	0.0220	25.4
3.2351	0.0767	2.42			
Av. 2.45			Av. 25.3		

Formic Acid in Kerosene			Kerosene in Formic Acid		
Sample	Found	In 100 g	Sample	Found	In 100 g
3.3003	0.0294	0.899	0.1003	0.0015	1.52
2.9977	0.0267	0.905	0.0681	0.0011	1.60
Av. 0.897			Av. 1.56		

Acetic Acid in Kerosene			Kerosene in Acetic Acid		
1.0690	0.1909	21.74	0.0735	0.0082	12.6
0.7638	0.1367	21.80	0.0802	0.0088	12.3
Av. 21.77			Av. 12.4		

## Partition Experiments

The results are given in the tables below, no completed determination being omitted, the first column showing the final percentage of acid in the water layer, the next three the amounts of water, oil and acid weighed in, while the fifth and sixth give the amounts of acid found in the two layers, the sum of these should equal the weight of acid in column four. In the seventh is found the molecular partition ratio or the acid dissolved by 1 mol. of water divided by that dissolved by 1 mol. of the oil. The m. wt. of cottonseed oil was assumed to be 885. In the case of kerosene this ratio is omitted. The next column gives the partition ratio for equal weights of water and oil and the last gives this weight ratio multiplied by the solubility of the acid in the oil when this is known.

TABLE I  
Partition of Formic Acid between Cottonseed Oil and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios		Weight ratio × 8.68
				Water	Oil	Molec- ular	Weight	
1.1	15.42	66.85	0.183	0.169	0.0115	1.29	63.6	552
2.3	16.94	70.53	0.423	0.399	0.0253	1.33	65.7	570
3.7	14.57	75.37	0.595	0.556	0.0430	1.36	66.8	580
4.2	22.54	72.63	1.036	0.990	0.0471	1.38	67.8	588
5.5	22.66	67.69	1.385	1.326	0.0592	1.36	66.9	581
8.1	12.05	81.52	1.163	1.064	0.1064	1.38	67.7	588
12.7	27.00	63.19	4.077	3.945	0.1224	1.54	75.4	654
14.4	6.84	5.91	1.166	1.152	0.0130	1.56	76.5	664
20.9	13.11	20.47	3.556	3.470	0.0680	1.62	79.7	692
30.3	5.57	6.576	2.500	2.429	0.0323	1.87	91.9	798
32.4	12.62	22.87	6.168	6.045	0.1192	1.81	88.8	771
51.1	4.54	5.051	4.827	4.747	0.0563	1.91	93.9	815
62.5	3.65	5.857	6.258	6.087	0.0997	1.99	97.9	850
71.3	3.16	4.981	8.043	7.854	0.1241	2.03	99.5	864
80.7	1.79	6.102	7.720	7.463	0.2222	2.34	114.8	996
86.3	0.799	7.728	5.493	5.023	0.3705	2.67	131.1	1138
87.2	0.728	8.589	5.894	4.972	0.4317	2.76	135.8	1179

TABLE 2  
Partition of Acetic Acid between Cottonseed Oil and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios		Weight ratio × 55.7
				Water	Oil	Molec-ular	Weight	
1.9	25.84	68.32	0.544	0.5105	0.0363	0.757	37.2	2071
2.1	24.32	66.23	0.550	0.5130	0.0364	0.781	38.4	2137
2.4	26.70	65.86	0.696	0.6504	0.0463	0.705	34.6	1930
7.5	27.51	71.33	2.408	2.238	0.1711	0.690	33.9	1888
8.2	26.31	64.31	2.513	2.346	0.1718	0.671	33.4	1859
12.7	26.68	68.80	4.185	3.877	0.3006	0.677	33.3	1853
14.1	28.28	69.97	4.9751	4.636	0.3471	0.672	33.0	1840
16.2	24.75	67.27	5.195	4.791	0.3940	0.673	33.1	1841
28.9	13.13	25.64	5.673	5.345	0.3177	0.667	32.9	1830
31.8	11.13	25.35	5.534	5.178	0.3453	0.695	34.2	1903
46.9	4.38	5.950	4.044	3.875	0.1424	0.752	36.9	2059
50.9	4.360	6.064	4.729	4.516	0.1720	0.743	36.5	2035
62.1	1.387	7.574	2.586	2.270	0.3118	0.809	39.7	2212
70.2	1.001	7.572	2.794	2.361	0.4311	0.843	41.4	2308
81.8	1.958	5.975	9.574	8.827	0.6483	0.845	41.5	2314

TABLE 3  
Partition of Propionic Acid between Cottonseed Oil and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios	
				Water	Oil	Molecular	Weight
3.4	38.15	48.33	1.620	1.347	0.2819	0.123	6.05
7.4	39.75	42.39	3.836	3.165	0.6580	0.104	5.13
14.3	20.05	20.09	4.045	3.335	0.7240	0.094	4.62
23.0	15.09	20.88	5.855	4.502	1.358	0.093	4.59
36.2	3.416	7.705	2.744	1.938	0.7779	0.114	5.60
59.8	2.988	5.516	5.311	4.438	0.8959	0.186	9.14
62.5	0.8750	7.750	2.853	1.458	1.366	0.192	9.45
67.3	0.4755	8.919	2.873	0.979	1.874	0.199	9.79

TABLE 4  
Partition of Butyric Acid between Cottonseed Oil and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios	
				Water	Oil	Molecular	Weight
2.7	16.135	24.590	0.747	0.4526	0.2764	0.0508	2.495
5.0	16.568	25.095	1.612	0.8798	0.7350	0.0369	1.813
9.2	6.530	6.562	1.164	0.6615	0.4906	0.0276	1.355
14.0	3.139	6.755	1.308	0.5106	0.7880	0.0284	1.395
30.5	3.911	6.597	3.458	1.714	1.692	0.0348	1.709
41.3	1.802	6.590	3.203	1.268	1.948	0.0484	2.380

TABLE 5  
Partition of Formic Acid between Kerosene and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratio Weight ratio	Weight ratio × 0.897
				Water	Oil		
17.9	10.634	65.717	2.324	2.316	0.00648	2209	1981
30.9	9.801	72.723	4.452	4.388	0.01586	2052	1841
38.9	9.778	65.189	6.283	6.224	0.02146	1933	1734
43.2	2.547	7.422	1.945	1.936	0.00308	1831	1642
59.8	2.725	5.645	4.160	4.060	0.00714	1180	1058
66.3	3.153	30.950	6.400	6.200	0.05358	1136	1019

TABLE 6  
Partition of Acetic Acid between Kerosene and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratio Weight ratio	Weight ratio × 21.77
				Water	Oil		
9.1	7.110	32.024	0.730	0.7127	0.02164	1483	32300
17.0	6.027	30.676	1.392	1.236	0.05796	1086	23600
27.2	6.786	29.831	2.665	2.532	0.1332	836	18200
46.9	2.503	8.479	2.330	2.214	0.09804	765	16700
59.2	2.819	6.243	4.273	4.089	0.1217	744	16200

TABLE 7  
Partition of Formic Acid between Benzene and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios		Weight ratio × 14.40
				Water	Oil	Molec-ular	Weight	
5.3	20.61	74.21	1.138	1.146	0.0126	75.1	327	4710
6.4	11.46	89.07	0.742	0.716	0.0175	73.5	319	4590
9.9	19.96	82.54	2.195	2.192	0.0329	63.5	275	3960
13.6	21.71	65.42	3.444	3.432	0.0382	62.4	270	3890
18.5	28.39	51.66	6.506	6.437	0.0434	62.3	270	3890
29.2	10.30	28.71	4.395	4.258	0.0449	61.0	264	3810
41.2	12.71	32.92	9.126	8.894	0.1060	50.8	220	3170
58.2	3.272	40.73	5.096	4.695	0.3279	41.1	178	2570

TABLE 8  
Partition of Formic Acid between Toluene and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios		Weight ratio × 11.08
				Water	Oil	Molec-ular	Weight	
5.3	21.04	79.04	1.174	1.177	0.0118	74.0	378	4190
7.9	20.43	64.20	1.799	1.761	0.0158	68.5	350	3880
16.5	10.319	88.00	2.086	2.039	0.0498	68.5	349	3870
31.0	9.210	84.70	4.257	4.148	0.1166	64.0	327	3620
41.7	5.618	30.87	4.181	4.019	0.0837	52.8	270	2990
59.7	3.276	32.68	5.186	4.834	0.2391	39.5	202	2230



TABLE 9  
Partition of Formic Acid between Xylene and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios		Weight ratio × 8.74
				Water	Oil	Molec- ular	Weight	
5.0	10.42	83.55	0.561	0.5521	0.0190	39.7	233	2040
5.1	9.867	94.58	0.559	0.5355	0.0225	38.6	228	1990
8.6	11.24	86.25	1.185	1.158	0.0362	41.6	245	2140
9.6	9.891	76.12	1.066	1.047	0.0319	42.8	252	2210
15.0	10.41	71.74	1.889	1.835	0.0411	52.4	308	2690
15.6	10.85	79.05	2.036	2.006	0.0439	56.5	334	2920
25.6	10.03	67.34	3.576	3.460	0.0778	50.8	299	2610
26.4	10.29	69.27	3.795	3.697	0.0776	54.5	321	2800
40.4	6.136	30.50	4.308	4.171	0.0680	51.8	305	2660
41.2	5.881	38.13	4.248	4.125	0.0963	47.2	278	2430
55.2	3.870	29.86	5.036	4.760	0.1498	41.9	245	2160
55.7	3.994	38.84	5.382	5.026	0.1923	43.1	254	2220
60.3	2.660	84.32	4.830	4.036	0.5611	38.7	228	1990

TABLE 10  
Partition of Formic Acid between Carbon Tetrachloride and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios		Weight ratio × 3.43
				Water	Oil	Molec- ular	Weight	
5.8	10.291	120.3	0.6534	0.635	0.00456	1910	1630	5590
8.6	9.978	107.4	0.9572	0.942	0.00861	1380	1180	4040
17.5	9.908	135.6	2.135	2.102	0.01541	2190	1870	6410
26.9	10.175	125.0	3.792	3.747	0.03416	1580	1350	4620
43.2	6.160	67.76	4.617	4.506	0.04213	1380	1180	4030
58.9	3.299	61.08	4.873	4.735	0.1040	990	840	2890

TABLE 11  
Partition of Formic Acid between Carbon Disulphide and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios		Weight ratio × 1.28
				Water	Oil	Molec- ular	Weight	
4.8	10.24	122.6	0.514	0.512	0.00390	3720	1570	1991
8.4	10.48	115.3	0.981	0.965	0.00661	3800	1606	2056
14.6	11.36	122.0	1.962	1.942	0.01281	3850	1628	2084
25.7	10.21	112.0	3.583	3.536	0.02403	3820	1614	2066
41.6	5.406	125.3	3.966	3.850	0.05497	3840	1623	2077
54.8	6.244	121.7	7.763	7.565	0.09122	3830	1616	2068

TABLE 12  
Partition of Formic Acid between Water and Bromoform

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios		Weight ratio × 2.45
				Water	Oil	Molec- ular	Weight	
3.1	9.746	243.0	0.5734	0.3084	0.2771	1.98	27.8	68
6.9	10.28	189.1	1.123	0.7613	0.3407	2.93	41.1	101
10.8	11.03	177.1	1.660	1.336	0.3121	4.87	68.7	168
23.1	10.39	192.3	3.898	3.123	0.7580	5.43	76.3	187
39.0	5.286	53.51	3.792	3.378	0.3630	6.70	94.2	231
53.6	3.430	58.99	4.762	3.960	0.7142	6.79	96.3	236

Summary

Formic acid has been partitioned at 25° between water and cottonseed oil, kerosene, benzene, toluene, xylene, carbon tetrachloride, carbon disulphide and bromoform. Acetic acid has been partitioned between water and cottonseed oil and kerosene, and propionic and butyric acids between cottonseed oil and water. The solubilities of these acids have been determined in the solvents named and vice versa so far as these were limited.

An attempt has been made to get clearer ideas of the relations involved when liquids are miscible in all proportions.

Baltimore, Md.

## THE MORDANTING OF WOOL WITH POTASH ALUM

BY W. W. PADDON

Although potash alum is one of the most common mordants used in the dyeing industry, little is known regarding its real action and the composition of the mordant on the fibre.

Knecht<sup>1</sup> states that, "it appears that not only the hydroxides but true basic aluminum salts are deposited by the mordanting process in the fibre." The only evidence given in support of this view is the fact that on dyeing well-washed wool with alizarin, the spent liquors invariably show an acid reaction. It is, however, unnecessary to postulate the presence of sulphuric acid in chemical combination, for adsorbed sulphuric acid should be displaced by the alizarin with equal readiness.

Fürstenhagen and Appleyard,<sup>2</sup> give data to show that the amount of sulphate in the fibre remains constant when mordanted from solutions of potash alum containing 10 to 20% of the alum on the weight of the wool. No information is given to show whether the sulphuric acid is adsorbed by or combined chemically with the alumina.

Havrez<sup>3</sup> and von Georgievics<sup>4</sup> are of the opinion that from baths containing above 24% of potash alum on the weight of the wool, alumina and sulphuric acid are adsorbed in the same relative amounts as they occur in  $Al_2(S_4O)_3$ . Up to 24% the amount of sulphuric acid taken up by the wool increases relatively to the wool as the concentration rises.

None of these investigators have determined the amounts of both alumina and sulphuric acid removed by wool from potash alum baths of different concentrations. Data of this nature have been found in the following way.

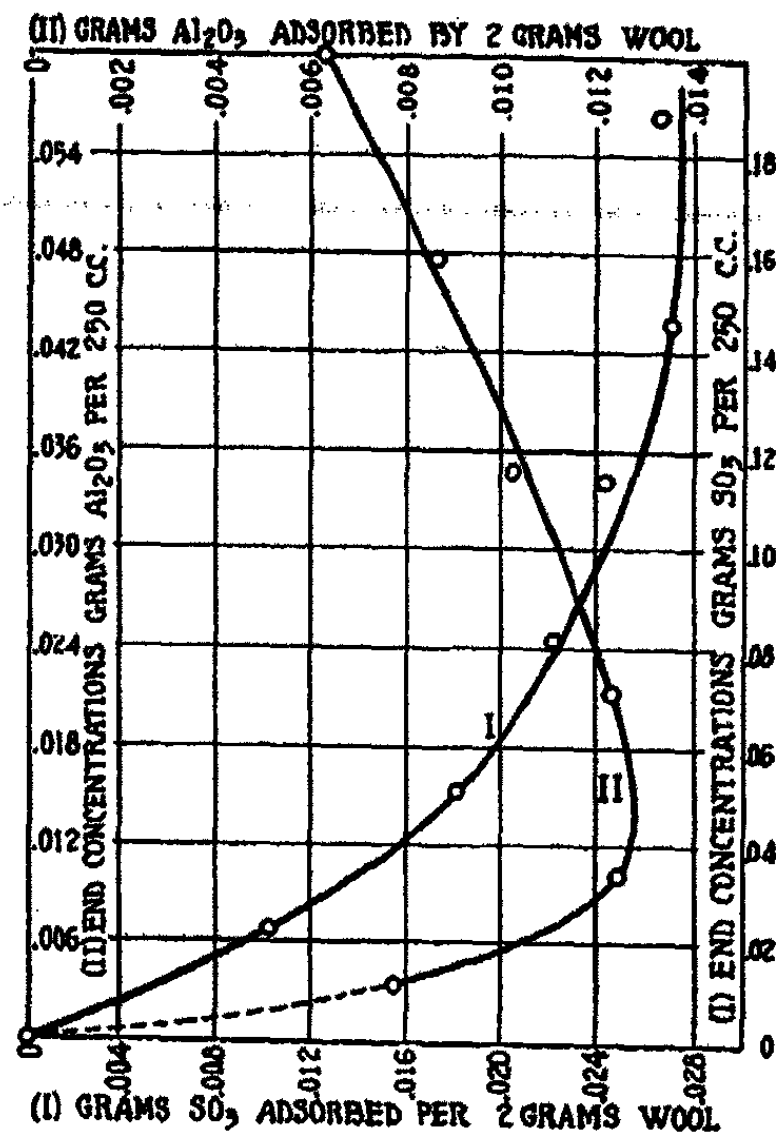
<sup>1</sup> Knecht, Rawson, and Lowenthal: "A Manual of Dyeing," p. 237 (1910).

<sup>2</sup> Fürstenhagen and Appleyard: Jour. Soc. Dyers and Colourists, 1888, 105.

<sup>3</sup> Chem. Centralblatt, 1874, 696.

<sup>4</sup> Jour. Soc. Chem. Ind., 14, 653 (1895).

Two-gram samples of well-washed wool were boiled for 1 hour in baths of potash alum of varying concentrations. After the one hour, the wool was removed when hot and an aliquot portion of the bath analyzed in the usual gravimetric manner for aluminum and for sulphates. The results have been expressed both in grams and in percentages referred to the alum and to the wool, the aluminum as  $\text{Al}_2\text{O}_3$  and the sulphuric acid



as  $\text{SO}_3$ . In the baths of higher concentrations, it was noticed that, upon boiling, a precipitate formed on the bottom of the flasks. This precipitate was found to contain aluminum, with only slight traces of sulphates. The amount of this aluminum was determined and added to the amount already found in each case to have been left in the bath. The values obtained are tabulated below.

TABLE I

% Potash alum on weight of wool	Orig. conc. $\text{Al}_2\text{O}_3$ grams/250 cc	End conc. $\text{Al}_2\text{O}_3$ grams/250 cc	Grams $\text{Al}_2\text{O}_3$ adsorbed per 2 g wool
5.12	0.0112	0.0035	0.0077
10.25	0.0225	0.0101	0.0124
15.37	0.0337	0.0215	0.0122
20.50	0.0450	0.0348	0.0102
25.62	0.0562	0.0476	0.0086
30.75	0.0676	0.0614	0.0062

% Potash alum on weight of wool	Orig. conc. g $\text{SO}_3$ /250 cc	End conc. g $\text{SO}_3$ /250 cc	Grams $\text{SO}_3$ adsorbed per 2 g wool
5.12	0.0346	0.0224	0.0122
10.25	0.0692	0.0511	0.0181
15.37	0.1037	0.0815	0.0222
20.50	0.1383	0.1141	0.0242
25.62	0.1730	0.1461	0.0269
30.75	0.2075	0.1811	0.0264

10.77%  $\text{Al}_2\text{O}_3$  and 33.7%  $\text{SO}_3$  in potash alum.

% Potash alum on weight of wool	$\text{Al}_2\text{O}_3$ referred to alum		$\text{Al}_2\text{O}_3$ referred to wool	
	Conc. in %	% in soln.	% in wool	% in soln.
5.12	3.3	7.4	0.17	0.38
10.25	4.8	5.9	0.49	0.60
15.37	6.8	3.9	1.07	0.60
20.50	8.3	2.4	1.74	0.49
25.62	9.1	1.6	2.38	0.42
30.75	9.8	0.9	3.07	0.30

% Potash alum on weight of wool	$\text{SO}_3$ referred to alum		$\text{SO}_3$ referred to wool	
	Conc. in %	% in soln.	% in wool	% in soln.
5.12	21.8	11.9	1.1	0.6
10.25	24.9	8.8	2.5	0.9
15.37	26.5	7.2	4.1	1.1
20.50	27.8	5.9	5.7	1.2
25.62	28.5	5.2	7.3	1.3
30.75	29.5	4.2	9.1	1.3

The data have been plotted in the form of the curves shown. In the case of the  $\text{SO}_3$ , a smooth curve is obtained, indicating the adsorption of  $\text{SO}_3$  by the wool and the absence of sulphate compounds in the mordanted wool. In the case of alumina, the curve is likewise free from sudden breaks that would indicate the formation of chemical compounds. It passes through a peculiar maximum. This is probably due to the fact that considerable alumina was precipitated on boiling, presumably as  $\text{Al}(\text{OH})_3$ , and the concentration of the alumina in the bath, as far as the wool was concerned, was considerably altered thereby.

As far as the data obtained in these experiments are concerned there is no basis for Knecht's belief in the presence of basic aluminum compounds on the fibre. The formation of such compounds would evidence itself as sudden breaks in the adsorption isotherm. No such breaks were found. Fürstenhagen and Appleyard, in obtaining their results, apparently took into account only the  $\text{SO}_3$  present in  $\text{Al}_2(\text{SO}_4)_3$  of the potash alum and neglected both in their analytical work and their calculations the  $\text{SO}_3$  present in the  $\text{K}_2\text{SO}_4$  of the alum. Above conc. of 20% of alum on the weight of the wool, the amount of  $\text{SO}_3$  adsorbed is quite constant, but this does not indicate the formation of a basic sulphate for at the same concentrations the amount of alumina adsorbed steadily decreases, and moreover the  $\text{SO}_3$  adsorption isotherm shows no sudden break.

It can therefore be concluded that the mordanting of wool with potash alum does not lead to the formation of definite chemical compounds on the fibre, but that it is strictly an adsorption phenomena, involving both alumina and sulphuric acid.

This work was carried out under the direction of Professor Bancroft, and was made possible by a grant from the Chemical Foundation.

*Cornell University*

## NEW BOOKS

**Fluidity and Plasticity.** By Eugene C. Bingham. 21 X 15 cm; pp. xi + 440. New York and London: McGraw-Hill Book Company, 1922. Price: \$1.00.—In the preface the author says that "even from the first the flow of liquids has been a subject of practical importance, yet the subject of Hydraulics has never become more than an empirical subject of interest merely to the engineer. Unfortunately the theory is complicated in that the flow of matter may be hydraulic (turbulent), viscous (linear), or plastic, dependent upon the conditions. It was in 1842 that viscous flow was first differentiated from hydraulic flow, and only now are we coming to realize the important distinction between viscous and plastic deformation."

The first part of the book deals with viscosity and the chapters are entitled: methods of measurement; the law of Poiseuille; the amplification of the law of Poiseuille; viscosity as a definite physical quantity; the viscometer. The second, and much longer, part deals with fluidity and plasticity and other physical and chemical properties. The chapters are entitled: viscosity and fluidity; fluidity and the chemical composition and constitution of pure liquids; fluidity and temperature, volume, pressure—collisional and diffusional viscosity; fluidity and vapor pressure; the fluidity of solutions; fluidity and diffusion; colloidal solutions; the plasticity of solids; the viscosity of gases; superficial fluidity; lubrication; further applications of the viscometric method. In addition there are appendices on practical viscometry, practical plastometry, technical viscometers, and the measurements of Poiseuille."

The author distinguishes three kinds of flow, p. 4. "It is characteristic of viscous or linear flow that the amount of deformation is directly proportional to the deforming force, and the ratio of the latter to the former gives a measure of viscosity. It has been questioned at times whether this ratio is truly constant, but it appears that only one qualification is necessary. In very viscous substances time may be necessary for the flow to reach a steady state, aside from any period of acceleration, because the viscous resistance develops slowly with substances like pitch, so that the above ratio gradually increases when the load is first put on; but, even in this case, the ratio finally reaches a value which is independent of the amount of the load. As, however, the deforming force is steadily increased, a point may be reached where the above ratio suddenly decreases. At this point the régime of turbulent or hydraulic flow begins. . . . . There are substances, on the other hand, for which the value of the above ratio increases indefinitely as soon as the deforming force falls below a certain minimum. These substances are said to be plastic. In plastic flow it is generally understood that a definite shearing force is required before any deformation takes place; but it has not been established whether this is strictly true or not."

On p. 61 the author says that "in expressing viscosities, it is possible to secure simultaneously the advantage of expression in absolute units with the advantages of viscosities relative to some common substance as standard. It is proposed to name the absolute unit of viscosity after Poiseuille the 'poise,' and consequently the submultiple of this unit, which is one-hundredth as large,

the 'centipoise' (*cp*). It so happens that one centipoise is almost exactly the viscosity of water at 20° C; hence absolute viscosities expressed in centipoises are also specific viscosities referred to water at 20° C expressed as standard. To be sure the viscosity of water is not exactly one centipoise at 20° C; but as 1.005, which is unity within the limits of possible experimental error in ordinary measurement."

One of the two main theses which the book tries to establish is stated on p. 83. "There are numerous reciprocal relations besides viscosity and fluidity, such as electrical resistance and conductance, or specific heat and heat capacity, or specific gravity and specific volume. It has been pointed out repeatedly that if one of these is additive, its reciprocal cannot be. It is singular enough that among all of these reciprocal relations, viscosity is the only one for which the decision has not been reached as to whether viscosity is additive or not, or if it is under what conditions. In electricity for example we have absolutely no doubt but that resistances are additive under certain conditions, viz., when the conductors are in series, and likewise that conductances are additive under other equally definite conditions, viz., when the conductors are in parallel. It seems probable that the present unsatisfactory condition as regards viscosity has arisen due to the extraordinary sensitiveness of this property to molecular changes in fluids, either combination or dissociation." The conclusion reached is that viscosities are additive in emulsions and fluidities in solutions. Unfortunately, the two cases grade one into the other, so this cannot be used as a test for the occurrence of colloidal solutions, even if one knew the viscosity of the dispersed phase.

On p. 145 the author explains why the fluidity of a liquid is proportional to the free volume. "When the molecules of a liquid are closely packed, the volume reaches its minimum value and the fluidity is zero. With tetrahedral close-packing of the molecules, shear would require rupture of the molecules themselves. If there are pore spaces between or within the molecules, they do not give rise to fluidity, so that the molecules somewhat resemble close-fitting solid figures. As the fluid expands, due to molecular agitation, the volume of the molecules themselves, i. e., the inner molecular volume may remain the same, but the ordinary, i. e., the outer molecular volume increases. The law states that the fluidity originates solely in the free space which is the difference between the outer molecular volume, or the volume occupied by the molecules, and the inner molecular volume or the space filled by the molecules in the sense indicated above. Given two substances with the same outer molecular volume, it is evident that the one with the larger molecular kernel will have the smaller fluidity. It is therefore natural to expect that the limiting molecular volumes should be additive as Batschinski has found to be the case. This opens the way to a study of the relation between fluidity and chemical composition and constitution which is most fascinating. It is very simple to measure the outer molecular volume, and if this with the fluidity will give a certain and easy method for determining the inner molecular volume, it is a result much to be desired. It is apparent that density and fluidity determinations should go hand in hand."

There is an interesting discussion of emulsions and emulsion colloids on p. 210. "In our discussion of the critical solution temperature, it was made



clear that the separation of the components of a mixture in the form of an emulsion is attended by an increase in the viscosity. It seems probable that this increase is due to the viscosities in emulsions being additive, for it follows of necessity that when the viscosities are additive the viscosity will be greater than in a homogeneous mixture of the same composition. As in the case of suspensions, there is considerable evidence that decreasing the size of particle of the disperse phase brings about a corresponding decrease in the fluidity. Martici (1907) experimented with oil-soap emulsions and found that the fluidity becomes less as the drops become smaller. Buglia (1908) has found the fluidity of milk is lessened when the milk is homogenized by being squirted against an agate plate, thereby increasing the number of fat globules. The apparent decrease in fluidity with emulsification finds excellent practical examples in the manufacture of solid lubricants and of certain household products such as mayonnaise, "whipped cream," and beaten egg albumen. In engine grease less than one percent of water emulsified by means of a solution of soap with mineral oil produces a salve-like grease. Such bodies have the properties of solids and may also be considered in connection with the plasticity of solids.

"The question inevitably arises: How is it possible that water with a high fluidity can decrease the fluidity of a heavy oil, or air decrease the fluidity of albumen, so that the resulting product, emulsion or foam as the case may be, has the rigidity of a solid? To answer this question it is necessary to return to the consideration of our simple case of lamellae of different liquids at right angles to the direction of shear. The theory that viscosities of emulsions are additive, will account for the fluidity being less than the fluidity of the homogeneous mixture but it will in no way account for the case we have here where the fluidity of the emulsion is less than the fluidity of either component.

"As the shear progresses, it is to be noted that the lamellae are greatly elongated. But in immiscible liquids this thinning out of the layers is opposed by the surface tension which tends to keep the surface area a minimum. If therefore the shearing force is less than the maximum force arising from the surface tension, continuous deformation will not result. There will be a certain amount of temporary deformation but this too will disappear as soon as the shearing force is removed. In other words, the substance shows not only rigidity but also elasticity; if the shearing force is greater than the elastic limit, continuous deformation will take place, but since we are dealing with immiscible liquids, the lamellae will not be thinned out indefinitely, but torn into portions which will gather into drops under the influence of surface tension. Thus in an emulsion, shear tends to make the droplets continually smaller, and consequently to raise the viscosity. This corresponds to the cold working of metals. This effect is opposed by the spontaneous coalescence of the particles on standing, analogous to the annealing of metals, so it appears that an equilibrium results and the maximum in viscosity in emulsions may depend upon the rate of shear.

"As the lamellae of the simple case, which we have taken for consideration, are broken up, the viscosities are no longer strictly additive. The droplets become smaller and smaller, the surface tension becomes more and more effective, the droplets become true spheres with an inappreciable amount of flow

within the spheres, so that finally the distinction between emulsion and suspension disappears.

"We pass finally to that class of polar colloids typified by gelatine, soap and rubber. In some ways they are in sharp contrast with the type which we have just been considering, because their viscosity increases tremendously on standing and decreases as a result of shear, but they are alike in the more fundamental respect of exhibiting the properties of rigidity and elasticity.

"It is assumed that the process of gelatinization is the result of polar forces producing a network of crystals or crystal-like material interlacing through the liquid, without necessarily taking up more than a small portion of the space. The solid network performs the function of the lamellae at right angles to the direction of shear in our simple case. The cohesion of the solid opposes the shear and gives rise to the rigidity of the gel. The ability of the solid to be deformed without fracture determines its elasticity. This property of elasticity is enormously developed in rubber, and we have seen that it is noticeable in forms and emulsions. Barus (1893) has noted the considerable degree of elasticity in marine glue which may be regarded as a very viscous liquid. It also is of importance in suspensions, as for example in the manufacture of pencils, the leads expand considerably, as they are forced out of the die previous to baking.

"If gelatinization is analogous to crystallization, we should expect the viscosity to increase on standing and that it would be hastened by 'seeding' the solution with a more viscous colloid. We can readily see that shearing the material would result in the destruction of the polar structure of the material and consequently in a decrease in the viscosity. We refer the reader to the rich material furnished by Garrett (1903)."

The reviewer does not see why gelatine, soap, and rubber should be classed as polar and this is not the ordinary use of the term. If marine glue is to be regarded as a very viscous liquid, it is not clear why it should show a considerable degree of elasticity. Another criticism is that the author seems to consider suspensions as more like solutions than like emulsions. For the present the reviewer cannot subscribe to that belief. He thinks that the author has been led astray by overlooking the differences in concentrations. Very dilute emulsions certainly behave like suspensions. So far as the reviewer knows, the change from viscous to plastic flow occurs at higher concentrations with emulsions than with suspensions. When discussing the occurrence of plastic flow in suspensions, the author does not give an adequate discussion of the factors determining zero fluidity. The question of adsorption as affecting voids is ignored pretty completely. The reviewer is skeptical as to the propriety of applying Stokes' Law to diffusion in true solution, p. 194, especially in view of the fact that diffusion may take place upwards.

There is a very interesting chapter on lubrication, in which it is pointed out that the superiority of fixed oils over mineral oils is due to the greater adsorption of the former by metals, p. 271.

The paragraph on nitrocellulose, p. 293, is worth quoting. "It is of course well known that the so-called solutions of nitrocellulose, gelatine and other colloids are not true solutions, nevertheless the term solution as applied to colloidal dispersion often leads to confusion. This acetone is one of the best

'solvents' for nitrocellulose, being superior, let us say, to amyl acetate. But what does this statement mean? It cannot possibly mean that acetone will actually dissolve more nitrocellulose than will a similar amount of amyl acetate, for there is no point of saturation for either, i. e., both liquids will 'dissolve' or better disperse an indefinite amount of colloid; hence the term solubility has here a very special, albeit a very definite, meaning, viz., that dispersive medium is the best solvent which with a given amount of colloid gives an emulsion having the maximum mobility. Here, however, there enters the fact, which seems from the literature not to have been sufficiently considered, that acetone has a far greater fluidity than amyl acetate to start with, and this must of necessity affect the mobility of dispersions in these media. It is evident that this must be taken into account if we are to get a true measure of the dispersive power of different media."

The author has written a very good book on a subject which has been ignored too much in the past. He seems to the reviewer to have made good on his two main contentions, that fluidity is the additive property in solutions, and that we must distinguish sharply between plastic flow and viscous flow. The reviewer could not quite make out to what extent the concentration giving zero fluidity is independent of the size of the capillary, the size of the particles, and of the pressure. It seems as though with emulsions the point of zero fluidity must vary with the size of the drops because homogenizing milk increases its viscosity, p. 211. The reviewer has been much impressed by the future importance of fluidity determinations as a means of studying solutions; but it will be necessary to work out the theory much more exactly than has yet been done because of the extraordinary sensitiveness of the method. The possibilities of error are so great that it is scarcely an exaggeration to say that no conclusions based on fluidity determinations with solutions are binding as yet; but the method evidently has extraordinary possibilities. The book is welcome as giving a critical, scientific presentation of a problem which is of great importance theoretically and technically.

*Wilder D. Bancroft*

*Philosophy and the New Physics.* By Louis Rougier. Translated by Morton Masius. 19 X 12 cm; pp. xv + 150. Philadelphia: P. Blakiston's Son and Co., 1921. Price: \$1.75.—Two years ago (24, 592) the author's book, entitled "La Matérialisation de l'Énergie," was reviewed and the hope was expressed that the book might soon be available in an English translation. This is a translation of a corrected text of the book in question, though the title has suffered a sea change. The following quotations, pp. 61, 63, 67, 91, 102, 132, 146, will give some idea of the general style of the book.

"According to it [the Lorentz synthesis] there is no matter, only electrons, positive and negative, in an ocean of uniform ether; all forces are of electromagnetic origin or behave like such; and the measurements effected in a moving system are relative to the dimensions of the instruments, to the forces taken as comparison terms, and to local time. In this conception matter, conduction currents and magnetism become mere modes of manifestation. The only constitutive principles are the ether and grains of vitreous (positive) and resinous (negative) electricity. We shall see how the English physicists have taken

hold of this conception and pushed the reduction in the number of things still further: according to certain of them not only is the existence of matter denied but also that of electricity; and nothing but ether and empty space exists."

"As Lord Salisbury picturesquely said in his Oxford presidential address to the British Association, the first and principal reason for the existence of the ether is to supply a subject to the verb to undulate."

"Re-arming themselves with the ideas of Faraday and Maxwell, the English physicists, and the most famous of them, J. J. Thomson, regard the inertia of the electron as due to the ether surrounding it. An electron at rest is a surface charge without material support, and may be considered as a cavity in the ether. This cavity is the center from which the electric lines of force constituting the electrostatic field of the electron diverge. The ether adheres to these lines of force, so that the electron cannot move without displacing it. The inertia of the electron results from the inertia of the entrained ether, which alone opposes its motion. Knowing the volume and the mass of an electron, the density of the ether adhering to it may be calculated; it is found to be equal to about 2000 million times the density of lead. Matter ceases to exist, since, being composed of electrons, the sole reason we have to believe in it, namely its inertia, does not properly belong to it, but is borrowed from the ether. Electricity likewise disappears as a substance with an existence of its own, since the electrons are reduced to cavities in the ether. Two principles only survive, ether and empty space, of one of which the ancients would have said that it is the non-being and consequently that it does not exist. The world is merely a bubble of ether in the non-thing."

"This theory of the disincarnation of matter, leading to a complete etherization, should, in spite of its alluring aspect, be taken with considerable caution. It is threatened with downfall on account of the concept that forms its base, that of an ether endowed with mechanical properties, the hypothetical existence of which seems, moreover, to be contradictory."

"In accordance with what is true for inertia, a change in internal energy is accompanied by a simultaneous change of mass and weight. A body is heavier when in motion than when at rest, when hot than when cold, when in a state of electrification than when neutral, detonating gas than the water it produces, uranium than its disintegration products."

"Empty space is not the absolute and infinite void of Newton's followers: it is the pure field of gravitation on which no matter is superimposed. From the physical point of view there is no amorphous void, endowed with pure receptivity, in which material points could be imagined, attracting or repelling one another according to certain laws, like Newton's law, and thus communicating absolute accelerations to one another. We cannot speak of empty space, except where there is a field of gravitation, not merely coexistent with this space, but veritably the creator of space, of its metrical properties, and, we may say, its extent. The world must be thought of no more as an assemblage of bodies lost in an infinite void, but as systems of bodies and of electromagnetic or luminous fields, superimposed on gravitational fields of finite dimensions. The absolute, void, amorphous, and infinite space of Newton vanishes like other *idola fori*

and Kant's antinomies advanced in regard to it are abolished as referring to a pseudo-problem."

"A second confirmation, due to Einstein and to Nernst, is drawn from the study of the specific heats of solids at low temperature. It is known that the specific heats of solids decrease rapidly when the temperature is lowered. Thus, for diamond at the temperature of liquid hydrogen, the specific heat is reduced to about one-seventh of what it is at ordinary temperatures. Everything takes place as if the molecules lost degrees of freedom in cooling, as if their joints became ankylosed from the effect of the frost. This is contrary to the theorem of the equipartition of energy, which provides a method of calculating the atomic heats of solids and of deducing Dulong and Petit's law, according to which the atomic heats are equal for all bodies and independent of the temperature.

"Planck defined the specific heat of a single resonator as the increase for one degree centigrade, of the mean energy, reduced to calories, that a resonator of given frequency must have at a definite temperature to be in equilibrium with black radiation. Einstein introduces the following simplifying hypotheses. He considers the solid bodies as possessing only a single kind of resonators and only one resonator per molecule; the products of Avogadro's constant by the specific heat of a single resonator then gives him the specific heat, referred to a gram-molecule, of the solid considered. According to his formula the specific heat of a solid hardly varies with the change of temperature at high temperatures; but at low temperatures it decreases rapidly and tends towards zero when the absolute zero is approached. Nernst complicates Einstein's hypothesis a little by adding to the latter's unique system of resonators other resonators tuned to the octave and so succeeds in obtaining a surprising coincidence with the numbers obtained experimentally by himself and his pupils, for a very large number of bodies at temperatures that extend from the ordinary temperatures down to the lowest temperatures that Kamerlingh-Onnes has been able to obtain in his cryogenic laboratory at Leyden. This theory amounts to the following: if a solid is regarded as an aggregate of atoms or of molecules oscillating about an equilibrium position, the energy of each oscillator thus realized must be, as in the case of Planck's electric oscillators, an integral multiple of  $h\nu$ . The diminution of the specific heat of the solid at low temperatures is then readily explained. When the temperature decreases, the supply of disposable energy offered to each of the material oscillators falls below the quantum of a large number of them; instead of vibrating a little they cease to vibrate at all, so that the total energy diminishes more rapidly than in the old theories. On the contrary, at high temperatures, the quantum  $h\nu$  becomes so small that we again get Dulong and Petit's law obtained by starting from the law of the equipartition of energy."

"To explain a phenomenon is, for primitive man, to interpret it anthropomorphically by a supernatural agent endowed with psychological life in his own image; for a scholastic it is to explain it by ultimate causes; for Bacon to explain it by causes; for Maxwell it is to deduce it from the principles of mechanics; for Gibbs and Boltzmann it is to account for it by the calculus of probabilities, by starting from a system of elements subject to given conditions."

This is a delightful book and well worth reading. *Wilder D. Bancroft*

# HYDROGEN ION CONCENTRATION AND THE PROPERTIES OF THE EMULSOID COLLOIDS<sup>1</sup>

BY ROBERT HERMAN BOGUE<sup>2</sup>

1-1851

## Introduction

Much has been written in the last few years upon the importance of a consideration of the hydrogen ion concentration with respect to the properties and behavior of colloids, and of the proteins in particular. Michaelis<sup>3</sup> and Sörenson<sup>4</sup> have studied the effect of the concentration of these ions on body tissues. Robertson,<sup>5</sup> Clark,<sup>6</sup> and Zoller<sup>7</sup> have studied particularly casein. Loeb,<sup>8</sup> Sheppard,<sup>9</sup> Davis *et al.*,<sup>10</sup> and Bogue<sup>11</sup> have reported similar investigations on gelatin. Many other workers in this field have also made valuable contributions to the subject.

In nearly all of these studies, however, the treatment of *hydrogen ion concentration* has been merely incidental to the main investigation, and a corollation of the several studies should be made with the focus of attention centred at that most interesting and important point.

In the present paper such a corollation is attempted, and in many places where the evidence has seemed to be contra-

<sup>1</sup> Published by courtesy of the American Chemical Society. Presented before the 63rd General Meeting of the American Chemical Society, Birmingham, Alabama, April 3 to 7, 1922.

<sup>2</sup> Industrial Fellow of the Mellon Institute of Industrial Research of Pittsburgh, and Research Chemist for Armour and Company, of Chicago.

<sup>3</sup> L. Michaelis: *Biochem. Zeit.*, 1909-1914.

<sup>4</sup> S. P. L. Sörenson: *Comptes rendus Lab. Carlsberg*, 1909-1913.

<sup>5</sup> T. B. Robertson: "The Physical Chemistry of the Proteins," (1920.)

<sup>6</sup> W. M. Clark: *Jour. Ind. Eng. Chem.*, 12, 1162 (1920).

<sup>7</sup> H. T. Zoller: *Ibid.*, 13, 510 (1921); *Jour. Gen. Physiol.*, 3, 365 (1921).

<sup>8</sup> Jacques Loeb: *Jour. Gen. Physiol.*, 1917-1921.

<sup>9</sup> S. E. Sheppard: *Jour. Ind. Eng. Chem.*, 12, 1007 (1920); 13, 423 (1921).

<sup>10</sup> C. E. Davis, E. T. Oakes, and H. H. Browne: *Jour. Am. Chem. Soc.*, 43, 1526 (1921).

<sup>11</sup> R. H. Bogue: *Chem. Met. Eng.*, 23, 5, 61, 105, 154, 197 (1920); *Jour. Am. Chem. Soc.*, 43, 1764 (1921); *Jour. Ind. Eng. Chem.*, 14, 32 (1922).



dictory or insufficient further experiments have been conducted with the hope of making clear or complete these deficiencies.

Very little effort has been made in the past upon the linking up of the findings obtained in the laboratory with the applicability of those findings in plant practice or control. As a result, it is inevitable that the relative importance of the several discoveries should be many times incorrectly accentuated. This is a distinct disadvantage to the chemist. The latter may report very large variations in viscosity, for example, with hydrogen ion concentration, and a plant man, upon repeating the test, may find no variation whatsoever. The reason is obvious, for the chemist may have used a very delicate viscosimeter, sensitive to 0.001 centipoise, and the plant man an instrument sensitive only to about 1 centipoise. But these distinctions are not always apparent to the practical glue tester, and the result is an injured reputation for the chemist: not for that one alone, but, which is much worse, for the profession at large. Some points bearing on this aspect will be mentioned in this paper.

#### Investigations on Hydrogen Ion Concentration

*Hydrogen Ion Concentration and Viscosity: Solvation: Hydration.*—Loeb<sup>1</sup> has shown that the viscosity of any given sample of gelatin varies considerably with the hydrogen ion concentration of the material. If a pure isoelectric gelatin<sup>2</sup> is obtained, the viscosity is found to be at a minimum at that point. The hydrogen ion concentration, or  $C_H$ , was found by Michaelis<sup>3</sup> to be  $2 \times 10^{-6}$  N at the isoelectric point, or in terms of Sørensen's logarithmic symbol,  $\text{pH} = 4.7^4$ .

<sup>1</sup> Jacques loeb: loc. cit.

<sup>2</sup> Obtained by treating a finely granulated gelatin with N/128 hydrochloric acid at 15° C, and washing out the excess of acid with water. It is then dissolved in water and made up to 1 percent solution, and the viscosity measured at 40° C with an Ostwald viscosimeter. Isoelectric gelatin is gelatin at the point of electro-neutrality.

<sup>3</sup> L. Michaelis: "Die Wasserstoffionenkonzentration," (1914).

<sup>4</sup>  $\text{pH} = 1/\log C_H$ .

When the hydrogen ion concentration was increased (the pH decreased), as by the addition of more acid, the viscosity was found to increase rapidly until a pH of about 3.5 was reached, after which the viscosity fell upon further additions of acid. When the hydrogen ion concentration was decreased (the pH increased), as by the addition of more alkali, the viscosity was found to increase somewhat more slowly, until a pH of about 9.0 was reached, after which the viscosity fell upon further additions of alkali.

These results have been confirmed, on the acid side, by Davis, Oakes, and Browne,<sup>1</sup> and on both the acid and the alkali side by Bogue.<sup>2</sup> It is probable that the former also would have obtained the same characteristic rise on the alkali side of the isoelectric point if they had started with an ash-free gelatin. The presence of calcium as calcium gelatinate would greatly inhibit the tendency of increased viscosity at pH values greater than 4.7.

Similar results have been obtained by earlier investigators, but their results are expressed in terms of concentration of acid or base added, rather than of the hydrogen ion concentration to which the solution is brought by such addition.<sup>3</sup> Loeb has pointed out the necessity of following the latter procedure.

It has also long been known that gelatin swells to different degrees depending upon the amount of acid or alkali added to the water in which the gelatin is immersed. Curves illustrative of this are shown by Wo. Ostwald<sup>4</sup> and by D. J. Lloyd,<sup>5</sup> and Fischer and Hooker<sup>6</sup> find similar results with polybasic acids and their salts. Bogue<sup>7</sup> has shown that swelling and viscosity are parallel functions within certain limits, except

---

<sup>1</sup> Davis, Oakes and Browne: *loc. cit.*

<sup>2</sup> R. H. Bogue: *loc. cit.*

<sup>3</sup> See P. von Schroeder: *Zeit. phys. Chem.*, **45**, 75 (1903).

<sup>4</sup> Wo. Ostwald (Fischer): "Handbook of Colloid Chemistry," p. 247 (1915).

<sup>5</sup> Dorothy J. Lloyd: *Biochem. Jour.*, **14**, 147 (1920).

<sup>6</sup> Martin Fischer and Marion Hooker: *Jour. Am. Chem. Soc.*, **40**, 272 (1918).

<sup>7</sup> R. H. Bogue, *Jour. Am. Chem. Soc.*, **43**, 1764 (1921).



that the percentage of change in the former may be far greater than the percentage of change in the latter upon similar alteration in hydrogen ion concentration.

*Hydrogen Ion Concentration and Jelly Strength: Gelation: Solution.*—Fischer and Coffman<sup>1</sup> have pointed out that the solution of a protein is an essentially different process from swelling, and should not be regarded as an extreme case of swelling. They urge that hydration (swelling) is to be regarded as a change through which the protein enters into physicochemical combination with its solvent (water); and solution as the expression of an increase in the degree of dispersion of the colloid. Their findings show that there is a progressive increase in the tendency of gelatin to go into solution in mixtures of the salts of polybasic acids as the amount of acid or alkali in these mixtures is increased from a given low point.

Bogue<sup>2</sup> has shown that the same tendency exists in mixtures of gelatin and sodium silicates upon increasing the hydroxyl ion concentration, either by the use of those silicates which are progressively more completely hydrolyzed in water, or by the direct addition of sodium hydroxid. The curves and data show that at a pH of about 8.5, a 1 percent solution of pure gelatin will just fail to form a firm jelly at 10° C, while at a pH of about 9.5 the solution will remain quite liquid. At pH values between 4.7 and 8.5 a firm jelly is formed.

On the acid side of the isoelectric point the jelly has been found to remain firm to a pH of about 3.5 and to again be quite liquid at a pH of about 2.5.

Sheppard and his collaborators<sup>3</sup> have studied the jelly strength of gelatins and glues by means of an instrument which measures both the breaking load and the percentage twist at break. The factor, breaking load  $\times$  twist / cross section, is

<sup>1</sup> Martin Fischer and W. D. Coffman: *Jour. Am. Chem. Soc.*, **40**, 303 (1918).

<sup>2</sup> R. H. Bogue: *Jour. Ind. Eng. Chem.*, **14**, 32 (1922).

<sup>3</sup> S. E. Sheppard, S. S. Sweet and J. W. Scott, Jr.: *Jour. Ind. Eng. Chem.*, **12**, 1007 (1920); S. E. Sheppard and S. S. Sweet: *Jour. Am. Chem. Soc.*, **43**, 539 (1921).

taken as the jelly strength. They report that there seems to be no simple relation between the jelly strength of a glue and the concentration of glue in the jelly; nor between the jelly strength and the hydrogen ion concentration. The tensile strength of the dried material was also found to bear no simple relation to the jelly strength. They report that the cooking of a glue solution lowers both the tensile strength and the jelly strength, but not in equivalent amounts.

*Hydrogen Ion Concentration and Melting Point: Setting Point.*—In 1920 Bogue<sup>1</sup> demonstrated that the melting point determination of gelatins or glues differentiated these products in a way that was more accurately representative of actual value (as determined by either gelatin content or joining strength) than either the jelly strength test or the viscosity (at 60° to 80° C) test.

Sheppard and Sweet<sup>2</sup> have studied the setting and melting points of gelatins by means of an instrument which determines the temperature of an arbitrarily selected degree of rigidity of the jelly or gelatinous solution. They find that the melting or setting point curves bear no consistent relation to concentration, the curves for different gelatins at varying concentrations sometimes cutting each other. The slope of these curves is very different from that of the jelly strength curves, these increasing in setting temperature very rapidly with the first increases in concentration, and showing only slight further rises in temperature at concentrations greater than 20 percent while the jelly strength curves increase slightly at first, but very rapidly at concentrations above 15 or 20 percent. The type of curve represented by the melting and setting point determinations is also the type which obtains in actual joint strength tests.

No work has been reported bearing *directly* upon the relations of hydrogen ion concentration to melting point.

*Hydrogen Ion Concentration and Joining Strength of Glues.*—The joining strength is to the joining and veneer trade the most

<sup>1</sup> R. H. Bogue: Chem. Met. Eng., 23, 61, 197 (1920).

<sup>2</sup> S. E. Sheppard and S. S. Sweet: Jour. Ind. Eng. Chem., 13, 423 (1921).

important property of glues. It is of the greatest importance to that trade that every means by which the actual joining strength may be raised should be understood and applied with intelligence.

Much has been said and written upon the changes which may be brought about in the viscosity, the jelly strength, and the melting point by a variation in the hydrogen ion concentration, and upon the relations which these several properties bear to joining strength. It has, for example, been pointed out that a change in the pH of a glue solution from 4.7 to 3.5 by the addition of an acid, or to 8.5 by the addition of an alkali will likewise result in an increase in the viscosity in either case. If the pH of the original sample is about 6.0 or 7.0 (which is the usual value), the addition of small amounts of acid, since that brings the pH nearer to that of the isoelectric point, 4.7, will decrease the viscosity. Larger amounts, since that will bring the pH beyond 4.7 and nearer to 3.5, will again raise the viscosity. Still greater amounts of acid will cause it once more to fall. Alkali added in any amount up to a pH of 8.5 will raise the viscosity, and beyond that produce a lowering.

What has been said of viscosity is true, in a general sense, of jelly strength and of melting point. But it has also been shown that the joining strength may be indicated by the melting point, or by the viscosity at 32° to 35° C<sup>1</sup>. Does it follow that the joining strength may be caused to vary by alterations in the hydrogen ion concentration of the glue solution, or which is the same thing, by the addition of acids or alkalies?

From an examination of the curves by Davis, Oakes, and Browne<sup>2</sup> (Fig. 7 of original paper) it will be observed that with a 1 percent solution the viscosity increased from about 1.27 centipoises at pH 4.7 to about 1.62 centipoises at pH 3.4. The difference between these two points is about 0.35 centipoise. This may be accepted as a fair indication of the variation obtained in 1 percent solutions of gelatin or high grade glue upon

<sup>1</sup> R. H. Bogue: *Jour. Ind. Eng. Chem.*, 14, 435 (1922).

<sup>2</sup> C. E. Davis, E. T. Oakes and H. H. Browne: *loc. cit.*

altering the hydrogen ion concentration from its least favorable to its most favorable value.

The instrument most commonly used in glue laboratories for measuring viscosity is some kind of pipette. The time outflow of a definite volume of the solution at a stated temperature (60° to 80° C) is noted by a stop-watch. An instrument which allows 180 cubic centimeters of water to pass through in 42 seconds is often used. In such an instrument a difference in time of flow of one second is nearly equivalent to 10 centipoises. Its sensitiveness is not greater than one half second, or 5 centipoises.

If a 20 percent solution of the glue is used for the test, the maximum variation in viscosity which may be expected would be  $20 \times 0.35$  centipoise (the variation in a 1 percent solution) or 7.0 centipoises. In the pipette described, this difference would be observed by a variation of less than a second in time of outflow. It would be just within the limits of detectability. But it would scarcely impress the plant technologist as an operation of especial merit.

The MacMichael viscosimeter is sensitive, in ordinary practice, to about one centipoise, and a variation of 7 centipoises would be inevitably observed. But the difference between any two grades (for example the Peter Cooper grades) is, in a 20 percent solution at 32° to 35° C, about 10 to 20 centipoises. It is obvious, therefore, that the improvement in viscosity which may be obtained by a change in hydrogen ion concentration is of but slight importance in the practical control of grade. It is doubtful if such control could raise the value of the product more than one full grade in any case, and its effect would usually be much less than that.

*Hydrogen Ion Concentration and Gelatin Content of Gelatins and Glues.*—Schryver<sup>1</sup> has recommended the use of 2 cubic centimeters of dilute (1 to 4) sulfuric acid to each 100 cubic centimeters of solution for the complete precipitation of protein from a solution with half saturated magnesium sulfate.

<sup>1</sup> S. B. Schryver: "Allen's Commercial Organic Analysis," vol. 8, p. 484.

Bogue<sup>1</sup> demonstrated that, with gelatins which he was testing, the maximum precipitation occurred upon the addition of only  $\frac{1}{2}$  cubic centimeter of the dilute (1 to 4) sulfuric acid to each 100 cubic centimeters of solution. Either greater or lesser amounts of acid diminished the amount of protein thrown out.

The reasons for this were not at that time apparent, but it is now obvious that the greatest insolubility occurs at the isoelectric point, and that at that point the maximum precipitation will take place when treated with salts.

The content of undegraded gelatin does not vary with hydrogen ion concentration (except that large amounts of either acid or alkali promote hydrolysis) but the readiness with which it may be precipitated does vary. This is because the precipitation is essentially a dehydration process, and the more nearly the gelatin approaches this condition before the addition of the salt, the less will be the amount of salt required to finish the process. Or, at a given salt concentration, the greater will be the amount dehydrated, or thrown out of solution.

The amount of acid required to be added to bring the solution to the isoelectric point will, of course, depend upon the original hydrogen ion concentration of the gelatin, and any instructions which specify the amount must be regarded as dependable only insofar as they effect this condition.

*The Significance of Hydrogen Ion Concentration in Research; in the Plant; and in Evaluation.*—There is probably no condition that it is more necessary to control in any physico-chemical investigation of a protein water system than the hydrogen ion concentration. Nearly every other property of the system is in some degree variable with its content of hydrogen ions. The reason for this is that the behavior of the protein in the formation of salts, and the ionization of these salts is determined by the hydrogen ion concentration.

At a pH of 4.7 there is in gelatin no tendency whatsoever toward salt formation, and any inorganic ions which may be

<sup>1</sup> R. H. Bogue: Chem. Met. Eng., 23, 106 (1920).

present are easily washed out of the gelatin with pure water, or with water brought to a pH of 4.7. If a little hydrochloric acid is then added, the pH will fall, and the gelatin will show a tendency to combine with the chlorid ion to form gelatin chlorid. This salt readily ionizes. According to the law of the Donnan Equilibrium,<sup>1</sup> if such a gelatin is allowed to dry out and then placed in a weak solution of the electrolyte, the concentration of the acid inside and outside of the jelly would, at equilibrium, not be the same, but would be greater in the exterior solution. Working on this principle, Procter and Wilson<sup>2</sup> have developed a theory to account for the swelling of gelatin, and Loeb<sup>3</sup> has deduced his "Occlusion Theory" which purports to account for the varying osmotic pressure, viscosity, etc., of gelatin water systems at varying hydrogen ion concentrations. Bogue<sup>4</sup> has studied particularly the sol-gel equilibrium, and urged a fibrillar structure theory for elastic gels and sols.

If an alkali, as sodium hydroxid, were added to the isoelectric gelatin, the pH would be raised and sodium gelatinate would be formed. This also is readily ionized, and the effects produced on the acid side would be largely duplicated on the alkali side.

The other papers quoted earlier in this report fully corroborate the importance of a control of hydrogen ion concentration in any investigational work with gelatins.

In the plant, a control of hydrogen ion concentration within certain limits is very desirable, but for different reasons than in investigational work. An alkaline gelatin or glue is much more readily attacked by molds in the course of manufacture than a slightly acid material. This is of considerable

<sup>1</sup> F. G. Donnan: *Zeit. Elektrochemie*, 17, 572 (1911); Donnan and Harris: *Jour. Chem. Soc.*, 99, 1554 (1911); Donnan and Garner: *Ibid.*, 115, 1313 (1919).

<sup>2</sup> H. R. Procter: *Jour. Chem. Soc.*, 105, 313 (1914); Procter and Wilson: *Ibid.*, 109, 307 (1916).

<sup>3</sup> Jacques Loeb: *Jour. Gen. Physiol.*, 3, 827 (1921); 4, 73, 97 (1921).

<sup>4</sup> R. H. Bogue: *Jour. Am. Chem. Soc.*, 44, 1313, 1343 (1922).

importance to successful plant operation, especially in hot and humid summer weather.

There is also a belief among joiners that an alkaline glue deteriorates in the joint, eventually resulting in a large number of failures. This point, however, needs confirmation.

When the product is to be used for certain delicate operations, as the sizing of fabrics, it is often necessary to ensure the absence of acid or alkali as these may react with the color base.

The improvement of grade by a control of the hydrogen ion concentration in manufacture is, however, of doubtful value, except in special cases. But it would certainly be the part of wisdom to avoid the region of the isoelectric point. Troubles of insolubility, opaque product, or the separation of a flocculent precipitate have many times been traced to this particular concentration of hydrogen ions.

It has been suggested that, since the viscosity, the jelly strength, and the melting point of gelatins and glues have been found to vary with the hydrogen ion concentration of the solutions, the tests for these properties should be made at some selected pH which should be regarded as standard.

There are two objections to this procedure. First, the test of the material should represent the value of the product as it is, rather than as it would be if it were treated with an arbitrarily selected amount of some acid or alkali. If it is argued that the test should represent the maximum obtainable value, we will add that dialysis to eliminate the ash, and precipitation to eliminate the hydrolytic products, might be included in the preliminary treatment, but we see no object in such extravagance of interpretation.

Second, it has already been pointed out that although wide differences are found to exist, by the use of sensitive instruments, between gelatins at varying hydrogen ion concentrations, yet in significant grades the maximum variation will rarely be the equivalent of one full grade. These arguments make it clear that it is neither desirable nor useful to attempt to evaluate gelatins or glues at a standard, but arbitrarily selected, hydrogen ion concentration.



**Summary**

It has been shown that the various physical properties of the emulsoid colloids, including the viscosity, jelly strength, melting point, and joining strength, are at a minimum at a hydrogen ion concentration corresponding to the isoelectric point. Several exact studies have been cited. As the acidity or the alkalinity of the solution is increased from this point, these properties rise in value.

It is shown that salt precipitations for gelatin contents should be made at the isoelectric condition if maximum precipitation is desired.

The necessity for a careful control of hydrogen ion concentration in investigational work on proteins is emphasized and the desirability of a similar control in the gelatin and glue plant during manufacture is pointed out. The limitation of benefit from such control makes questionable, however, the practicability of such methods for the purpose of the improvement of grade.

The estimation of hydrogen ion concentration as one of the tests in the evaluation of gelatin and glue is urged, but it is not recommended that all tests of viscosity, jelly strength, etc., be made at a specified pH value.

*Mellon Institute of Industrial Research  
University of Pittsburgh  
February 1, 1922*



## A PRELIMINARY STUDY OF ZIRKITE ORE

276-920 BY J. G. THOMPSON

This investigation consists of a study of zirkite ore (crude zirconium oxide), with attempts to improve the refractory properties by the elimination of certain of the impurities present in the raw material.

Pure zirconium oxide, if available in sufficient quantity, would aid materially in solving the problems of the users of high-temperature refractories, particularly those problems connected with the extreme temperatures encountered in the use of the electric furnace. As a refractory for high temperatures zirconium oxide is far superior to any of the materials commonly employed for this purpose and in some respects it approaches the ideal refractory. It possesses<sup>1</sup> a melting point higher than that of any other known metallic oxide; it is non-volatile below its melting point; it is neutral in character and inert to the action of practically all of the common reagents; it possesses low coefficients of thermal and electrical conductivity. These properties ensure the successful use of pure zirconium oxide as a refractory, even for the most extreme service conditions, at any time when it becomes available in quantity.

Zirconium was discovered by Klaproth in 1789; but, for many years after its discovery, it was considered one of the rare earths, and occasional samples of zircon, the orthosilicate of zirconium, were the only sources of supply. At present deposits of zircon sands, usually associated with monazite sands, are known to exist in many localities but the deposits usually are of limited extent and the zircon content is small. Zirconium also occurs in small amounts in a number of rare ores but these are important only for the traces of radio-active elements

<sup>1</sup> Meyer: Met. Chem. Eng., 12, 791 (1914); 13, 263 (1915); Hedvall: Zeit. anorg. Chem., 93, 313 (1915); Bradford: Chem. Trade Jour., 62, 284 (1918); Arnold: Jour. Soc. Chem. Ind., 37, 724 (1918); Granger: Chem. News, 118, 115, 121 (1919).

which they contain. Present interest centers solely upon the oxide ores of zirconium generally known as "Baddeleyite" ores. This group includes a number of ores of indefinite and variable composition in which the zirconium oxide content varies up to 99 percent. The name "Zirkite" has been restricted to the baddeleyite ore from the huge Brazilian deposits which now supply practically all of the demand for zirconium. Zirkite ore is variable in composition but careful sorting at the mine furnishes a product which is fairly uniform in composition averaging about 80 percent zirconium oxide. It is stated<sup>1</sup> that an unlimited supply of this ore is available as the deposits are of vast extent. The only factors limiting the output are the difficulties due to primitive methods of mining and transportation.

The use of zirconium oxide always has depended upon its refractory properties; but this use, until recently, was confined to the small amounts of very pure material required for the incandescent element in the Nernst, Drummond, and Bleriot lamps; as an additional element mixed with the thoria and ceria in Welsbach mantles; etc. The discovery of the huge Brazilian deposits of high-grade ore has awakened much interest in the possibility of using this ore on a large scale as a refractory.

Many of the properties of the raw ore<sup>2</sup> are comparable with those of the pure oxide but the melting point (2950°–3000° C for pure ZrO<sub>2</sub>) drops to 1200°–2000° C for the raw ore, depending upon the composition. Zirkite is an excellent refractory within the limits set by its softening and melting points but the low melting point obviously detracts greatly from the refractory value of the ore. It has been used successfully as raw material in the manufacture of combustion boats, tubes, etc., for high temperature work in the laboratory;

<sup>1</sup> Meyer: Foote Mineral Company publication for November, 1916.

<sup>2</sup> Meyer: *Met. Chem. Eng.*, 12, 791 (1914); Audley: *Trans. Eng. Ceram. Soc.*, 16, 121 (1917); Rosenhain: *Trans. Faraday Soc.*, 12, 178 (1917); Devereux: *Met. Ind.*, 16, 414 (1920).

but the successful use of the material on a large scale awaits the development of means of raising the melting point.

The problem obviously is the elimination of the element or elements which exert so detrimental an effect upon the melting point of the ore. No definite information is available regarding the specific effect of the various impurities upon the melting point of pure zirconium oxide, but silicon and iron, which together constitute the bulk of the impurities, naturally are regarded as the chief sources of trouble.

Methods of purification, as recorded in the literature, may be divided into two classes:

(1) Methods for the preparation of pure zirconium compounds.<sup>1</sup>

(2) Methods for partial purification of the ore by elimination of impurities, either by leaching<sup>2</sup> or by volatilization.<sup>3</sup>

Those methods in the first class which are successful are adaptable only for the production in the laboratory of small amounts of pure zirconium compounds. The methods in class two have been confined almost entirely to the removal of iron. The refractory silicates of zirconium were not affected at the relatively low temperatures used in Phillips' chlorination experiments and are not susceptible to leaching unless they have been decomposed by a preliminary fusion.<sup>4</sup> The methods in this class are better adapted for large scale operation but are successful only to a limited extent in producing satisfactory refractory material from the raw ore.

<sup>1</sup> Berlin: Jour. prakt. Chem., 58, 147 (1853); Hermann: Ibid., 97, 330, 340 (1866); Bailey: Chem. News, 53, 55, 260, 287 (1886); Doremus: Jour. Am. Chem. Soc., 8, 91 (1886); Bayer: Zeit. angew. Chem., 23, 485 (1910); Anonymous: Ceramique, 14, 204 (1911); Loveman: U. S. Patent No. 1,261,984 (1918); Imray: British Patent No. 16,555 (1913); Leuchs: German Patent No. 285,344 (1914); Meyer: loc. cit., and Granger: loc. cit.

<sup>2</sup> Wedekind: Zeit. angew. Chem., 21, 2270 (1908); Weiss and Lehmann: Zeit. anorg. Chem., 65, 178 (1909); Wedekind: Ber. deutsch. chem. Ges., 43, 290 (1910); Ramsden: Met. Ind., 16, 3 (1920); Audley; Granger; Rosen: loc. cit.

<sup>3</sup> Phillips: Jour. Am. Ceramic Soc., 1, 791 (1918).

<sup>4</sup> Weiss and Lehmann: loc. cit., Jost and Plocker: German Patent No. 285,981 (1914).

The remarkable stability at high temperatures of certain compounds of zirconium, particularly the oxide and carbide, together with the fact that these compounds are not appreciably volatile below their decomposition points, suggested the use of electric heating as a means of purifying zirkite ore by the elimination of impurities whose oxides and carbides presumably are less refractory than the corresponding zirconium compounds. Hitherto the electric furnace has been employed<sup>1</sup> only as a preliminary step in the purification of zirkite, apparently for the sole purpose of decomposing refractory silicates. This investigation, therefore, was undertaken for the sake of ascertaining to what extent zirkite might be freed from impurities by direct heating in an electric furnace.

Before the experimental portion of this investigation could be undertaken, a scheme of analysis had to be outlined. A search of the literature revealed many conflicting statements and considerable time was devoted to the investigation of the various methods before a satisfactory scheme was obtained. A brief, critical review of some of the methods proposed, together with a description of the scheme adopted, is therefore included in this report.

#### The Analysis of Zirconium Compounds

The characteristic properties of zirconium ores which make them valuable, i. e., the refractory properties and chemical inertness, formed the first obstacles to be overcome in the decomposition of the ore.

- Four general methods of attack have been proposed:
- (1) Fusion with hydrofluoric acid or with fluorides<sup>2</sup>
  - (2) Conversion to carbides in the electric furnace<sup>3</sup>

---

<sup>1</sup> Moissan: *Comptes rendus*, 116, 1222 (1893); Troost: *Ibid.*, 116, 1428 (1893); Podszus: *Jour. Soc. Chem. Ind.*, 36, 217 (1917); Barton: U. S. Patent No. 1,342,084 (1920); Weiss and Lehmann: *loc. cit.*

<sup>2</sup> Marignac: *Ann. Chim. Phys.*, (3) 60, 260 (1860); Weiss and Neumann: *Zeit. anorg. Chem.*, 65, 248 (1909); Anonymous: *The Brass World*, 7, 46 (1911); Meyer: Foote Mineral Company Publication for November 1916; Weiss and Lehmann: *loc. cit.*

<sup>3</sup> Granger; Moissan; Podszus; Troost; Weiss and Lehman: *loc. cit.*

(3) Fusion with sulphuric acid or its derivatives<sup>1</sup>

(4) Fusion with alkalies<sup>2</sup>

Fusion with sodium tetraborate (borax) was found to furnish the best means for the decomposition of the materials encountered in this investigation. Borax fusions usually produce complete decomposition in one operation but the boric acid must be eliminated thereafter if a complete analysis is desired. Fusion with alkalies produces decomposition of the silicates and phosphates but is not applicable to oxide ores. Fusion with pyrosulphates decomposes oxide ores but is not applicable to silicates. Methods involving fusion with fluorides or conversion to carbides in the electric furnaces are objectionable on account of loss through volatilization. A combination of alkali fusions, followed or preceded by pyrosulphate fusions, eventually produces complete decomposition and total solution of any zirconium compound, but the procedure is tedious and involved. In all cases the method employed for decomposition is determined by the nature and characteristics of the material.

After the ore has been decomposed by fusion methods and brought into complete solution, the problem of the separation of the various elements arises.

#### Analytical Separations

Silicon is removed from the solution without difficulty owing to the insolubility in acids of its dehydrated oxide.

Iron interferes with almost all of the methods for the precipitation of zirconium from solution, and should be removed before such precipitation is attempted. Leaching of

<sup>1</sup> Baskerville: *Jour. Am. Chem. Soc.*, 16, 475 (1894); Dittrich and Freund: *Zeit. anorg. Chem.*, 56, 337 (1907); Weiss: *Ibid.*, 67, 456 (1910); Wedekind: *Ber. deutsch. chem. Ges.*, 43, 290 (1910); Johnstone: "The Rare Earth Industry" (1915); Powell and Schoeller: *Analyst*, 44, 397 (1919); Weiss and Lehmann; Bayer: *loc. cit.*

<sup>2</sup> Jewett: "Bibliography of Zirconium" (1893); Dennis and Spencer: *Jour. Am. Chem. Soc.*, 18, 674 (1896); Abegg: *Handbuch*, IV, 490 (1913); Schlotz: *Chem. Abstracts*, 12, 661 (1918); Travers: *Chim. Ind.*, 2, 385 (1919); Lundell and Knowles: *Jour. Am. Chem. Soc.*, 42, 1439 (1920); Bayer; Berlin; Johnstone; Powell and Schoeller: *loc. cit.*

freshly precipitated or ignited oxides by acid solutions, including oxalic and sulphurous acids<sup>1</sup> is not successful.<sup>2</sup> Smith<sup>3</sup> claims to have effected complete separation of iron and zirconium by electrolytic methods, using a mercury cathode, and Price<sup>4</sup> records the formation of soluble perzirkonates by methods which would leave the iron insoluble. Neither of these results could be duplicated during this investigation.

Only two really successful methods have been devised for the separation of iron from solutions containing zirconium. These are based, respectively, upon selective solubility of ferric chloride in ether,<sup>5</sup> and the fact that iron is and zirconium is not precipitated by hydrogen sulphide from ammoniacal solutions containing tartaric acid.<sup>6</sup> The ether separation method is the better of the two for the removal of large amounts of iron such as are encountered in the analysis of zirconium steels or ferro-zirconium. The precipitation method is not as satisfactory for the removal of large amounts of iron, owing to the difficulties encountered in handling large volumes of precipitated ferrous sulphide. It is indispensable however, for the removal of the traces of iron which almost invariably survive the ether separation, and is adaptable for the analysis of zirconium ores in which the iron oxide content does not greatly exceed five percent.

A few attempts to precipitate zirconium and titanium separately are recorded in the literature,<sup>7</sup> but the success of some of these attempts has been questioned.<sup>8</sup> For analytical

<sup>1</sup> Dubois and Silveira: *Ann. Chim. Phys.*, (1) 14, 110 (1820); Berthier: *Ibid.*, (2) 50, 362 (1832); Wunder and Jeanneret: *Zeit. analyt. Chem.*, 50, 733 (1911).

<sup>2</sup> Berlin; Hermann: *loc. cit.*

<sup>3</sup> Smith: "Electro-Analysis" (1911).

<sup>4</sup> Price: "Per-Acids and Their Salts" (1912).

<sup>5</sup> Noyes, Bray and Spear: *Jour. Am. Chem. Soc.*, 30, 481 (1908).

<sup>6</sup> Wedekind: *loc. cit.*

<sup>7</sup> Bailey: *Jour. Chem. Soc.*, 49, 149, 481 (1886); Crookes: "Select Methods in Chemical Analysis" (1894); Dittrich and Freund: *loc. cit.*; Browning, Simpson and Porter: *Am. Jour. Science*, 42, 106 (1916); Headden: *Chem. Abstracts*, 11, 2311 (1917).

<sup>8</sup> Mathews: *Jour. Am. Chem. Soc.*, 20, 815 (1898); Weiss and Lehmann: *loc. cit.*

purposes the separation of zirconium from titanium is unnecessary as titanium is readily determined by Weller's<sup>1</sup> colorimetric method using hydrogen peroxide. The presence of zirconium does not interfere with this determination.

A variety of methods have been proposed for the simultaneous precipitation of zirconium and titanium. Dittrich and Freund<sup>2</sup> claim that sodium acetate will produce complete precipitation of zirconium and titanium. The use of sulphurous acid or its derivatives has been proposed,<sup>3</sup> but Johnstone<sup>4</sup> says that this reagent also precipitates some of the rare earths as well as traces of iron and aluminum and Hermann<sup>5</sup> reports that the separation resulting from the use of sulphur dioxide is not satisfactory. A number of these separations were attempted during the present investigation with complete lack of success. The manipulation is tedious, precipitation seldom is complete, and the precipitate usually is badly contaminated. Precipitation of zirconium and titanium by weak organic bases has been recommended,<sup>6</sup> and a number of these precipitations were attempted, using phenylhydrazine as the most promising member of this class. The experiments uniformly were unsuccessful, the precipitation was slow and incomplete, and the precipitate usually was contaminated. Variations of Hillebrand's method for the precipitation of zirconium phosphate<sup>7</sup> have been recommended. Lundell and Knowles<sup>8</sup>

<sup>1</sup> Weller: *Ber. deutsch. chem. Ges.*, 15, 2599 (1882).

<sup>2</sup> Dittrich and Freund: *loc. cit.*

<sup>3</sup> Berthier: *Ann. Chim. Phys.*, (2) 50, 362 (1832); (3) 7, 84 (1843); Chancel: *Jour. prakt. Chem.*, 74, 471 (1858); Imray: *Jour. Soc. Chem. Ind.*, 9, 941 (1890); Trautmann: *Zeit. angew. Chem.*, 24, 62 (1911); Baskerville; Dittrich and Freund; Weiss and Lehmann; Travers; Granger; Powell and Schoeller: *loc. cit.*

<sup>4</sup> Johnstone: *loc. cit.*

<sup>5</sup> Hermann: *Ibid.*

<sup>6</sup> Hess and Campbell: *Jour. Am. Chem. Soc.*, 21, 776 (1899); Jefferson: *Ibid.*, 24, 540 (1902); Allen: *Ibid.*, 25, 421 (1903); Hartwell: *Ibid.*, 25, 1128 (1903).

<sup>7</sup> Hillebrand: *U. S. Geol. Survey, Bull. No. 148*; Biltz and Mecklenburg: *Zeit. angew. Chem.*, 25, 2110 (1912); Ferguson: *Eng. Min. Jour.*, 106, 356, 793 (1918); Steiger: *Jour. Wash. Acad. Sci.*, 8, 637 (1918); Nicolardot and Reglade: *Comptes rendus*, 168, 348 (1919); Browning, Simpson and Porter: *loc. cit.*; Schiötz: *loc. cit.*

<sup>8</sup> Lundell and Knowles: *Jour. Am. Chem. Soc.*, 41, 1801 (1919).



discuss the method in detail and point out that the variations in composition of the precipitate prevent the use of the method except for very small amounts of zirconium. The most satisfactory method for the analytical determination of zirconium and titanium was found to be precipitation by cupferron, the ammonium salt of nitrosophenylhydroxylamine. The use of this reagent has been proposed by several authors<sup>1</sup> and has been recommended recently by Lundell and Knowles<sup>2</sup> who discuss the method in detail, including a list of the elements which interfere with the precipitation and a discussion of the precautions which must be observed.

The filtrate from the cupferron precipitation contains the aluminum, rare earths, and traces of other elements. The scheme of separation for the elements in this filtrate depends upon the nature and number of elements present, as determined in the preliminary qualitative examination.

From the foregoing data a complete scheme of analysis, adaptable to low-phosphorus baddeleyite ore, was evolved. In view of the time and labor required for a complete analysis, a modified scheme was adopted for the numerous analyses which attended the progress of this investigation. This modified scheme allows only the determination of silicon, iron, titanium, and zirconium, as follows:

#### **Modified Scheme for Routine Analysis**

The sample is ground to 80–100 mesh. 0.5 gram of the sample is weighed out and fused<sup>3</sup> in platinum with 5 grams of borax until a clear, fused mass results. When fusion is complete (usually requiring about one-half hour at the full heat of a Meker burner) the crucible is removed from the

---

<sup>1</sup> Ferrari: *Chem. Abstracts*, 9, 1019 (1916); Thornton and Hayden: *Am. Jour. Sci.*, 38, 187 (1914); Thornton: *Ibid.*, 42, 151 (1916); Brown: *Jour. Am. Chem. Soc.*, 39, 2358 (1917).

<sup>2</sup> Lundell and Knowles: *Jour. Ind. Eng. Chem.*, 12, 344 (1920).

<sup>3</sup> The usual practice is to dehydrate the borax in the crucible, add the weighed sample, and proceed with the fusion. Carbide samples should be ignited to the oxides before attempting the fusion.



flame. While solidification of the melt is taking place, the crucible is kept in motion so that when cold the fusion is distributed around the sides of the crucible. The cooled melt is dissolved in 5 percent hydrochloric acid in a porcelain casserole, solution being hastened by gentle warming. When solution is complete, the crucible is removed and rinsed out, 10-15 cc concentrated sulphuric acid are added, and the solution is evaporated on a hot plate until fumes of sulphur trioxide appear. The final fuming is done over a free flame, agitating the solution to prevent spattering. The residue is cooled, dissolved by diluting with water, and filtered. The precipitate on the filter is washed with hot water, ignited, weighed, treated with hydrofluoric and sulphuric acids, again ignited and weighed, and the loss of silica determined. A slight residue, mainly iron, is recovered by fusion with pyrosulphate and added to the original filtrate.

The filtrate from the removal of silica is diluted to about 500 cc, precipitated with ammonia, and boiled to coagulate the precipitate. After settling, the supernatant liquid is decanted as completely as possible to remove the bulk of the alkalis and boron. The ammonia precipitate is redissolved by adding 5-10 cc of concentrated sulphuric acid. One gram of tartaric acid is added and the solution is made distinctly ammoniacal. The volume of the solution at this point should be 150-200 cc. The solution is treated with hydrogen sulphide for twenty minutes, boiled for 3-4 minutes, allowed to cool, and filtered. The precipitate is covered and allowed to drain thoroughly but is not washed, owing to the decided tendency of the ferrous sulphide to pass through the filter when any washing solution is used. The filtrate is subjected to a second precipitation with hydrogen sulphide and is again boiled and filtered. The two precipitates of ferrous sulphide are redissolved in dilute aqua regia and the iron is determined gravimetrically. The presence of hydrochloric acid and small amounts of organic matter (from the tartaric acid) precludes the determination of iron by volumetric methods.

The filtrate from the removal of ferrous sulphide, boiled to remove most of the hydrogen sulphide, is made acid with a known excess of sulphuric acid, boiled again, and the precipitated sulphur filtered off and discarded. The filtrate is cooled, diluted to 600 cc containing 7.5–10 percent free sulphuric acid, chilled in ice water, and precipitated by the addition of a cold 6 percent aqueous solution of cupferron. During this precipitation the temperature must not exceed 15° C. The precipitate is allowed to stand one-half hour and is then filtered using gentle suction and washing with cold, 5 percent hydrochloric acid. The filtrate and washings are discarded. The precipitate is ignited and weighed as  $ZrO_2 + TiO_2$ .<sup>1</sup> The weighed precipitate is fused with pyrosulphate, dissolved in 5 percent sulphuric acid and the titanium determined colorimetrically.

On account of the variable amounts of carbon in the different samples, the analytical results were computed to a metallic basis, and the ratio of the elements determined on the basis of 100 parts of metallic zirconium. For the comparison of the various electric furnace products a study of this ratio is more easily understood than a study of the percentage composition of the samples.

### Experimental

The zirconium ore employed in this investigation was a finely ground zirkite, 65 percent of which passed through a 100-mesh sieve. Duplicate analyses of ignited samples of the ore gave the following composition:

---

<sup>1</sup> Any iron which escapes the precipitation with hydrogen sulphide will appear in this precipitate. Experience has shown, however, that the amount of iron which survives a double precipitation with hydrogen sulphide is so small that it may be disregarded for all except the most exact determinations. The color of this ignited precipitate is a reliable indicator of the composition. A pure white color indicates that zirconium alone is present. Titanium produces a yellow color, and a reddish or brownish tinge indicates the presence of iron.

	Percent	Percent
ZrO <sub>2</sub> .....	72.55	72.78
SiO <sub>2</sub> .....	17.34	17.26
Fe <sub>2</sub> O <sub>3</sub> .....	4.11	4.14
TiO <sub>2</sub> .....	0.80	0.81
Al <sub>2</sub> O <sub>3</sub> .....	5.28	5.91
Rare Earths (cerium group).....	1.04	1.13
P <sub>2</sub> O <sub>5</sub> .....	0.49	0.45
MnO <sub>2</sub> .....	0.25	0.27
MgO.....	trace	trace
Total.....	101.86	102.75 <sup>1</sup>
Loss on ignition.....	2.88	2.88

Ratio, on a metallic basis, of the elements present in the ore:

100 Zr: 15.1 Si: 5.37 Fe: 0.89 Ti

Owing to the time and labor consumed by the necessary analytical work, it was decided to limit this investigation to the three impurities silicon, iron, and titanium. Since silicon is present in far larger amounts than any other impurity, this investigation was directed primarily towards the elimination of silicon. The removal of iron is a secondary object of the investigation.

Two possibilities were considered for the removal of silicon and iron in the electric furnace:

(1) Reduction of the oxides to the metals in the presence of an excess of iron, forming ferro-silicon which could be removed subsequently by mechanical means.

(2) Reduction of the oxides to the metals or carbides with subsequent volatilization resulting from the application of higher temperatures.

The first method was tried out in a small crucible furnace heated by a direct arc. Iron oxide was added to the charge in an amount sufficient to unite with all of the silicon to form

<sup>1</sup> The error in the analyses probably is due to adsorption of alkalis by the cupferron precipitate; but may be due in part to the existence in the ore of elements, e. g., iron and manganese, in different states of oxidation than the ones represented in the above table. The composition of the silicates of zirconium, which occur in zirkite ore, has not been determined definitely.

ferro-silicon containing 50 percent iron. Several runs were made but no evidence of the formation of ferro-silicon was obtained. In every case the iron and silicon remained distributed uniformly throughout the charge, probably on account of the high viscosity of the melt which prevented the desired formation and coalescence of ferro-silicon. Increasing the temperature would increase the fluidity of the melt and a point might be reached at which the ferro-silicon would coalesce and settle out. The indications are, however, that the desired degree of fluidity would not be reached below the temperature at which silicon becomes volatile. If it is necessary to employ temperatures high enough to cause at least partial volatilization of the impurities, it would seem advisable to rely wholly upon volatilization to remove the impurities. The latter method also would avoid contaminating the ore by the addition of iron, which is necessary if the ferrosilicon scheme is followed. Accordingly the attempts to eliminate silicon and iron, as ferro-silicon, were abandoned in favor of attempts to volatilize the impurities directly.

Preliminary experiments conducted in a small arc furnace indicated that zirconium carbide is stable at temperatures above the decomposition point of silicon carbide (carborundum).<sup>1</sup> This led to the belief that conversion of the entire ore to carbides, followed by the exposure of the mixed carbides to temperatures above 2220° C, at which temperature silicon carbide decomposes, would eliminate silicon and perhaps some or all of the iron and other impurities. If this elimination of impurities were successful, it would then be possible to ignite the zirconium carbide to the oxide thus producing pure and highly refractory zirconia.

The first experiments were carried out in a furnace of the silicon carbide type, sufficient carbon being added to ensure the transformation of all the oxides present into carbides. Later experiments were performed in an arc furnace, the amount of carbon being varied from run to run.

---

<sup>1</sup> Gillett: *Jour. Phys. Chem.*, 15, 213 (1911).

### Experiments with a Resistance Furnace

The resistance furnace was built in the form of a rectangular trough 7 inches wide at the bottom, 8 inches wide at the top, 9 inches deep, and 29 inches long. The floor was built of zirkite brick supported by a double layer of fire brick. The sides were built of fist-size lumps of zirkite, backed with the fire brick and faced smooth with ground zirkite bonded with a little water-glass. The sides and floor were permanent. The end walls were faced with zirkite brick, which were backed up with fire brick, and were torn out after each run to facilitate removal of the charge. The electrodes were pieces of 4-inch square carbon electrodes which entered through the center of the end walls and protruded four inches into the furnace. The outer ends of the electrodes were water-cooled and connected to bus bars by flexible leads. Power was supplied by a 75 kilowatt motor-generator set. Two thousand amperes was the largest current available, representing the maximum output of the motor-generator set.

The complete conversion of 100 parts of ore to the various carbides and carbon monoxide requires approximately 33 parts of carbon. To ensure the presence of an excess of carbon, a ratio of 45 parts of carbon to 100 parts of ore was used. Petroleum coke, 10-20 mesh in fineness, supplied the carbon for most of the runs, although in one or two cases granular electrode carbon was tried.

Four runs were made in the resistance furnace. Since the runs were all more or less alike, the first one only will be described in detail, as follows:

#### Run 1

Ratio of ore to carbon in charge.....	100 : 45
Total weight of charge.....	86.5 pounds
Core.....	A double line of graphite electrode pieces, one inch in diameter, the junctions packed in petroleum coke to ensure contact
Duration of run.....	1 hour, 52 minutes
Power consumption.....	60 K.W.H.

The charge was packed loosely in the furnace up to the level of the electrodes. The core was inserted and the remaining charge added, filling the furnace. At first it required a potential of 46 volts to produce a current of 400 amperes through the furnace. Small gas volcanoes appeared almost at once, followed by flames, bright yellow at the base with reddish yellow tips. The power input was maintained as high as possible, being limited by the violence of the gas evolution which resulted in loss of charge when the power input became too high. After the first violent evolution of gas subsided, the charge presented the appearance of gentle boiling. After half an hour, when the total power input had reached 15 K.W.H., one end of the charge ceased boiling and settled to form a crust. This effect spread gradually until the entire charge was crusted over and quiet. Heating was continued about half an hour more. The entire charge finally became bright red in color but the temperature could not be raised further. At first the current was carried almost entirely by the core; but the charge itself soon began to conduct with the result that the current rose and the voltage fell off rapidly, until at the end of the run the current reached 1750 amperes and the voltage dropped to 5. These results made it evident that the conductivity of the core and heated charge was too great to allow the input of power at a rate sufficient to produce the very high temperature desired.

When the cooled charge was examined, a grayish black granular core about 4 inches in diameter was found in the center, extending the length of the charge between the electrodes. Small deposits of spongy material, metallic in appearance and rather bluish in color, which subsequent examination proved to be zirconium carbide, were found in close proximity to the original core. The total weight of "sponge" was about six pounds. The remaining contents of the furnace consisted of unchanged charge. The original graphite core was not attacked, indicating the presence of an adequate supply of carbon in the charge. Some slight indications of

the volatilization of silica were found on the furnace walls, but the power input evidently was too low.

The three subsequent runs were made in an attempt to increase the power input, but without marked success. The results of the four runs may be summarized as follows:

TABLE I

K. W. H.	Av. Kw.	Carbide "sponge" pounds	Metal in Sponge when Zr = 100		
			Si	Fe	Ti
60	32	6.0	3.7	4.48	0.79
75	34	6.5	11.0	5.50	0.78
100	38	10.0	12.2	7.60	0.79
80	40	7.5	5.5	2.60	0.87
		Original Ore	15.1	5.37	0.89

The behavior of the carbide "sponge" on analysis showed that most of the silicon was present as the carbide, thus indicating that in general the temperature of the mass was not high enough to ensure the removal of the silicon by volatilization. As the data indicate, the removal of silicon varied in a very irregular manner, being fairly complete in some cases but very incomplete in others. Other samples from portions of the charge farther removed from the core showed higher ratios of silicon to zirconium. This follows naturally, since volatilization of silicon would occur first in the hottest portion of the charge, i. e., around the core, and would be less evident in regions at a greater distance from the source of heat.

The data indicate little or no elimination of titanium or of iron, except in the fourth run where considerable iron was apparently removed. In this run, however, about 9 pounds of common salt was added to the charge resulting in the elimination of approximately half the iron, presumably through the formation of the volatile chloride. All things considered, the results obtained with the resistance furnace were unsatisfactory and this type of furnace was abandoned in favor of one of the arc type.

**Experiments with an Arc Furnace**

The furnace shell of the arc furnace consisted of an iron pot, lined with fist-sized pieces of zirkite ore. The lining was faced smooth with ground zirkite bonded with a little water glass, and contained the same ratio of carbon to zirkite as the charge proper. The resulting hearth was cone-shaped, 8 inches in diameter at the top, 4 inches in diameter at the bottom, and 8-10 inches deep. This lining was torn out after each run to facilitate removal of the charge. The lower, horizontal electrode, composed of two 2-inch square graphite electrodes, formed the floor of the hearth, entering through a rectangular opening in the side of the cast iron pot. The upper electrode was a 4-inch square carbon electrode, suspended in a vertical position and counter-weighted to allow adjustment. Both electrodes were clamped in water-cooled electrode holders and connected to bus bars by means of flexible cables.

The first run performed in this furnace will be described in detail, as being typical of all the runs carried out subsequently.

**Run 5**

Ratio of ore to carbon in charge.....	100 : 45
Total weight of charge.....	11 pounds
Time of run.....	45 minutes
Power consumption.....	32.5 K.W.H.

The run was started by striking an arc between the bare electrodes. The walls of the cone immediately began to slag down so that the first addition of charge was made as soon as possible after starting the arc. The charge was fed in slowly and was observed to solidify when it reached the zone of the arc. During the early stages of the run the arc was smothered by the charge but after all the charge had been added the arc was run open, and remained fairly quiet. The current was maintained at about 1000 amperes until the evolution of fumes had almost ceased when the arc became noisy and hard to maintain. The run was stopped when this point was reached.

The top of the charge oxidized during cooling, forming



a layer of fine white oxides, below which lay a brittle, black mass weighing approximately 3.5 pounds. A sample for analysis was taken from the center of this cake and gave the following ratio:

100 Zr: 4.85 Si: 6.38 Fe: 0.70 Ti

A series of runs was made in which the ratio of carbon (petroleum coke) to zirkite ore was varied systematically. The results are assembled in the following tables.

TABLE II  
Effect of Varying Ratio of Ore to Carbon

Run	Charge Pounds	Carbon per 100 ore	K.W.H.	Yield purified product pounds
5	11.0	45	32.5	3.5
9	12.5	25	18.25	3.0
10	12.0	20	17.5	3.1
11	15.4	15	21.5	5.0
18	15.4	10	19.3	7.0
19	16.8	5	27.0	9.9

Metal Ratio in Product

Run	Zr	Si	Fe	Ti
5	100	4.85	6.38	0.70
9	100	3.03	6.50	0.64
10	100	2.21	5.00	0.55
11	100	0.88	5.92	0.70
18	100	1.31	8.73	0.69
19	100	1.86	6.67	0.73
Ore	100	15.70	5.37	0.89

TABLE III  
Elimination of Impurities

Run	Carbon per 100 ore	Percentage elimination of		
		Si	Fe	Ti
5	45	68	-19	21
9	25	80	-21	28
10	20	85	7	38
11	15	94	-10	21
18	10	91	-62	22
19	5	88	-24	18

The data obtained with the arc furnace show a maximum in the removal of silicon when the ratio of zirkite to carbon is 100:15. Calculations based on the silica content of the ore show that a little more than 10 parts of carbon to 100 parts of ore is just enough to transform all of the silica into carbide (carborundum) and carbon monoxide. We have, therefore, come to the conclusion that the best high-temperature elimination of silicon is obtained when little more than enough carbon is used to form carbide with the silicon only, leaving the zirconium oxide undecomposed.

When more than 15 parts of carbon are used the elimination of silicon becomes steadily less complete. Under these circumstances it is known that zirconium carbide is actually produced in the arc. The zirconium carbide therefore appears to retain some of the silicon and the suggestion is offered that stable double carbides of silicon and zirconium may be produced or that the two carbides form solid solutions or mixed crystals. Runs in which granular electrode carbon was substituted for petroleum coke showed that better results may be obtained on a small scale with the more finely divided coke.

An interesting fact brought out by these experiments is the high melting point and stability, in a reducing atmosphere, of the carbide of zirconium. As long as there was an excess of carbon present, over and above the amount required for the complete conversion of the oxides to carbides, it was impossible to melt the product even under the direct action of a 40-50 kilowatt arc.

The partially purified carbide apparently had a higher melting point than the oxide product with the same relative composition. This was shown in the runs in which the ore melted and formed a pool under the arc, the pool solidifying as soon as more carbon was added. In order to use the carbide as a refractory, however, it would be necessary to protect it from oxidation. The black carbides all burned readily in the air to form light, fluffy oxides. Heating the powdered carbides to dull redness is sufficient to start the oxidation which then proceeds slowly but persistently.

The data show that some titanium was also eliminated but no iron, there being an apparent increase in the amount of the last impurity. This apparent increase in the iron content, especially in the case of Run 18, is due to the difficulties encountered in analysis. The samples of furnace products must be pulverized for analysis and, since the amount of silicon present is of primary importance, grinding such abrasive material in an agate mortar is out of the question. The only other method available was the use of a cast-steel bucking board, which resulted, naturally, in contamination of the samples. In view of the time required for analysis it was not considered advisable to grind additional samples in an agate mortar for the determination of iron. From a consideration of the data in Table III, therefore, one may safely conclude only that little if any iron was eliminated under the conditions of experiment.

Other runs were made in which sodium chloride was added to the charge of ore and coke to aid in the removal of iron, but curiously enough no iron was eliminated in this way. It is possible that the rapid attainment of the high temperature under the arc decomposed the chloride before it could be volatilized away.

Since the treatment in the electric furnace was not successful in eliminating the iron, other means of accomplishing this end were sought.

#### **Experiments on the Removal of Iron**

Different samples of the various electric furnace products all showed magnetic properties, due presumably to the presence of iron either as carbide or alloy. Accordingly attempts were made to use these magnetic properties as a basis of separation of the iron but the attempts were not successful. The magnetic portions contained approximately half of the zirconium and the non-magnetic portions contained appreciable amounts of iron.

Attempts were next made to remove the iron by leaching with 5 percent sulphuric acid.<sup>1</sup> Both the carbide and the

<sup>1</sup> Barton: *loc. cit.*

corresponding oxidized products of the electric furnace runs were leached with hot and with cold 5 percent sulphuric acid. The iron in the carbide appears to be more susceptible to leaching than is the iron in the oxidized material; but, even in the case of the carbide, less than half of the iron could be removed in this way.

A series of experiments was next carried out on the removal of iron by treatment of the carbides or mixed oxides with chlorine<sup>1</sup> at both low and high temperatures. The experiments were carried out in a small, horizontal, tube furnace and the frequent clogging of the apparatus by the volatile products of the reactions, especially at high temperatures, showed plainly that a furnace of special design is essential for investigation of this possibility. Nevertheless, results were obtained which indicated that iron may be removed in this way from zirconium carbide at low temperatures and, at high temperatures, from zirconium oxide from which silicon had been largely eliminated in the arc furnace. It would seem, therefore, that a fairly pure zirconia for refractory purposes might be made from crude zirkite ore by eliminating in an electric furnace as much as possible of the silicon and by following this by treatment with chlorine or phosgene<sup>2</sup> to remove the iron.

This investigation is admittedly incomplete in many ways. The limited time at our disposal and the difficulty of, and the time consumed by, the analytical work involved, may be offered as an excuse. It is hoped, however, that attention will be called to the problem of large-scale purification of zirconium oxide, so that the latter may become more generally available as a refractory material for very high temperatures. A summary of the results obtained follows:

#### Summary

(1) Ninety to ninety-five percent of the silicon may be removed from siliceous zirkite ore by heating a mixture

<sup>1</sup> Phillips: *loc. cit.*

<sup>2</sup> Baskerville: *Science*, 50, 443 (1919).

of ore and carbon to a temperature greater than 2220° C in an electric furnace.

(2) The best results appear to be obtained by feeding into an arc furnace a mixture of ore and coke, the amount of carbon being approximately that required to transform only the silicon to the carbide.

(3) The existence of stable double carbides of silicon and zirconium or of solutions of silicon carbide in solid zirconium carbide has been suggested as an explanation of the incomplete removal of silicon when carbon in excess of that required to form only silicon carbide is used.

(4) It is suggested that zirconia sufficiently pure for refractory purposes might be obtained from zirkite ore by removing the silicon in an electric furnace and following this treatment with chlorine or phosgene to remove the iron.

(5) Attention has been called to the refractory properties of zirconium carbide and the factors which limit its use.

(6) Methods of analysis of zirconium compounds have been reviewed briefly and a modified scheme of analysis has been outlined for the determination of zirconium and the three major impurities, silicon, iron, and titanium.

## BORON HYDRIDES

2-973  
BY MAURICE L. HUGGINS<sup>1</sup>

According to Stock and his coworkers,<sup>2</sup> there are at least ten boron hydrides, of which the formulae of four are known:  $B_2H_6$ ,  $B_4H_{10}$ ,  $B_6H_{12}$ , and  $B_{10}H_{14}$ . Stock considers that in these compounds boron is quadrivalent, but, in the light of present day evidence in regard to atomic structure, it does not seem possible that boron can be quadrivalent in the sense that carbon is quadrivalent—that in these substances each boron atom can be directly bonded, through electron pairs, to four other atoms. Also, the compound  $B_{10}H_{14}$  is not simply accounted for in this way; and furthermore, why is it that boron exhibits such a valence only in its hydrogen compounds?

Because of the above considerations, the author has been led to look for some other type of structure for these compounds, based on the idea that boron possesses but three valence electrons. The structures arrived at are illustrated in Figures 1 to 4.

The analogy between these structures and those of the carbon compounds, ethylene ( $H_2C = CH_2$ ), butadiene ( $H_2C = CH - CH = CH_2$ ), benzene<sup>3</sup> (Fig. 5), and naphthalene (Fig. 6), is very striking.

It has been pointed out by the author<sup>4</sup> that the "residual affinity" supposedly possessed by "unsaturated atoms" in many organic molecules is more properly considered a property of the double or triple bond, and results in the attraction of other unsaturated structures and the formation (usually only

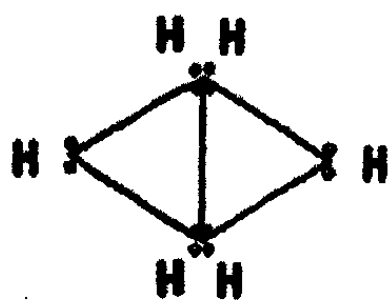
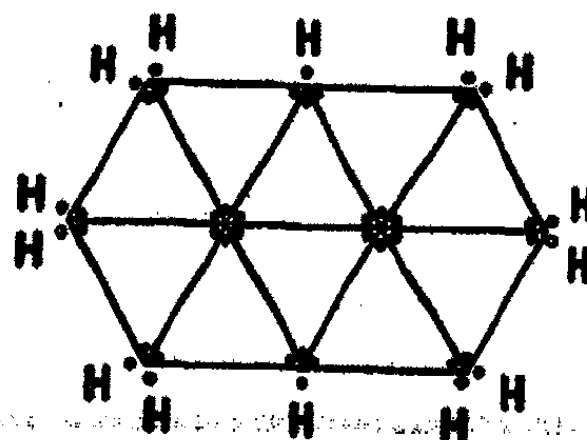
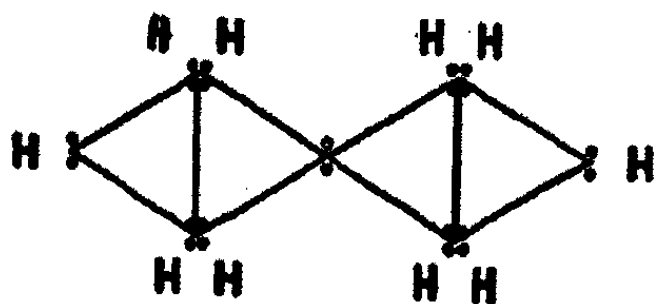
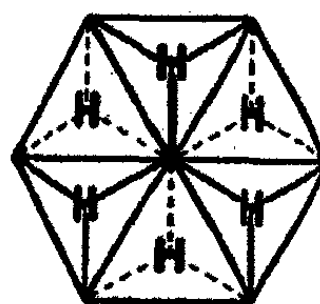
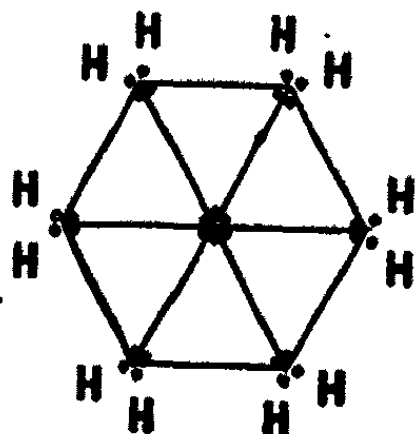
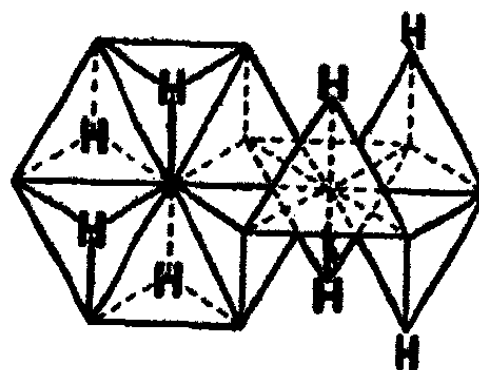
<sup>1</sup> DuPont Fellow in Chemistry at the University of California, 1921-1922.

<sup>2</sup> Stock and Massenez, *Ber. deutsch. chem. Ges.*, 45, 3539 (1912); Stock and Friederici, *Ibid.*, 46, 1959 (1913); Stock, Friederici and Priess, *Ibid.*, 46, 3353 (1913); Stock, *Zeit. Elektrochemie*, 19, 779 (1913); Stock, Kuss and Priess, *Ber. deutsch. chem. Ges.*, 47, 3115 (1914).

<sup>3</sup> Concerning the benzene and naphthalene structures, cf. Huggins, *Jour. Am. Chem. Soc.*, 44, 1607 (1922); *Science*, 55, 678 (1922).

<sup>4</sup> *Jour. Am. Chem. Soc.*, 44, 1607 (1922).

temporarily) of a bond of three or four (or sometimes more) electrons. Now if we suppose that boron atoms have a greater tendency to form and maintain such complexes than have carbon atoms, the structures illustrated are accounted for.

FIG. 1 -  $B_2H_6$ FIG. 4 -  $B_{10}H_{14}$ FIG. 2 -  $B_4H_{10}$ FIG. 5 -  $C_6H_6$ FIG. 3 -  $B_6H_{12}$ FIG. 6 -  $C_{10}H_8$ 

Altho the "residual affinity" of the boron-boron double bond is strong enough to hold onto hydrogen atoms, it may be incapable of holding onto larger atomic kernels.

Although the figures picture the hydrogens as in the same plane as the boron nuclei and the bond electrons, it is more

probable that the electrons in each four-electron bond and the atomic kernels around each such bond are tetrahedrally arranged. It is also possible that in  $B_6H_{12}$  and  $B_{10}H_{14}$  (and perhaps in the others) the boron nuclei are alternately to one side or the other of the plain containing the electronbonds (the plane of the paper, in the figures), the three valence electrons forming, with the two electrons in each boron kernel, a very much distorted tetrahedron around each nucleus.

Little is known of the properties of these substances which would serve as evidence for or against this theory. Further experimental evidence is needed before these or any other proposed structures may be considered proved.

#### Summary

1. Structures are proposed for the compounds  $B_2H_6$ ,  $B_4H_{10}$ ,  $B_6H_{12}$ , and  $B_{10}H_{14}$ .
2. These structures are analogous to those of the carbon compounds ethylene, butadiene, benzene, and naphthalene, respectively.
3. The hydrogen atoms are held by means of four-electron bonds, such as often exist (temporarily at least) in unsaturated organic compounds. Each such bond is surrounded by four atoms.

*Chemical Laboratory  
University of California  
Berkeley, California*



## ADSORPTION OF IONS BY FRESHLY PRECIPITATED MANGANESE DIOXIDE.

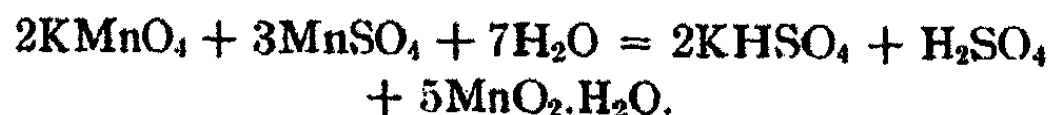
BY P. B. GANGULI AND N. R. DHAR

### Introduction

It is well known that the precipitate which comes down when an electrolyte is added to a sol, shows a certain amount of adsorption of one of the ions of the electrolyte; a negatively charged colloid adsorbing the cation and *vice versa*. According to the Schulze-Hardy Law one would expect that the amount adsorbed would vary inversely as the valency of the adsorbed ion; the higher the valency of the ion the less will be the adsorption. In the following experiments the amount of adsorption of different ions by manganese dioxide during the course of its precipitation by mixing potassium permanganate with manganous sulphate, have been determined. Manganese dioxide has been found to be a negatively charged colloid and shows considerable adsorption of cations. The influence of the anions on the adsorption of cations by manganese dioxide have also been studied by using electrolytes having the same metallic ion but different anions.

### Experimental

When to a solution of potassium permanganate a solution of manganous sulphate is added and the mixture shaken, a precipitate of manganese dioxide comes down. According to Volhard, the reaction takes place in the following manner:



The manganese dioxide in the above reaction is not precipitated at once; but if sufficiently dilute solutions be used, a fairly stable colloidal solution is formed, which can be kept for a sufficiently long time with the help of a stabiliser like gelatine. Normally however the manganese dioxide settles down with time especially in concentrated solutions. There is thus a marked

tendency for the manganese dioxide precipitated in the above reaction to separate first as a colloidal solution and then owing to the presence of electrolytes, and the unstable nature of the colloid itself to get precipitated. This behavior was also observed by Deiss,<sup>1</sup> who prepared a solution of manganese dioxide by reduction of permanganate by sodium arsenite. In view of the above considerations manganese dioxide precipitated in the above manner seems well suited for adsorption experiments.

Weiser<sup>2</sup> has found appreciable adsorption of anions by barium sulphate generated from sodium sulphate and the barium salt of the various acids giving rise to the anions. We have found that a pure dry sample of barium sulphate gives no appreciable adsorption with either copper sulphate or copper chloride. This points to the view that a fine precipitate is more active while it is in the course of being precipitated, than when once it has been precipitated. In the following experiments, instead of using a dry old sample, the conditions of the experiments have been so arranged that the electrolytes came in contact with the manganese dioxide while it was being precipitated. To secure the above object 5 cc of a  $\frac{1}{8}$  N solution of potassium permanganate was placed in a dry bottle. 5 cc of a N solution of the electrolyte under examination was next introduced into the bottle and finally 5 cc of a solution of manganous sulphate equivalent to 5 cc of the permanganate solution were run in. The strength of the manganous sulphate was adjusted by estimation of its manganese content. The resulting solution was titrated against its own volume of the potassium permanganate solution. After the solutions had been added, the bottle was securely stoppered and shaken for half an hour in a mechanical shaker. It was seen as a result of a trial experiment that a shaking of five minutes is sufficient to bring about equilibrium in the system. The contents of the bottle were next filtered and washed with cold water till the filtrate was free from all traces of the electrolyte under

<sup>1</sup> Zeit. Kolloidchemie, 6, 69 (1910).

<sup>2</sup> Jour. Phys. Chem., 23, 205 (1919).

examination, and the cation content of the total filtrate estimated by suitable gravimetric or volumetric methods.

In the cases of monovalent sodium and lithium salts an aliquot part of the filtrate was analysed without the addition of any wash water to the filtrate.

Nearly normal solutions of about thirty different electrolytes were investigated in the above manner. The exact cation contents of the electrolytes were determined beforehand by suitable methods and knowing the cation content after adsorption, the amount adsorbed was known.

The experimental results are given in Table I, and in Table II are given the number of gram-mols of electrolyte adsorbed by one gram of manganese dioxide.

*Discussion of Results.*—As we have already said, according to the Schulze-Hardy Law, the amount of an ion adsorbed by a fixed quantity of a sol, would vary inversely as the valency of the ion. An examination of the experimental results obtained shows that monovalent silver ion has a higher percentage of adsorption than all the bi-, tri-, and quadrivalent ions studied. Trivalent aluminium ions have a lower percentage of adsorption than the monovalent and most of the bivalent ions, being about  $\frac{1}{10}$ th the value of monovalent silver ions. These results are in agreement with the Schulze-Hardy Law.

Trivalent cerium and quadrivalent thorium ions have a higher percentage of adsorption than bivalent nickel ions from nickel chloride, mercuric ions from mercuric chloride and magnesium ions from either the chloride or the sulphate. Monovalent lithium ions have a percentage adsorption of 4.8, which is smaller than the values for trivalent cerium or quadrivalent thorium. Trivalent cerium and quadrivalent thorium ions have both the same percentage of adsorption, viz. 5.4. The values of the percentage adsorption of the divalent ions vary over a wide range, the ratio between the highest and lowest value being 1:9. Magnesium chloride has a percentage adsorption of 2.2 which is equal to the value of trivalent aluminium sulphate, while divalent lead nitrate has a value 19.8 which approximates to the value of monovalent silver nitrate,

TABLE I  
Adsorption of Electrolytes by Manganese Dioxide

Salt	Concentration before adsorption	Concentration after adsorption	Percentage adsorbed	Method of estimation
AgNO <sub>3</sub>	N	.787N	21.25	Volumetrically by KCNS
NaCl	N	.899	10.01	Gravimetrically as anhydrous NaCl
LiCl	N	.951	4.81	Gravimetrically as anhydrous LiCl
CdSO <sub>4</sub>	N	.988	11.15	Gravimetrically as anhydrous CdSO <sub>4</sub>
Cd(NO <sub>3</sub> ) <sub>2</sub>	N	.921	7.85	Gravimetrically as anhydrous CdSO <sub>4</sub>
Cu(NO <sub>3</sub> ) <sub>2</sub>	1.1 N	.961	12.6	Gravimetrically as CuO
CuCl <sub>2</sub>	1.02N	.899	11.88	Gravimetrically as CuO
CuSO <sub>4</sub>	N	.839	16.02	Gravimetrically as CuO
BaCl <sub>2</sub>	N	.917	8.27	Gravimetrically as BaSO <sub>4</sub>
Ba(NO <sub>3</sub> ) <sub>2</sub>	0.57N	.50	12.3	Gravimetrically as BaSO <sub>4</sub>
ZnSO <sub>4</sub>	N	.940	6.0	Gravimetrically as ZnO
Zn(NO <sub>3</sub> ) <sub>2</sub>	1.2 N	1.122	6.5	Gravimetrically as ZnO
CoCl <sub>2</sub>	1.08N	.926	14.2	Gravimetrically as metallic Co
Co(NO <sub>3</sub> ) <sub>2</sub>	1.07N	.982	8.24	Gravimetrically as metallic Co
CoSO <sub>4</sub>	1.02N	.846	17.0	Gravimetrically as metallic Co
NiCl <sub>2</sub>	N	.960	4.0	Gravimetrically as NiO
Ni(NO <sub>3</sub> ) <sub>2</sub>	N	.930	7.0	Gravimetrically as NiO
MgCl <sub>2</sub>	1.08N	1.056	2.2	Gravimetrically as Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>
MgSO <sub>4</sub>	1.2 N	1.168	2.6	Gravimetrically as Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>
Sr(NO <sub>3</sub> ) <sub>2</sub>	0.98	.884	9.8	Gravimetrically as SrSO <sub>4</sub>
Pb(NO <sub>3</sub> ) <sub>2</sub>	0.61N	.49	19.6	Gravimetrically as PbSO <sub>4</sub>
HgCl <sub>2</sub>	0.2 N	.194	3.2	Volumetrically by KI
Ferric alum	1.07N	.713	33.4	Gravimetrically as Fe <sub>2</sub> O <sub>3</sub>
FeCl <sub>3</sub>	N	.610	38.94	Gravimetrically as Fe <sub>2</sub> O <sub>3</sub>
FeCl <sub>3</sub>	N	.629	37.06	Gravimetrically as Fe <sub>2</sub> O <sub>3</sub>
Fe(NO <sub>3</sub> ) <sub>3</sub>	N	.53	47.0	Gravimetrically as Fe <sub>2</sub> O <sub>3</sub>
Potash alum	N	.981	1.94	Gravimetrically as Al <sub>2</sub> O <sub>3</sub>
Potash alum	N	.968	3.2	Gravimetrically as Al <sub>2</sub> O <sub>3</sub>
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	1.06N	1.037	2.2	Gravimetrically as Al <sub>2</sub> O <sub>3</sub>
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	1.06N	1.026	3.2	Gravimetrically as Al <sub>2</sub> O <sub>3</sub>
Al(NO <sub>3</sub> ) <sub>3</sub>	0.92N	.782	15	Gravimetrically as Al <sub>2</sub> O <sub>3</sub>
Al(NO <sub>3</sub> ) <sub>3</sub>	0.92N	.745	19	Gravimetrically as Al <sub>2</sub> O <sub>3</sub>
CeCl <sub>3</sub>	1.09N	1.03	5.4	Gravimetrically as CeO <sub>2</sub>
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	N	.918	8.2	Gravimetrically as U <sub>3</sub> O <sub>8</sub>
Th(NO <sub>3</sub> ) <sub>4</sub>	N	.946	5.4	Gravimetrically as ThO <sub>2</sub>

TABLE II  
Gram-mols. of Electrolyte adsorbed by one Gram of Manganese Dioxide

Salt	Strength of the solution	Percentage adsorbed	No. of gram-mol of electrolyte adsorbed by 1 gram of MnO <sub>2</sub>
AgNO <sub>3</sub>	N	21.25	.006107
NaCl	N	10.01	.002876
LiCl	N	4.81	.001382
CdSO <sub>4</sub>	N	11.15	.001600
Cd(NO <sub>3</sub> ) <sub>2</sub>	N	7.85	.001128
Cu(NO <sub>3</sub> ) <sub>2</sub>	1.1 N	12.6	.001992
CuCl <sub>2</sub>	1.02N	11.88	.001690
CuSO <sub>4</sub>	N	16.02	.002300
BaCl <sub>2</sub>	N	8.27	.001188
Ba(NO <sub>3</sub> ) <sub>2</sub>	0.57N	12.3	.001007
ZnSO <sub>4</sub>	N	6.0	.000862
Zn(NO <sub>3</sub> ) <sub>2</sub>	1.2 N	6.5	.001120
CoCl <sub>2</sub>	1.08N	14.2	.002203
Co(NO <sub>3</sub> ) <sub>2</sub>	1.07N	8.24	.001267
CoSO <sub>4</sub>	1.02N	17.0	.002491
NiCl <sub>2</sub>	N	4.0	.000574
Ni(NO <sub>3</sub> ) <sub>2</sub>	N	7.0	.001006
MgCl <sub>2</sub>	1.08N	2.2	.000341
MgSO <sub>4</sub>	1.2 N	2.6	.000448
Sr(NO <sub>3</sub> ) <sub>2</sub>	0.98N	9.8	.001380
Pb(NO <sub>3</sub> ) <sub>2</sub>	0.61N	19.6	.001718
HgCl <sub>2</sub>	0.2 N	3.2	.000018
Ferric alum	1.07N	33.4	.003442
FeCl <sub>3</sub>	N	38.0	.003702
Fe(NO <sub>3</sub> ) <sub>3</sub>	N	47.0	.004483
Potash alum	N	2.57	.000246
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	1.06N	2.7	.000276
Al(NO <sub>3</sub> ) <sub>3</sub>	0.92N	17.0	.001496
CeCl <sub>3</sub>	1.09N	5.4	.000563
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	N	8.2	.000586
Th(NO <sub>3</sub> ) <sub>4</sub>	N	5.4	.000385

viz. 21.26. These results are all opposed to the Schulze-Hardy Law.

If we arrange the electrolytes in the order of their percentage adsorption, we get the following series:

Potash alum, MgSO<sub>4</sub> > Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, MgCl<sub>2</sub> > NiCl<sub>2</sub> > CeCl<sub>3</sub> > LiCl > Th(NO<sub>3</sub>)<sub>4</sub> > ZnSO<sub>4</sub> > Zn(NO<sub>3</sub>)<sub>2</sub> > Ni(NO<sub>3</sub>)<sub>2</sub> > Co(NO<sub>3</sub>)<sub>2</sub> > Cd(NO<sub>3</sub>)<sub>2</sub> > UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> > BaCl<sub>2</sub> > Sr(NO<sub>3</sub>)<sub>2</sub>

NaCl > CdSO<sub>4</sub> > CuCl<sub>2</sub> > Ba(NO<sub>3</sub>)<sub>2</sub> > Cu(NO<sub>3</sub>)<sub>2</sub> > CoCl<sub>2</sub> > CuSO<sub>4</sub> > CoSO<sub>4</sub> > Al(NO<sub>3</sub>)<sub>3</sub> > Pb(NO<sub>3</sub>)<sub>2</sub> > AgNO<sub>3</sub> > Ferric alum > FeCl<sub>3</sub> > Fe(NO<sub>3</sub>)<sub>3</sub>.

In the above series the positions of MgSO<sub>4</sub>, CeCl<sub>3</sub>, LiCl, Th(NO<sub>3</sub>)<sub>4</sub>, NaCl, Al(NO<sub>3</sub>)<sub>3</sub>, and the ferric salts, are anomalous.

The number of gram-mols of electrolyte adsorbed by one gram of the manganese dioxide, has been calculated. From these numbers we get the following order for the coagulative powers:

HgCl<sub>2</sub> > Potash alum > Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> > MgCl<sub>2</sub> > Th(NO<sub>3</sub>)<sub>4</sub> > MgSO<sub>4</sub> > CeCl<sub>3</sub> > NiCl<sub>2</sub> > UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> > ZnSO<sub>4</sub> > Ni(NO<sub>3</sub>)<sub>2</sub> > Ba(NO<sub>3</sub>)<sub>2</sub> > Zn(NO<sub>3</sub>)<sub>2</sub> > Cd(NO<sub>3</sub>)<sub>2</sub> > BaCl<sub>2</sub> > Co(NO<sub>3</sub>)<sub>2</sub> > Sr(NO<sub>3</sub>)<sub>2</sub> > LiCl > Al(NO<sub>3</sub>)<sub>3</sub> > CdSO<sub>4</sub> > CuCl<sub>2</sub> > Pb(NO<sub>3</sub>)<sub>2</sub> > Cu(NO<sub>3</sub>)<sub>2</sub> > CoCl<sub>2</sub> > CuSO<sub>4</sub> > CoSO<sub>4</sub> > NaCl > Ferric alum > FeCl<sub>3</sub> > Fe(NO<sub>3</sub>)<sub>3</sub> > AgNO<sub>3</sub>.

In the above series the two trivalent aluminium salts occur at about the beginning, the divalent electrolytes generally occur in the middle, while monovalent silver nitrate is the last member of the series. In so far a general tendency to follow the Schulze-Hardy Law is discernible. But the positions of mercuric chloride, magnesium chloride, thorium nitrate, magnesium sulphate, lithium chloride, aluminium nitrate, the ferric salts, etc., are not in accordance with the Schulze-Hardy Law. In fact the positions of lithium ion between divalent strontium and cadmium ions, of quadrivalent thorium between divalent magnesium ions, of trivalent cerium ion between divalent magnesium and nickel ions are very difficult to reconcile with the Schulze-Hardy Law. Weiser (*loc. cit.*) has also found that the order obtained from the adsorption of anions by barium sulphate did not follow at all the Schulze-Hardy Law.

In estimating the filtrates after adsorption in the cases of lead and barium salts, allowances had to be made for the lead and barium sulphates precipitated along with the manganese dioxide owing to the sulphate ions arising from the manganous sulphate added. Barium sulphate during the course of its precipitation however does not interfere with the adsorption of cations by manganese dioxide, because colloidal solutions

of barium sulphate are positively charged and do not show any appreciable adsorption of cations.

All the ferric salts studied have shown a high percentage of adsorption, varying from about 35 to 40%. Aluminium ions from aluminium nitrate have also a much higher value, being about eight times greater than the value of alum. The abnormally high values seem to be due to the hydrolysis of the electrolytes. It is well known that a solution of ferric alum decomposes with the separation of ferric hydroxide when boiled for some time. That a partial decomposition of these ferric salts took place was seen from the color of the manganese dioxide. In other cases it was black, while in the cases of ferric salts, it had brownish color, strongly suggesting contamination with ferric hydroxide. The high value in the case of aluminium nitrate seems to be peculiar in view of the fact that aluminium sulphate gives a percentage adsorption of only 2.2, aluminium nitrate being about 18. There is no reason to believe that aluminium nitrate has a greater tendency to hydrolyse than aluminium sulphate.

The differences in the values shown by electrolytes with the same cation is very marked, which will be seen from Table III.

TABLE III  
Effect of Anions

Salt	%	Salt	%
CdSO <sub>4</sub>	11.15	CoCl <sub>2</sub>	14.2
Cd(NO <sub>3</sub> ) <sub>2</sub>	7.8	Co(NO <sub>3</sub> ) <sub>2</sub>	7
BaCl <sub>2</sub>	8.27	CoSO <sub>4</sub>	16
Ba(NO <sub>3</sub> ) <sub>2</sub>	12.2	CuCl <sub>2</sub>	12.6
ZnSO <sub>4</sub>	6	Cu(NO <sub>3</sub> ) <sub>2</sub>	11.88
Zn(NO <sub>3</sub> ) <sub>2</sub>	6.5	CuSO <sub>4</sub>	16.02
MgCl <sub>2</sub>	2.2	Potash alum	1.9 to 3.2
MgSO <sub>4</sub>	2.6	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2.2 to 3.2
NiCl <sub>2</sub>	4		
Ni(NO <sub>3</sub> ) <sub>2</sub>	7		

The wide variations in the values obtained for electrolytes with the same cation but different anions, is very marked. There seems however no regularity in the variations shown by

these electrolytes having the same cation. Generally the sulphates show a higher percentage of adsorption than either the chloride or the nitrate of the same metal.

From our experimental results we see that among the electrolytes of the metals occurring in the same group in the periodic table, the values of the percentage adsorption of cations by the manganese dioxide are in the order of their atomic weights, which will be seen from Table IV.

TABLE IV  
Percentage Adsorption of Cation

Salt	At. wt. of metal	Percentage adsorption	At. wt. of metal	Percentage adsorption of nitrates	Percentage adsorption of the sulphates
LiCl	7	4.81	Mg 24.4	..	2.6
NaCl	23	10.01	Zn 65.4	6.5	6.0
Sr(NO <sub>3</sub> ) <sub>2</sub>	87.6	9.8	Cd 112.4	7.85	11.15
Ba(NO <sub>3</sub> ) <sub>2</sub>	137	12.3			

But in the cases of nickel and cobalt salts no such relation can however be seen. On the contrary though they have very nearly equal atomic weights, the values of the percentage adsorption of nickel and cobalt chlorides by manganese dioxide, varies from 4 in the case of nickel to 14.2 in the case of cobalt.

**Summary**

The coagulative powers of different electrolytes as calculated from the percentage of the cation adsorbed from nearly normal solutions of the electrolytes, by manganese dioxide, have been found to follow the Schulze-Hardy Law but partially.

The effects of the anions on the adsorption of cations by manganese dioxide have been found to be very marked. There is however no regularity in the variations shown by the values of the percentage adsorptions of the cations, with variations of the anions, the cation remaining the same.

In the case of ferric salts abnormally high percentages of adsorption of ferric ions by manganese dioxide have been obtained. This is probably due to a partial decomposition of the salts with formation of ferric hydroxide.



Among the electrolytes of the metals occurring in the same group in the periodic table, the values of the percentage adsorption have been found to be generally in the order of their atomic weights.

*Chemical Laboratory  
Muir Central College  
Allahabad, India*

11  
J  
O  
11

# THE PHYSICAL CHEMISTRY OF DYEING. ACID AND BASIC DYES.

BY T. R. BRIGGS AND ARTHUR W. BULL<sup>1</sup>

## Introduction

The various theories which have been proposed from time to time to account for the phenomena of dyeing may be classified, in general, as either physical or chemical. In the latter class are grouped all explanations based on the assumption that a chemical reaction occurs between the dye and the fiber. In the physical interpretation the presence of chemical reactions is denied except in a few special cases, it being believed that in the majority of cases dyeing is due to physical forces or, more specifically, to adsorption of the dye by the fiber.

The adsorption or colloidal theory of dyeing has been summarized and elaborated by Bancroft.<sup>2</sup> Its application to acid dyes<sup>3</sup> may be stated briefly as follows. When any fiber is placed in a dyebath, it may adsorb any or all of the constituents of the bath. (In the case of acid dyes in acidified baths these constituents are hydrogen ions, sodium ions, (assuming the dye to have been a sodium salt), anions of the dye, anions of the acid, and undissociated compounds.) Hydrogen ions being, in general, more strongly adsorbed than other univalent cations will be taken up largely and the fiber will become charged positively relative to the solution. This positive charge, in turn, will lead to an increased adsorption of anions,<sup>4</sup> and by this secondary process of adsorption the charge on the fiber will be more or less neutralized. The

<sup>1</sup> A thesis submitted by Arthur W. Bull to the Faculty of the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Jour. Phys. Chem., 18, 1, 118, 385 (1914); 19, 50, 145 (1915).

<sup>3</sup> An acid dye is one which contains the color in the acid radical and which dissociates in water solution to give colored anions.

<sup>4</sup> Bancroft: Jour. Phys. Chem., 18, 10 (1914); "Applied Colloid Chemistry," 115 (1921).

anions of dye and of acid will both be taken up in amounts which are determined for a given fiber by the nature of the ions and by their concentrations. Since, in being adsorbed, the anions of an acid dye have to compete with the other anions of the bath, it follows that the addition of other strongly adsorbed anions will decrease the amount of dye taken up. In a similar way, the addition of a strongly adsorbed cation will cause an increase in the amount of an acid dye taken up, other factors remaining constant. In all cases there may be some concurrent adsorption of undissociated dyes. On the basis of this theory it is possible to explain the facts met with in dyeing with acid dyes.

The final effect produced by the addition of any given reagent to a dyebath may be the resultant of several different factors. In general, the added reagent may affect either the fiber or the dyebath. It may act on the fiber chemically as in the case of sodium hydroxide on wool, or it may be adsorbed by the fiber thereby modifying the extent of adsorption of other substances.

The effect on the dyebath may be more complex. The dye may be decomposed chemically by the formation of a salt or by the production of the free color acid or base. If the dye is in true solution, the reagent may change its solubility, thereby affecting the amount of dye adsorbed. If the dye is in suspension, the added reagent will produce some change in its degree of dispersion and will therefore influence the amount of dye adsorbed. This latter action is of prime importance in the case of substantive dyes. Finally, the added reagent may change the hydrogen ion concentration of the dyebath. It will be shown subsequently in this paper that the hydrogen ion concentration of the dyebath is the most important single factor affecting the process of dyeing.

In the experiments described in this paper no evidence of any chemical action of the reagents on the fiber was obtained, except with relatively high concentrations of sodium hydroxide. Experiments on the diffusion of the acid dyes employed in this work showed these dyes to be presumably

in true solution, at least in neutral, weakly acid, or weakly alkaline baths. Electrometric titration of Orange II indicated that the free acid of the latter is strongly ionized and the other acid dyes used are presumably similar in this respect since they are all sodium salts of sulfonic acid derivatives. It was therefore concluded that in all baths containing acid dyes, with the exception of certain special cases to be noted later, the color was present in solution almost entirely in the form of dye anions. With the basic dyes investigated, however, the evidence obtained from experiments on diffusion showed that these dyes, while in true solution in a neutral dyebath, became increasingly colloidal on the addition of sodium hydroxide, even in relatively small amounts.

The hydrogen ion concentration of the dyebath is probably the most important variable as emphasized previously; but, so far as we are aware, no former investigator has controlled this factor quantitatively, although Pelet-Jolivet<sup>1</sup> pointed out its importance. Many of the assistants or restrainers, used in dyeing, produce an appreciable and often a great change in the hydrogen ion concentration of the dyebath and their action in many cases is due more to this change than to any other specific action.

The colloidal or adsorption theory agrees well with the facts of dyeing but much of the earlier work on which the theory was based was not quantitative and uncontrolled variables were often present. It therefore seemed advisable to carry out a more rigid investigation, controlling, so far as possible, all the variables involved, but particularly the hydrogen ion concentration of the dyebath. This paper deals with the results obtained with acid and basic dyes.

#### Experimental

*Materials used.*—Two separate lots of wool (Fleisher's Knitting Worsted) purchased at different times, were used and found to give closely agreeing results. The yarn was first treated with a warm, dilute solution of Ivory soap and was then

<sup>1</sup> *Rev. gén. mat. color.*, 12, 97 (1908); *Abstracts*, 2, 2159 (1908).

rinsed thoroughly in tap water followed by many changes of hot distilled water. The air-dried yarn was kept in a large bell jar above a saturated solution of calcium chloride to keep the humidity constant, since Wright<sup>1</sup> has shown that changes in humidity cause an appreciable variation in the moisture content of wool. A small piece of yarn was also kept under the bell jar to serve as a control and was weighed from time to time to detect any such change. No appreciable variation was observed over a period of several months.

In making preliminary experiments to determine the time required for equilibrium to be established between wool and dye bath, it was discovered that the amount of Crystal Ponceau taken up from a neutral bath passed through a maximum as the length of the boiling period was increased, as shown in Table I.

TABLE I

Boiling period in minutes	45	60	75	90
Milligrams of dye adsorbed	9.6	17.5	15.6	12.7

This unexpected result was finally traced to the presence in the wool of small amounts of soap apparently retained from the previous washing. It is probable that long-continued boiling brought about hydrolysis of this soap and that the fatty acid thus formed was carried by steam to the lower portions of the return condenser where it solidified, leaving the solution slightly more alkaline. Since Crystal Ponceau is adsorbed by wool less readily from an alkaline solution than it is from a neutral or acid one, a portion of the dye already adsorbed was removed as the bath became alkaline.

All reagents except sodium hydroxide were of the standard grade marked "Chemically Pure." Carbonate-free alkali was prepared by an electrolytic method.<sup>2</sup> The dyes employed in the preliminary experiments were supplied through the courtesy of the National Aniline and Chemical Company. For the later experiments specially purified dyes were made

<sup>1</sup> Jour. Soc. Chem. Ind., 28, 1020 (1909).

<sup>2</sup> Jorissen and Filippo: Zeit. angew. Chem., 23, 726 (1910).

available through the co-operation of E. I. du Pont de Nemours and Company.

*Experimental Procedure.*—The following procedure was followed throughout this investigation. A dyebath of known composition and of a total volume of 250 cc was brought to boiling while attached to a return condenser to prevent evaporation. A one-gram sample of the fiber to be tested was placed in this bath and slow but steady boiling was continued for forty-five minutes. In many previous investigations the fiber was allowed to remain in the bath after boiling until the solution had cooled. The latter course is open to serious criticism. Lake<sup>1</sup> has shown that the amount of dye taken up may vary greatly with the temperature of the bath while it is also certain that equilibrium between the fiber and the solution is reached comparatively slowly at low temperatures. If the fiber is allowed to remain in the bath until the solution is cold, the amount of dye adsorbed is probably neither the amount taken up at the boil nor at room temperature, but will be some intermediate value depending on the degree of approach to the room temperature equilibrium. In this work, therefore, the dyed sample was removed directly from the boiling solution at the end of forty-five minutes.

The dyebath was then analyzed for the amount of dye left unadsorbed, the free acid present, or for any other substances as desired. Aliquot volumes were taken for analysis and it was thus unnecessary to correct for the amount of solution retained by the wool.

*Determination of the Amount of Dye Adsorbed.*—The amount of dye removed by the fiber under given conditions may be determined in two ways. The dyed fiber may be compared with a series of color standards in which the amount of dye is known, or the quantity of dye removed may be secured by difference after the amount of dye left behind in the bath is determined. The first method is difficult to apply to the deeper shades and the standards are hard to prepare. The dye left in the bath, however, can be estimated

<sup>1</sup> Jour. Phys. Chem., 20, 761 (1916).

rather easily in the case of certain dyes. In the earlier experiments the Kober colorimeter was used for this purpose. As the investigation progressed, however, certain difficulties and possible sources of error in the colorimetric method became evident. The colorimetric analysis of a dye solution is based on the assumption that the intensity of color is proportional to the concentration of dye. On testing this assumption experimentally it was found not to be in strict accord with the facts.<sup>1</sup> For accurate results it is therefore necessary to compare an unknown solution with a color standard of nearly equal concentration. On varying the hydrogen ion concentration of a dye bath, it was observed that acids and bases not only affected the color intensity of the latter, but in many instances also produced a distinct change in the color itself. The following experiment serves to illustrate this effect. 50 cc of a standard solution of Crystal Ponceau were placed in each of three Erlenmeyer flasks. To one flask 10 cc of water were added, to the second, 10 cc of N/10 sulfuric acid, and to the third, 10 cc of N/10 sodium hydroxide. The solutions were then compared colorimetrically. The acid solution was found to be apparently eight percent and the alkaline solution no less than three hundred percent more concentrated than the neutral solution, although the difference of color between the neutral and alkaline solutions rendered exact matching difficult. It is thus evident that color comparisons, at least with this particular dye, must be made between neutral solutions or between those containing the same concentration of acid or base. Salts have but little effect at low concentrations on the color intensity and shade, but in stronger solutions they must also be taken into account. The boiling of wool in the dye bath also renders the bath slightly cloudy and makes exact matching with a clear standard very difficult. Furthermore, the colorimetric method is tedious and the eyes become tired quickly. It was therefore deemed advisable to abandon the

---

<sup>1</sup> Compare Gordon: *Color Trade Jour.*, 6, 61 (1920); *Chem. Abstracts*, 14, 2420 (1920).

colorimetric method and to employ some other means of analysis.

Titration with titanium trichloride, as suggested by Knecht<sup>1</sup> was thereupon tried and was found to give satisfactory results with many dyes. It was found advisable to make a few preliminary experiments with each new dye to determine whether the addition of Rochelle salt was necessary. The titanium chloride reagent was standardized directly in terms of the dye under investigation by titrating a standard solution of the dye to a colorless end-point. All titrations were carried out in boiling solutions from which air was excluded, in accordance with Knecht's directions.

*Determination of Hydrogen Ion Concentration.*—Throughout this investigation the hydrogen electrode was used to determine the hydrogen ion concentration of the exhausted dyebaths and in some cases also, in the titration of free residual acid. Various types of electrodes and electrode vessels were employed. Free acid was titrated with the Hildebrand<sup>2</sup> electrode. Clark's<sup>3</sup> rocking cell, the Bunker<sup>4</sup> electrode and a simplified form of the device of Lewis, Brighton, and Sebastian<sup>5</sup> were all used in this work at various times for the determination of pH.

The application of the hydrogen electrode proved difficult under the conditions met with in much of this work. Adsorption of dye by the electrode tended to lower the adsorption of hydrogen and to render the electrode inaccurate. Traces of grease on the wool were apparently transferred to the dyebaths on boiling and subsequently decreased the activity of the platinum black. Following a suggestion of Dr. E. T. Oakes<sup>6</sup> the activity of the electrodes was restored by immersion in chromic acid cleaning mixture after each de-

<sup>1</sup> Ber. deutsch. chem. Ges., 36, 1552 (1903); 40, 3819 (1907).

<sup>2</sup> Jour. Am. Chem. Soc., 35, 847 (1913).

<sup>3</sup> Jour. Biol. Chem., 23, 475 (1915).

<sup>4</sup> Ibid., 41, 11 (1920).

<sup>5</sup> Jour. Am. Chem. Soc., 39, 2250 (1917).

<sup>6</sup> Personal communication to the author.



termination of pH. Some dyes are reduced by hydrogen in contact with platinum black and this depolarizing action also introduces an error.

It may be mentioned here that an electrode which was known to be giving low readings in a dye solution was found to indicate correct values of pH when used in buffer solutions. It proved to be an easy matter to check buffer solutions; but dyebaths presented greater difficulties. The Lewis<sup>1</sup> type of vessel with a partially submerged electrode was found to be most satisfactory. The Bunker<sup>2</sup> electrode gave good results in solutions of inorganic electrolytes, but owing to its smaller surface it was more quickly contaminated than were the larger electrodes of the other types when placed in the dye solutions.

The hydrogen electrodes were supplied with electrolytic hydrogen from a tank. Immediately before use the gas was passed through a quartz tube containing a heated nichrome spiral, to make certain of the complete removal of oxygen.

Normal and saturated calomel electrodes were used as standards and were frequently checked for accuracy. Potentials were measured at room temperature to the nearest millivolt by means of a Leeds and Northrup "Student Type" potentiometer. In view of the sources of error met with in determining the pH of dyebaths, as discussed in the previous paragraphs, the use of a potentiometer of extreme precision was not deemed worth while.

*Adsorption of Hydrochloric Acid by Wool.*—The adsorption of acids by wool has been studied previously by several investigators.<sup>3</sup> Since the amount of acid taken up varies with the specimen of wool, and as the experimental conditions used by previous workers did not correspond entirely with those under which the present experiments on dyeing were to be

<sup>1</sup> Jour. Am. Chem. Soc., 39, 2250 (1917).

<sup>2</sup> Jour. Biol. Chem., 41, 11 (1920).

<sup>3</sup> Georgievics and Pollak: Monatsheft., 32, 655 (1911); Mills and Takamine: Jour. Chem. Soc., 43, 142 (1883).

carried out, it seemed advisable to redetermine the adsorption isotherm for hydrochloric acid and wool.

One gram portions of the yarn were placed in boiling solutions of hydrochloric acid of known concentrations, all the solutions having a volume of 250 cc. After boiling for forty-five minutes (tests had shown this time to be sufficient for the establishment of equilibrium), the yarn was removed and 100 cc portions of the cooled solutions were titrated to determine the amount of unadsorbed acid. The data are given in Table II.

TABLE II  
Adsorption of Hydrochloric Acid by Wool

cc N/10 HCl at start	cc N/10 HCl at end	cc N/10 HCl adsorbed
1.00	0.87	0.13
2.00	1.77	0.23
3.00	2.60	0.40
5.00	4.28	0.72
7.00	6.05	0.95
10.00	8.47	1.53
15.00	13.05	1.95
25.00	22.30	2.70

The isotherm (Figure 1) drawn from the data in Table II is more suggestive of solid solution following Henry's law than of adsorption, but when it is considered that the highest concentration of acid remaining behind in the bath amounted only to about one-hundredth normal, it is seen that the curve, as drawn, really constitutes the first portion of the complete adsorption isotherm and is, therefore, practically a straight line over the small range shown. Georgievics and Pollak<sup>1</sup> have shown conclusively that the taking up of acids by wool is strictly an adsorption phenomenon.

Experiments were next performed to determine the adsorption of acid from a bath containing both acid and dye to see whether the adsorption of acid by wool is affected by the simultaneous adsorption of dye. Fort and Swares and Fort and Andersen<sup>2</sup> have taken up this question and they present

<sup>1</sup> Monatsheft., 32, 655 (1911).

<sup>2</sup> Jour. Soc. Dyers and Colorists, 31, 80, 96 (1915).

data to show that when both dye and acid are present in a bath, less acid is taken up by the wool than when acid alone is present. There is apparently, therefore, a displacement of acid by the dye.

One gram portions of wool were treated as previously described in boiling dyebaths containing hydrochloric acid and Crystal Ponceau. The

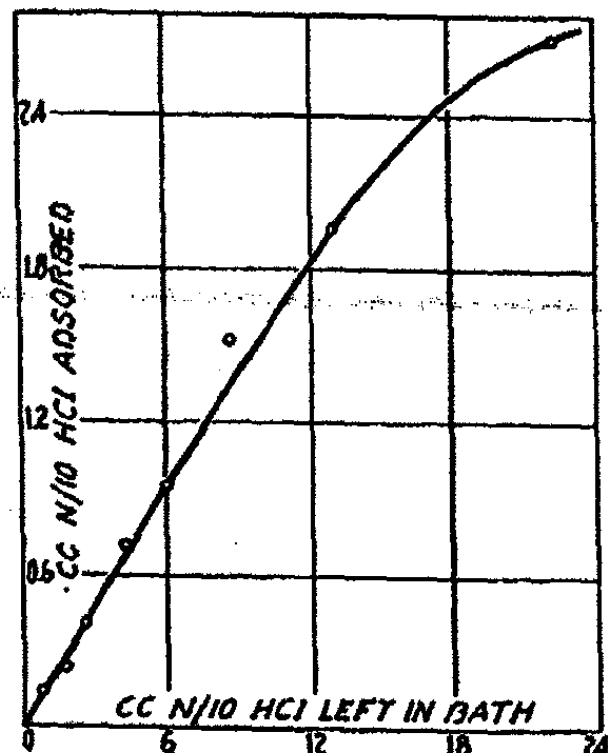


Fig. 1

Adsorption of Hydrochloric Acid by Wool

amounts of dye and free acid left in the bath were determined respectively with the colorimeter and the hydrogen electrode. In all cases the weight of dye at the start was seventy-five milligrams; the acid content was varied as stated in Table III; and the total volume of the bath was maintained at 250 cc. Larger quantities of acid were not used because at the highest concentration given, practically all of the dye was taken up by the wool. The values given are the averages of duplicate determinations.

TABLE III  
Adsorption of Hydrochloric Acid in the Presence of Crystal Ponceau

cc N/10 HCl at start	Final pH of bath	cc N/10 Acid left	cc N/10 Acid removed	Mgs dye adsorbed
0.00	5.3	—	—	4.5
1.00	5.1	0.15	0.85	34.9
2.00	4.2	0.47	1.53	56.3
3.00	3.6	1.20	1.80	67.9
5.00	3.0	2.93	2.07	73.4
7.00	2.75	4.65	2.25	74.2

If one compares these data or the corresponding isotherm (Figure 2) with the previous data and isotherm (Figure 1), it is at once apparent that much more hydrochloric acid has

disappeared from the bath containing acid and dye than was the case with the bath containing acid alone. It does not necessarily follow, however, that this increase represents a greater adsorption of hydrochloric acid. Crystal Ponceau has the formula  $C_{10}H_7N : NC_{10}H_4OH(SO_3Na)_2$  and contains 9.16 per-

cent sodium. It is probable that the dye, being a sodium salt, is largely dissociated in aqueous solution. In these acidified dyebaths we probably have hydrogen ions strongly adsorbed by the wool. In order that the fiber shall remain electrically neutral there must be an adsorption of some anion, in this case, the dye anion. As a result, sodium ions remain in the bath, together with the anions from the mineral acid, the adsorption process resulting in a replacement of the free mineral acid with its sodium salt. The disappearance

of hydrochloric acid in the above experiment may therefore be due, not to increased adsorption of the acid, but to its neutralization. If hydrochloric acid has been neutralized, all the chloride ions will be left in the bath while adsorption of the acid will remove chloride ions. The following experiments were performed to answer this question.

Two dyebaths were prepared containing 108.5 milligrams of Crystal Ponceau and 7.00 cc of N/10 hydrochloric acid in a total volume of 267 cc. One gram samples of wool were boiled in each bath for forty-five minutes and then removed. The

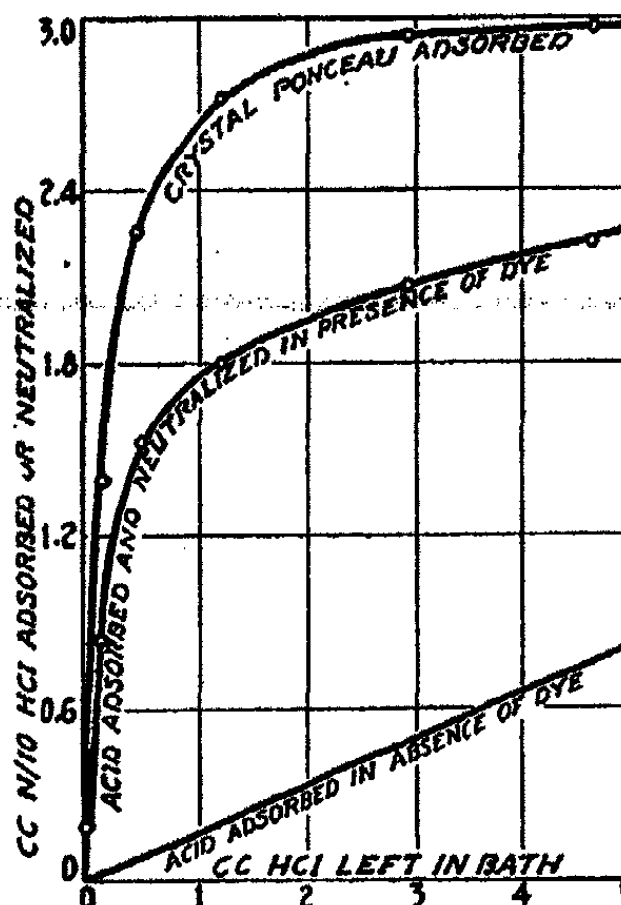


Fig. 2

Adsorption of Hydrochloric Acid and Crystal Ponceau by Wool. (1/4 the ordinates gives milligrams Crystal Ponceau adsorbed)

resulting solutions were analyzed for unadsorbed dye, for free acid, and for chlorides. Chlorides were determined by decolorizing the solutions with electrolytic hydrogen and then titrating with N/10 silver nitrate using potassium chromate as an indicator. The results are given in Table IV.

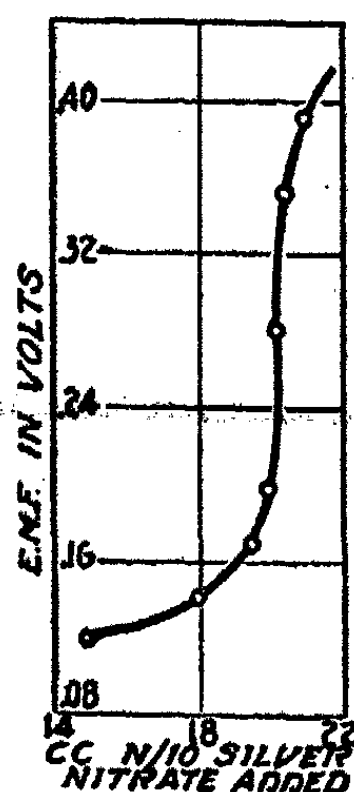


Fig. 3

Typical Curve obtained in the Electrometric Titration of 20 cc N/10 NaCl

(A saturated calomel electrode was used for the other half of the cell)

To determine whether other dyes behaved in a similar manner, experiments were performed in which Croceine Orange replaced Crystal Ponceau. In dyeing, the same procedure was followed, the dyebath containing seventy-five

TABLE IV  
Adsorption of dye and acid from the same bath

	I	II
(a) cc N/10 HCl at start.....	7.00	7.00
(b) Total N/10 chlorides left in bath.....	6.31	6.47
(c) HCl adsorbed (a - b).....	0.69	0.53
(d) cc free acid left in bath.....	4.26	4.39
(e) HCl neutralized by sodium in dye (b - d).....	2.05	2.08
(f) Milligrams of dye adsorbed.....	104.8	104.6
(g) Calculated possible HCl neutralized by dye.....	4.17	4.17
(h) Adsorption of HCl from solution without dye Figure 1.....	0.65	0.67

milligrams of the dye and a known amount of hydrochloric acid in a total volume of 250 cc. One gram portions of wool were placed in the boiling dyebaths for forty-five minutes. Unadsorbed dye was determined colorimetrically. Free acid was estimated by titration with the hydrogen electrode and

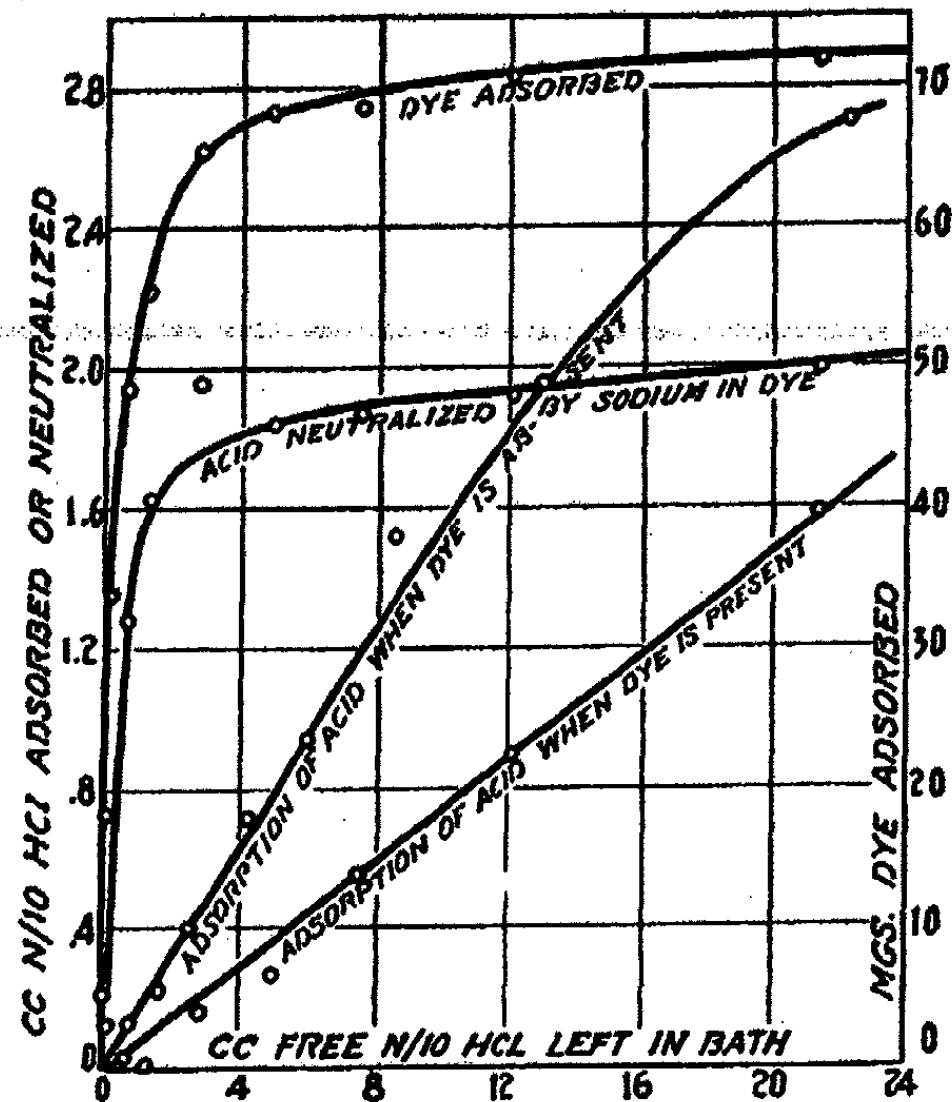


Fig. 4

Adsorption of Hydrochloric Acid and Croceine Orange by Wool

total chlorides were determined electrometrically. Croceine Orange cannot be readily decolorized with hydrogen so it became necessary to employ a volumetric method for the determination of chlorides in colored solutions. This problem was solved by the use of a silver electrode.<sup>1</sup> The average of

<sup>1</sup> Behrend: Zeit. phys. Chem., 11, 462 (1893). The potential of a silver electrode against any solution in which it is placed is a function of the silver ion concentration of the solution. If one measures the potential of a silver electrode immersed in a chloride solution to which silver nitrate is being added, the curve

duplicate experiments with Croceine Orange are given in Table V. They have been plotted in Figure 4.

TABLE V  
Adsorption of Croceine Orange and Hydrochloric Acid from the Same Bath

cc N/10 HCl at start	cc N/10 HCl at end	cc N/10 Cl' at end	Mg dye adsorbed	pH
0.00	—	—	5.1	6.8
1.00	0.13	0.87	33.8	5.0
2.00	0.68	1.96	48.5	3.8
3.00	1.36	2.99	55.4	3.3
5.00	2.89	4.88	65.5	2.9
7.00	4.88	6.73	68.2	2.6
10.00	7.57	9.44	68.5	2.4
15.00	12.18	14.11	70.7	2.2
25.00	21.44	23.43	71.8	2.0
cc N/10 HCl at start	cc N/10 HCl adsorbed	cc N/10 HCl found	neutralized calc.	pH
1.00	0.13	0.74	0.96	5.0
2.00	0.04	1.28	1.38	3.8
3.00	0.01	1.63	1.58	3.3
5.00	0.16	1.95	1.87	2.9
7.00	0.27	1.85	1.94	2.6
10.00	0.56	1.87	1.96	2.4
15.00	0.89	1.93	2.02	2.2
25.00	1.57	1.99	2.05	2.0

These curves and data show that Croceine Orange unquestionably diminishes the adsorption of hydrochloric acid by wool. Croceine Orange is a monobasic salt with the formula:  $C_6H_5N:NC_{10}H_6OH(SO_3Na)$  with 6.567 percent sodium. In this case the calculated values for the total possible amount of hydrochloric acid neutralized by the sodium in the dye agree

shown in Figure 3 is obtained. So long as silver chloride is precipitated, the silver ion concentration of the solution is extremely small and roughly constant. As soon as an excess of silver nitrate is added, however, the concentration of the silver ions in the solution rises rapidly and a sudden change in the potential of the electrode occurs. It is thus possible to determine chlorides in colored solutions, provided that no other substance is present which forms a precipitate or a complex ion with the silver nitrate. In measuring the potential of the silver electrode, it is, of course, necessary that the calomel electrode be connected with the solution through an ammonium nitrate or similar salt bridge to prevent contamination of the solution with potassium chloride from the electrode.

quite well with the experimental values. It is thus apparent that Croceine Orange is adsorbed by wool largely as the free dye acid. It should be observed that these calculations are based on the assumption that any decrease in chlorine ion concentration is due only to adsorption of hydrochloric acid. It is possible of course that the decrease may be caused by adsorption of sodium chloride. Experiments were performed to determine whether this was actually the case and no adsorption of sodium chloride by wool could be detected.

*Adsorption of Acid Dyes and pH of Dyebath. Addition Agents.*—The next step in the development of the general problem was to determine quantitatively the relation between the

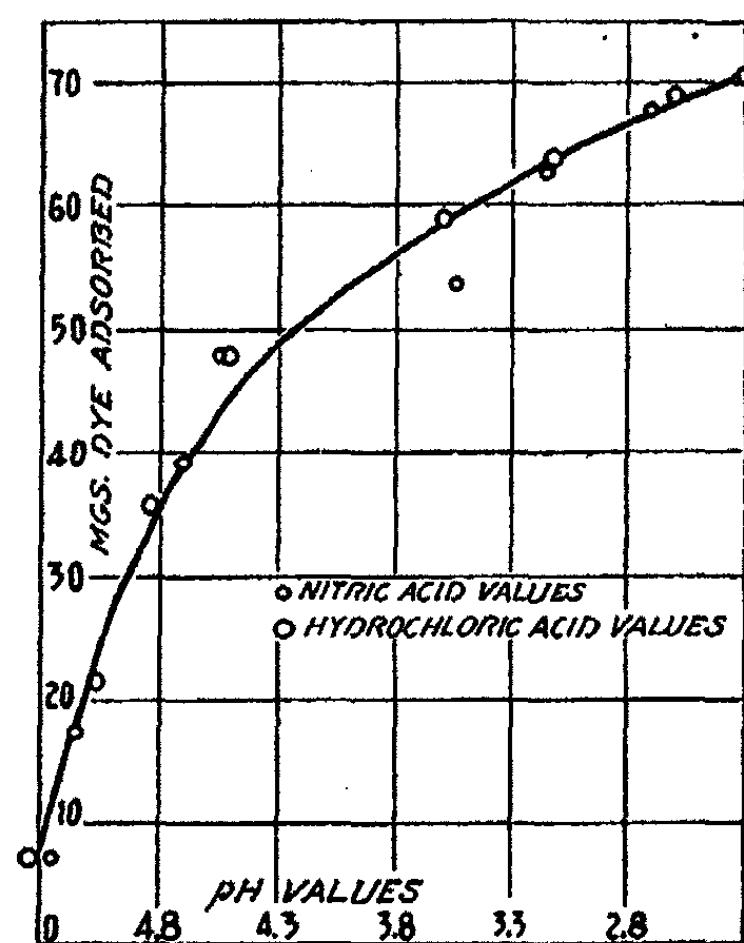


Fig. 5

Adsorption of Croceine Orange by Wool

hydrogen ion concentration of the dyebath and the adsorption of various acid dyes by wool and from this to proceed to the quantitative determination of the effect of various addition agents.



Using nitric and hydrochloric acids, two series of experiments were made on Croceine Orange to determine the relation between pH and the amount of dye adsorbed. One gram of wool was boiled for forty-five minutes in a bath containing seventy-five milligrams of dye in a total volume of 250 cc. The results are given in Table VI and in Figure 5.

TABLE VI  
pH and Adsorption of Croceine Orange

cc N/10 HCl added	Final pH	Mgs. dye adsorbed	cc N/10 HNO <sub>3</sub> added	Final pH	Mgs dye adsorbed
0.0	5.91	4.0	—	—	—
0.5	5.35	7.0	0.5	5.25	7.0
1.0	5.07	21.4	1.0	5.15	17.2
1.5	4.85	35.7	1.5	4.72	39.1
2.0	4.53	47.8	2.0	4.55	47.9
3.0	3.60	58.9	3.0	3.53	53.6
4.0	3.12	63.5	4.0	3.13	62.5
8.0	2.61	68.8	8.0	2.70	67.7
15.0	2.30	70.4	15.0	2.32	70.1

This curve shows that the amount of Croceine Orange adsorbed by wool increases as the hydrogen ion concentration is made greater. The fact that the chloride and nitrate ions have no specific effect may be accounted for by the assumption that they are either not adsorbed or that they are adsorbed equally.

To show that a change in hydrogen ion concentration produces a similar effect on the adsorption of other acid dyes, experiments were performed using Lake Scarlet R. The experimental conditions were kept the same as those used with Croceine Orange, except that the colorimetric method was abandoned and the amount of dye remaining in the baths was determined by titration with titanium chloride. Curve (a) of Figure 6 represents the data obtained (Table VII).

It is apparent that over a considerable range, the amount of Lake Scarlet R adsorbed by wool is directly proportional to the hydrogen ion concentration of the bath. As the total amount of dye in solution was only seventy-five milligrams, it is obvious that this is a limiting value which accounts for

the sudden upward bend in the curve, since this upward bend represents practically complete removal of the dye. If more dye had been used, it is probable that the proportionality between adsorption and pH would have continued over a still greater range.

TABLE VII  
pH and Adsorption of Lake Scarlet R

cc N/10 HCl added	Final pH	Mgs dye adsorbed
0.0	6.43	0.6
0.5	5.58	10.2
1.0	4.90	25.6
1.5	4.31	39.9
2.0	3.88	51.3
3.0	3.37	68.0
5.0	2.85	73.9
8.0	2.57	74.4
15.0	2.13	74.8

In accordance with the theory of dyeing previously outlined in the introduction to this paper, the addition to the dye-bath of substances forming strongly adsorbed anions will cause a decrease in the adsorption of an acid dye, and in general the greater the valence of the added anion, the greater will be its restraining action. The substitution of sulfuric or phosphoric acid for hydrochloric acid should therefore cut down the adsorption of acid dyes. A similar effect should be obtained if salts such as sodium sulfate, sodium phosphate or even sodium chloride are added to dyebaths containing hydrochloric acid.

Pelet-Jolivet,<sup>1</sup> Lake,<sup>2</sup> and others have investigated this point and have shown that the addition of sulfate and phosphate does actually decrease the amount of dye adsorbed by wool. But none of these investigators were careful to allow for the change in pH of the dyebath which the added salt might produce. The results already presented in this paper make it evident that a quantitative determination of the relative and absolute effect of restrainers such as chloride, sulfate, and

<sup>1</sup> "Die Theorie des Färbeprozesses" (1910).

<sup>2</sup> Jour. Phys. Chem., 20, 76 (1916).

phosphate, can only be made in dyebaths of equal hydrogen ion concentrations.

Data were therefore obtained to determine the action of restrainers on Lake Scarlet R. The experimental conditions were those described in the previous work, the dyebaths (250 cc) each containing seventy-five milligrams of dye plus different amounts of other reagents as denoted in the table of data (Table VIII). The final pH of each dyebath was ascertained as before and the amount of dye taken up by wool was determined. Curves were then drawn between pH and milligrams of dye adsorbed in the presence of the different addition agents. (Curves b, c, d, and e of Figure 6).

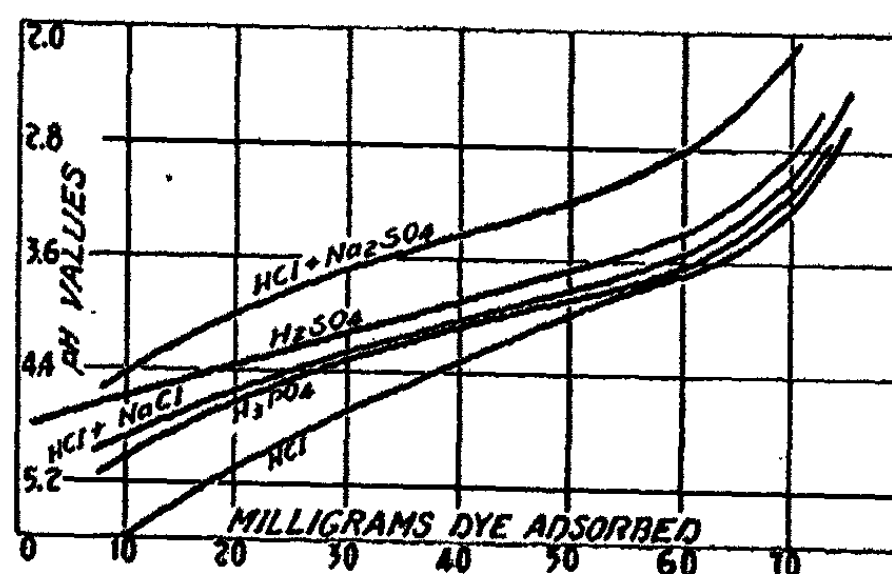


Fig. 6

Effect of Anions on the Adsorption of Lake Scarlet R.

An inspection of these curves brings out several interesting points. The amount of dye adsorbed always increases with the hydrogen ion concentration of the bath. In order to determine the relative effect of the different addition agents, it is essential that comparisons be made at equal values of pH. This is done readily by finding where the curves cross a line parallel to the X axis representing the desired pH. Thus at a pH of 4.0, the amount of dye adsorbed in the presence of hydrochloric acid was 48 mg, in the presence of phosphoric acid, 46.5 mg, and in the presence of sulfuric acid, 30 mg, the order of dye adsorption being  $\text{HCl} > \text{H}_3\text{PO}_4 > \text{H}_2\text{SO}_4$ .

TABLE VIII  
The Effect of Addition Agents on the Adsorption of Lake Scarlet R

cc N/10 H <sub>2</sub> SO <sub>4</sub>	Final pH	Mgs dye adsorbed	
0.5	4.81	1.3	
1.0	4.40	10.6	
1.5	4.13	28.1	
2.0	3.84	40.9	
2.8	3.50	57.5	
4.5	3.14	65.8	
cc N/10 H <sub>3</sub> PO <sub>4</sub>	Final pH	Mgs dye adsorbed	
1.2	4.98	10.8	
2.5	4.55	22.6	
4.2	4.25	39.0	
5.5	3.93	48.6	
7.0	3.62	57.8	
8.8	3.45	64.6	
12.5	3.11	68.7	
20.0	2.75	73.9	
cc N/10 HCl	cc N/10 NaCl	Final pH	Mgs dye adsorbed
0.5	25.00	4.90	10.0
1.0	25.00	4.55	20.9
1.5	25.00	4.15	35.7
2.2	25.00	3.77	49.1
3.3	25.00	3.28	65.9
5.0	25.00	3.00	69.1
8.0	25.00	2.68	71.6
cc N/10 HCl	cc N/10 NaSO <sub>4</sub>	Final pH	Mgs dye adsorbed
0.5	25.00	4.55	8.6
1.0	25.00	4.05	18.9
1.5	25.00	3.80	27.9
2.0	25.00	3.80	31.0
3.0	25.00	3.36	44.0
5.0	25.00	2.88	54.5
8.0	25.00	2.70	62.0
15.0	25.00	2.37	68.5
25.0	25.00	2.07	73.1

These results are in agreement with the theory. The strongly adsorbed divalent sulfate anion would be expected to cut down the amount of dye anion adsorbed. It is also evident that less dye was adsorbed from hydrochloric acid baths when sodium chloride was added and this is likewise in agreement with the theory. In a similar way, less dye

was adsorbed when sulfuric acid was substituted for hydrochloric acid in the dyebath, although the effect was not as marked for sulfuric acid alone as for hydrochloric acid plus sodium sulfate, because in the latter case the concentration of sulfate ions was greater and the two experiments are not comparable. It is often the custom among colloid chemists to regard phosphate solutions as a source of tri-valent phosphate ions.<sup>1,2</sup> Were this true we might therefore expect phosphate to be a more effective restraining agent than di-valent sulfate, assuming the valence rule. The data, however, show that phosphate is much less effective. The reason for this perhaps unexpected result probably lies in the fact that in phosphate solutions we do not really have tri-valent ions to any appreciable extent. Phosphoric acid dissociates very largely as a monobasic acid, slightly as a dibasic acid, and only very weakly as a tribasic acid. The effective valence of the anions in phosphate solutions should therefore be between one and two, and we should expect the curve for phosphoric acid to lie between the curves for hydrochloric and sulfuric acids. Inspection of Figure 6 shows that this is indeed the case. Lake<sup>3</sup> has reported that the addition of sodium phosphate to dyebaths containing hydrochloric acid almost completely prevented the taking up of acid dyes by wool. He ascribed the effect to the tri-valent phosphate ion. As Lake used an excess of di-sodium hydrogen phosphate, solutions of which have a pH value of about 9.2, it seems probable that the very considerable change in hydrogen ion concentration resulting from the addition of this salt was, to a large extent, the cause of the restraining action that he reported.

An attempt was made to use potassium ferri- and ferrocyanides as sources of tri-valent and tetravalent anions, but in each case these substances reacted with the dye, and the experiments could not be completed.

To show that the phenomena observed in the case of Lake

<sup>1</sup> Lake: *Jour. Phys. Chem.*, 20, 786 (1916).

<sup>2</sup> Compare Loeb: *Jour. Gen. Physiology*, 3, 248 (1920).

<sup>3</sup> *Jour. Phys. Chem.*, 20, 786 (1916).

Scarlet R were general for the acid dyes, another series of experiments was performed with du Pont Orange II. This dye can be titrated readily with titanium chloride in the presence of Rochelle Salt and is therefore easily determined in solution. In each of the experiments in this series one gram of wool was boiled for forty-five minutes in a dyebath (250 cc) containing seventy-five milligrams of dye plus the various addition agents specified in Table IX. In each of the sets of experiments comprising Table IX, however, the total amount of sulfate or phosphate was kept approximately the

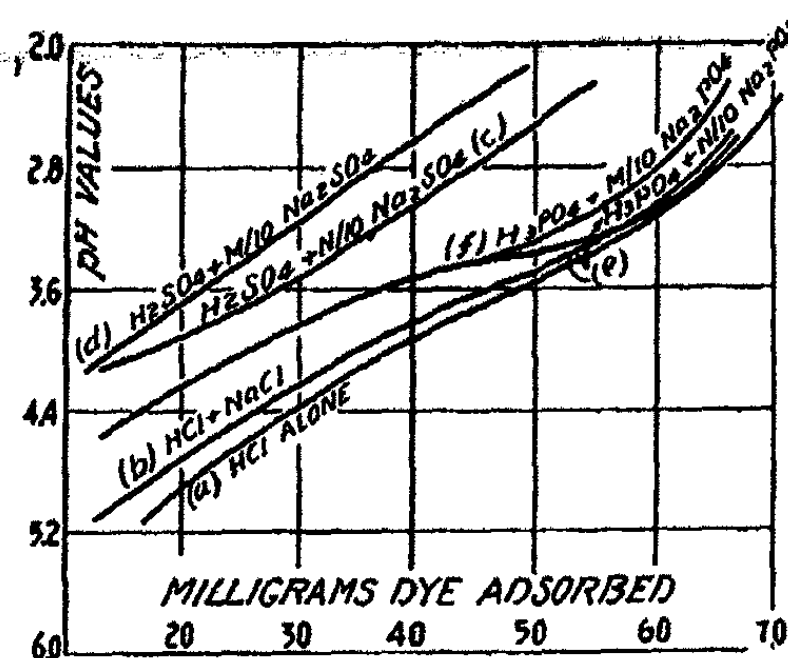


Fig. 7

Effect of Anions on the Adsorption of Lake Scarlet R

same and only the pH of the dyebaths was varied; in this regard the series differs from the one with Lake Scarlet R. Thus in the two sets of experiments with sulfuric acid and sodium sulfate, the quantity of acid and the quantity of salt were each varied, but their total was kept constant at 25 cc of either N/10 or M/10 sulfate solution in a dyebath of 250 cc. The results are plotted in Figure 7.

Attempts were made to determine the effect of di-valent and tri-valent cations, but the three (barium, magnesium, and aluminum) whose chlorides were added to the dyebath caused the dye to precipitate. It is well known, however,

TABLE IX  
The Effect of Addition Agents on the Adsorption of Orange II

Hydrochloric Acid Alone		
cc N/10 HCl	Final pH	Mgs dye adsorbed
0.5	4.34	28.8
0.7	4.23	33.6
0.8	4.16	34.8
1.0	4.03	35.4
1.3	3.70	47.0
1.5	3.60	51.7
2.0	3.38	54.5
3.0	3.18	59.2
6.0	2.76	63.0
10.0	2.49	69.7

Hydrochloric Acid plus Sodium Chloride			
cc N/10 HCl	cc N/10 NaCl	Final pH	Mgs dye adsorbed
0.3	24.7	4.88	16.4
0.6	24.4	4.68	20.2
0.8	24.2	4.30	29.0
1.0	24.0	3.84	35.0
2.0	23.0	3.56	48.0
3.0	22.0	3.29	57.0
4.5	20.5	2.97	61.7
7.0	18.0	2.68	63.5
10.0	15.0	2.45	66.7

Sulfuric Acid plus Sodium Sulfate			
cc N/10 H <sub>2</sub> SO <sub>4</sub>	cc N/10 Na <sub>2</sub> SO <sub>4</sub>	Final pH	Mgs dye adsorbed
0.3	24.7	4.12	13.5
1.0	24.0	3.83	25.0
2.0	23.0	3.50	29.9
3.0	22.0	3.27	36.1
4.5	20.5	2.96	42.5
7.0	18.0	2.71	48.0
11.0	14.0	2.32	53.2
cc N/10 H <sub>2</sub> SO <sub>4</sub>	cc N/10 Na <sub>2</sub> SO <sub>4</sub>	Final pH	Mgs dye adsorbed
0.15	24.85	4.08	13.5
1.50	23.50	3.24	28.8
5.50	19.50	2.33	45.9

## Phosphoric acid plus di-sodium hydrogen phosphate

N/10 H <sub>3</sub> PO <sub>4</sub>	N/10 Na <sub>2</sub> HPO <sub>4</sub>	Final pH	Mgs dye adsorbed
12.4	12.6	4.80	9.6
12.5	12.5	4.75	13.0
12.6	12.4	4.57	14.0
12.9	12.1	4.47	15.3
13.5	11.5	4.00	24.5
14.0	11.0	3.82	31.0
15.5	9.5	3.44	44.0
17.0	8.0	3.30	55.0
18.0	7.0	3.22	57.2
19.2	5.8	3.05	60.8
20.7	4.3	2.89	61.0
23.7	1.3	2.65	65.6
25.0	0.0	2.52	67.5
M/10 H <sub>3</sub> PO <sub>4</sub>	M/10 Na <sub>2</sub> HPO <sub>4</sub>	Final pH	Mgs dye adsorbed
12.83	12.17	4.30	18.4
15.34	9.66	3.08	55.1
23.67	1.33	2.28	66.0

that when the calcium or magnesium salt of an acid dye is soluble, it will be taken up more readily than the sodium salt of the same dye.

At low concentrations the effect of such anions as sulfate on the adsorption of an acid dye by wool is due, as stated before, to adsorption of the inorganic anion in place of some of the dye. It is easily possible, however, that at higher concentrations of sulfate the solubility of the dye may be diminished so that its tendency to be adsorbed may actually be increased. In other words, the restraining effect of sodium sulfate on acid dyes may pass through a maximum as the sulfate concentration is increased.

To test this point a series of experiments<sup>1</sup> was carried out with dyebaths which contained more sulfate than was the case previously. General conditions otherwise were kept as before. Each dyebath contained seventy-five milligrams of du Pont Orange II and five cc of N/10 sulfuric acid in 250 cc. One gram of wool was boiled in each bath for forty-five minutes.

<sup>1</sup> We are indebted to Mr. W. W. Paddon for aid in this series of experiments.



The partially exhausted baths were then analyzed for unadsorbed dye. Although equal amounts of acid had been added to all the baths, the hydrogen ion concentrations after dyeing were not the same throughout, probably because of the influence of the salt on the dissociation of the acid. Final hydrogen ion concentrations in this particular series of baths could not be determined by means of the hydrogen electrode because of some peculiar influence of the dye under these conditions. It was therefore necessary to resort to an indirect method for securing pH values. Mixtures of sodium sulfate and sulfuric acid were prepared corresponding to the concentrations existing in the dyebaths and the pH values of these solutions were secured. The values thus obtained were applied to the dyebaths.

In order that the effect of changing the sodium sulfate concentration may be determined, it is necessary that all other variables shall be controlled. The final pH values must therefore be the same throughout the series or the results must be corrected to a constant pH value. The latter method was employed and all adsorption values were corrected to a pH of 3.50, as follows. It was assumed that, over the short range of pH involved, the curves between milligrams of dye adsorbed and pH values were straight lines like those shown in Figure 7 for N/10 and M/10 sodium sulfate and that they were approximately parallel to these lines. For each of the baths a point was placed on Figure 7 at the position representing the milligrams of dye adsorbed and the pH as found. Lines were then drawn through these points parallel to the curve for M/10 sodium sulfate. The intersection of these new lines with the pH line equal to 3.50 gave, by direct reference to the X axis, the corrected milligrams of dye adsorbed.

Another method of comparing the effects of various concentrations of sodium sulfate is to compute the restraining action of the sulfate in each case by comparison with the adsorption curve in Figure 7 for hydrochloric acid alone at the same pH value. The results by both methods are given in Table XI. It is plainly evident that the restraining action

of the sodium sulfate passed through a maximum as its concentration was increased.

TABLE XI  
The Effect of Sodium Sulfate on the Adsorption of Orange II

No.	Bath conc. $\text{Na}_2\text{SO}_4$	pH	Mgs dye absorbed	Mgs dye adsorbed corrected	Method 2 restraining effect of sulfate
1	N/100	3.5	29.9	29.9	21.1
2	N/50	3.2	28.8	24.1	33.4
3	N/10	3.1	17.0	10.1	42.5
4	N/5	3.2	14.0	9.9	43.5
5	N	3.5	12.2	12.4	38.8
6	2N	3.6	27.3	28.4	21.7
7	3N	3.6	41.5	43.4	7.5
8	4N	3.7	47.1	50.8	-0.6

In order to show that the effect of the sulfate in the higher concentrations was actually due to a decrease in solubility, portions of baths 5, 6, 7, and 8 were placed in collodion thimbles after dyeing and immersed in solutions of sodium sulfate of the same concentrations as those inside the thimbles. At the end of forty-eight hours Number 5 showed strong diffusion, 6 slightly less, and 7 and 8 only very slight diffusion with 8 less than 7, showing that the sodium sulfate had lowered the solubility of the dye.

#### Basic Dyes

Experiments were next undertaken with basic dyes of which Methylene Blue was chosen first as a typical example. This dye proved to be a convenient one because it may be determined readily and accurately by titration with titanium chloride. Diffusion experiments<sup>1</sup> (Fig. 8) indicated that the

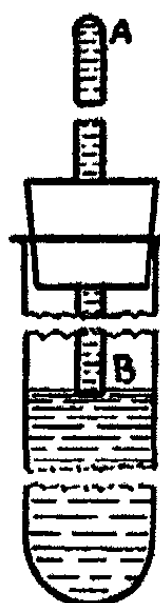


Fig. 8  
Diffusion Tube

<sup>1</sup> A glass tube (AB) of about 2 mm inside diameter and sealed at the top is filled with distilled water and then placed with its open end just below the surface of the dye solution to be tested. If the dye is in true solution, diffusion will be evident in a few hours and after several days the color will have extended nearly to the top of (AB). Colloidal suspensions show little or no diffusion. In case electrolytes have been added to the dye-bath, the tube (AB) should be filled with an equivalent solution of

dye forms true solutions in either neutral, weakly acid or weakly basic solutions. In more strongly basic solutions however, the dye forms a suspension and may be almost completely precipitated as the alkalinity is increased further.

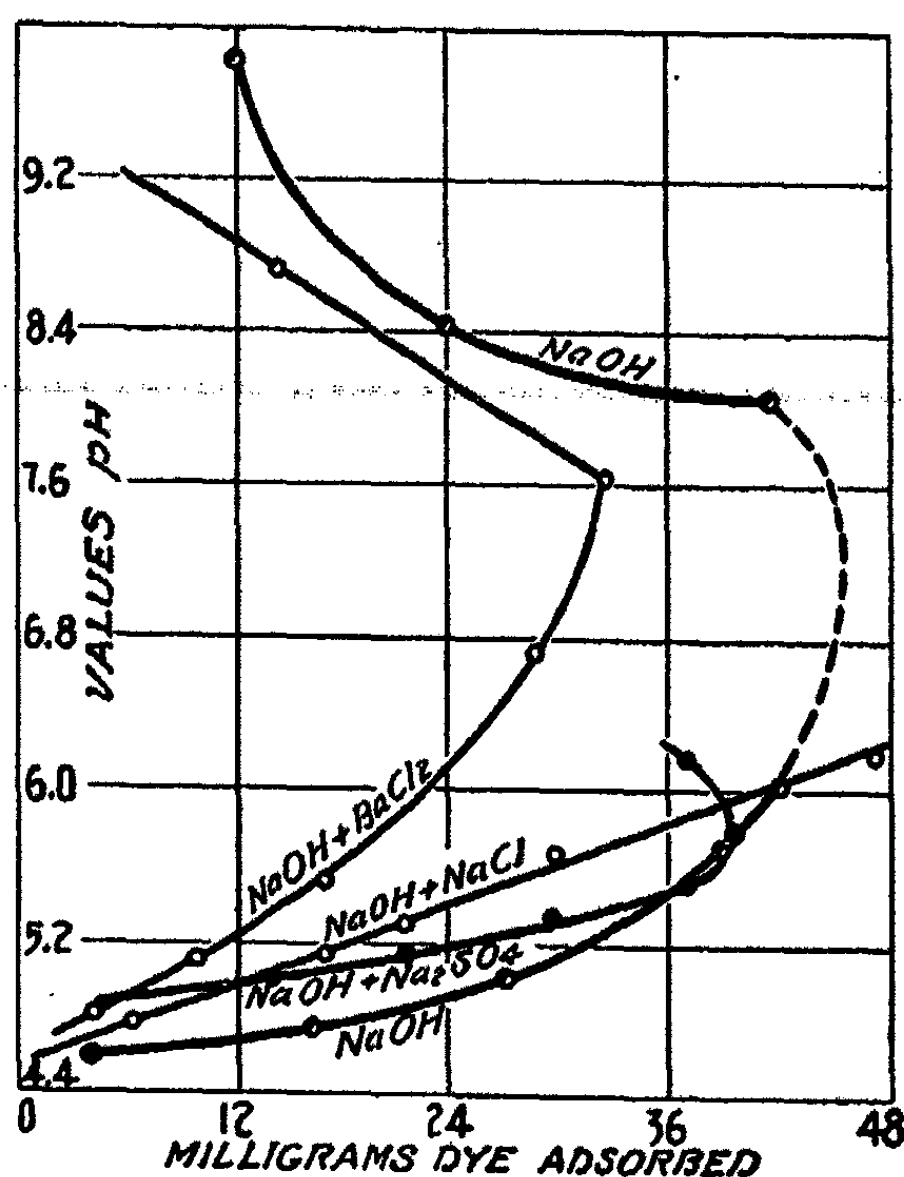


Fig. 9

Adsorption of Methylene Blue by Wool

By following the general procedure that was employed with the acid dyes, the amount of methylene blue taken up by wool in the presence of addition agents was determined. As in the previous work, one gram of wool was boiled for forty-five

these electrolytes instead of with pure water, to prevent any change in the condition of the dye as it diffuses up the tube. It should be recognized that between true solutions and colloidal suspensions we may and do have all degrees of combination of the two states. Part of the dye may be in true solution while the rest is colloidal.

minutes in a dyebath of 250 cc containing seventy-five milligrams of dye.

The first step was to ascertain the relation between hydrogen ion concentration and the amount of dye adsorbed. The data given in Table XII and in Figure 9 represent the results

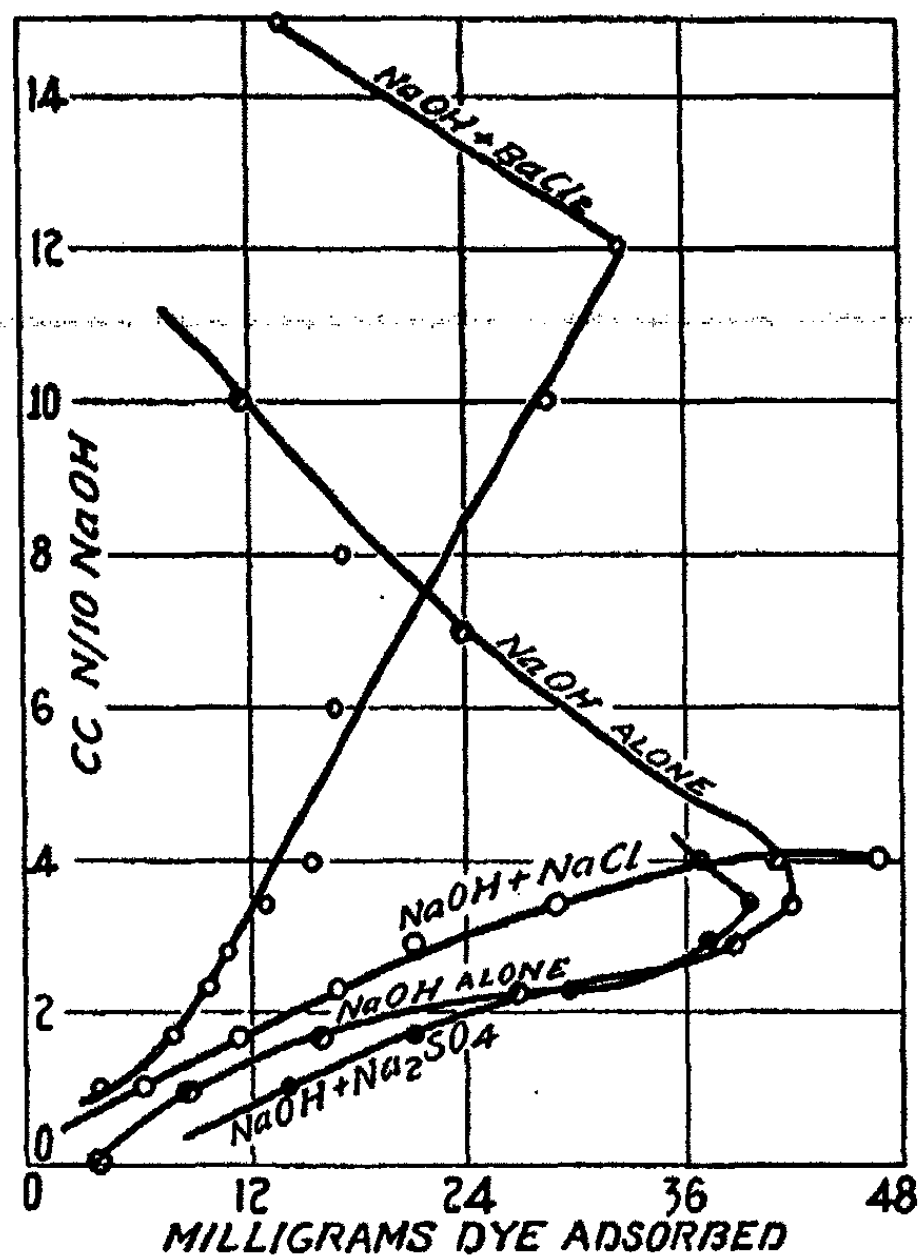


Fig. 10  
Adsorption of Methylene Blue by Wool

obtained. It will be noted that the effect of a change in pH is not so marked with this dye as it was in the case of acid dyes. It is also apparent that the total amount of base used is as important as the final pH of the solution. To bring out this point the curves in Figure 10 have been prepared by plotting total base added as ordinates instead of pH. Since the amount

TABLE XII  
The Adsorption of Methylene Blue by Wool

In the Presence of Sodium Hydroxide			
cc N/10 NaOH		Final pH	Mgs dye adsorbed
0.0		4.50	4.0
1.0		4.72	9.0
1.7		4.73	16.3
2.3		5.03	27.0
2.9		5.69	38.7
3.4		6.02	42.0
4.0		8.05	41.5
7.0		8.40	23.7
10.0		9.81	11.9

In the Presence of Sodium Chloride			
cc N/10 NaOH	cc N/10 NaCl	Final pH	Mgs dye adsorbed
1.0	25.0	4.80	6.4
1.7	25.0	4.80	11.6
2.3	25.0	5.12	17.1
2.9	25.0	5.29	21.4
3.4	25.0	5.66	28.9
4.0	25.0	6.18	46.9

In the Presence of Sodium Sulfate			
cc N/10 NaOH	cc N/10 Na <sub>2</sub> SO <sub>4</sub>	Final pH	Mgs dye adsorbed
1.0	25.0	5.00	14.2
1.7	25.0	5.13	21.4
2.3	25.0	5.35	29.4
2.9	25.0	5.48	37.6
3.4	25.0	5.78	39.6
4.0	25.0	6.17	37.1

In the Presence of Barium Chloride			
cc N/10 NaOH	cc M/10 BaCl <sub>2</sub>	Final pH	Mgs dye adsorbed
1.0	25.0	4.80	4.3
1.7	25.0	4.96	8.4
2.3	25.0	5.08	9.9
2.8	25.0	5.05	10.8
3.4	25.0	5.17	13.2
4.0	25.0	5.35	15.6
6.0	25.0	5.50	17.0
8.0	25.0	6.06	17.6
10.0	25.0	6.70	28.5
12.0	25.0	7.61	32.3
15.0	25.0	8.72	14.2

of dye adsorbed at first is practically proportional to the total base added, it seems probable that the dye base is taken up more strongly than its hydrochloride and that the adsorption of dye is roughly proportional to the amount of free dye base present.

A striking feature of each of these curves is the presence of a point of maximum adsorption. There are apparently two reasons for such a point. It will be recalled from the experiments on diffusion previously described that methylene blue passes from true to colloidal solution as sodium hydroxide is added and that when the latter is present in fairly large quantities, flocculation occurs. It is probable that sodium hydroxide removes hydrochloric acid from the methylene blue and sets free the dye base which is insoluble in water and which remains in suspension.

The dye now being distinctly in colloidal solution, a modification of the dyeing process results. All dyes behave like the substantive or direct dyes if their solutions become colloidal. For this reason, Methylene Blue, as soon as it has been rendered colloidal by the addition of sodium hydroxide, acts as a substantive dye and no longer behaves as a true basic dye. Briggs and Kakiuchi and Briggs and Woodward<sup>1</sup> have shown that the adsorption curves for substantive dyes pass through a maximum as the concentration of electrolytes is increased. Since Methylene Blue is colloidal in alkaline solution, it is to be expected that it would behave in a similar way. This supposition is confirmed by the data given in Table XII.

The other factor tending to produce a maximum point in the curves, is the action of the sodium hydroxide on the wool. The samples dyed at the higher concentrations of alkali showed very appreciable decomposition.

In those experiments the Methylene Blue was adsorbed strongly by the hydrogen electrode and after a few minutes the readings of the electrode showed a gradual falling off. Table XIII contains a series of readings made under such conditions.

---

<sup>1</sup> Results will be published in a subsequent paper.

TABLE XIII

Voltage reading...	.460	.562	.560	.558	.558	.556	.553	.548
Time in minutes...	1	2	3	5	7	10	20	27

"Time in minutes" means minutes elapsed from the time hydrogen was first started bubbling through the solution under test. The voltage rises quickly, remaining at a nearly constant value for several minutes and then gradually falls off again. This secondary decline is probably due to an adsorption of the dye by the electrode. By treating the hydrogen electrode with chromic acid cleaning mixture after each determination, the film of dye is stripped off and the surface renewed.

If the theoretical hydrogen ion concentrations of the dye-baths given in Table XII are calculated, it will be found that in all cases the observed pH values are lower than one would

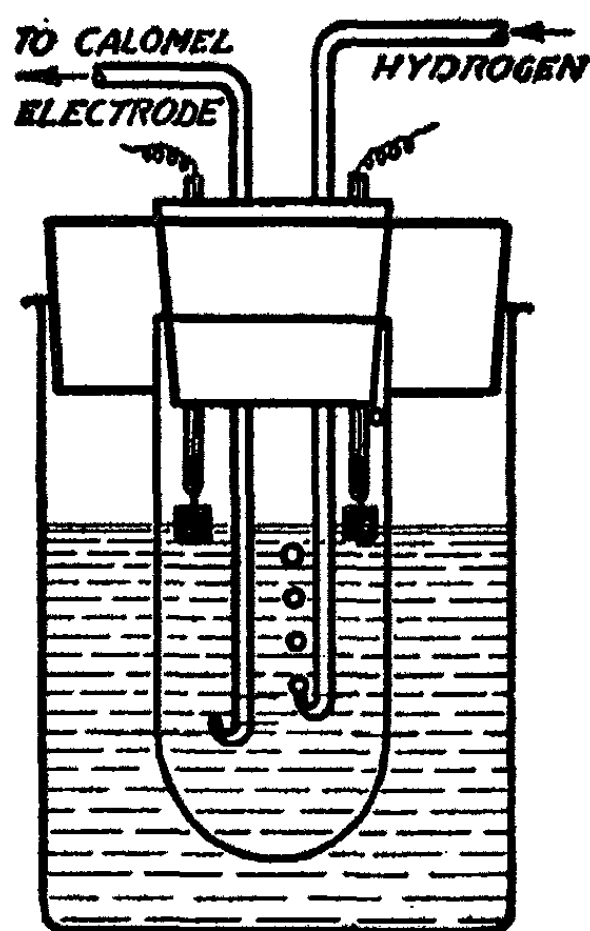


Fig. 11

expect, even though one allows for the hydrochloric acid liberated from the Methylene Blue. In order to make sure that the dye had not affected the hydrogen electrode and caused it to give consistently low readings, the apparatus shown in Figure 11 was prepared. In this device the hydrogen electrodes were partially immersed in distilled water contained in a collodion sac (S). The latter was then immersed in a dye bath of Methylene Blue whose pH value had been previously determined in the usual way. The bath chosen was a strongly alkaline one which had gone almost completely colloidal on boiling. Alkali began at once to pass into the sac and the rate of diffusion was followed by observing the change in the potential of the electrode. The dye did not diffuse through the col-

lloid.

lodian membrane so its possible effect on the electrodes was eliminated. The final pH value obtained in this way corresponded closely (8.72 and 8.79) with the value obtained in the usual manner where the electrodes were immersed directly in the dyebath.

One gram of wool was boiled forty-five minutes in 250 cc of sodium hydroxide solution containing 15.0 cc of N/10 sodium hydroxide. The free base left after this treatment was titrated with hydrochloric acid using phenolphthalein as indicator. It was found that only 5.0 cc of free base remained. The action of the alkali on the wool and its removal by the latter will therefore account for the high concentrations of hydrogen ion found in the experiments on Methylene Blue.

#### Summary

1. The process of dyeing wool with acid and basic dyes has been investigated from the standpoint of the adsorption theory of dyeing as formulated by Pelet-Jolivet and Bancroft.

2. The effect of dyes on the adsorption of acids by wool and of acids on the adsorption of dyes has been determined quantitatively for typical acid dyes.

3. It has been shown that the taking up of dyes is a case of adsorption and that the amount of dye adsorbed varies continuously with a change in the hydrogen ion concentration of the dyebath. No evidence of chemical action between dyes and wool has been found.

4. The use of the hydrogen electrode has made it possible to control a hitherto neglected variable.

5. The action of assistants has been studied and has been found to be strictly in accord with the theory.

The writers take this opportunity to express their thanks to Professor W. D. Bancroft for his unfailing interest and help.

This work was made possible by a fellowship grant from E. I. du Pont de Nemours and Company to whom our thanks are also due.

*Cornell University*



# THE BOILING POINTS OF AMMONIA, SULFUR DIOXIDE, AND NITROUS OXIDE

(An investigation of the error caused by using unjacketed  
boiling vessels.)

A-1853

BY F. W. BERGSTROM

## Introduction

It was desirable in connection with work described in a preceding paper<sup>1</sup> to check the static vapor pressure measurements made upon ammonia and sulfur dioxide by direct determinations of their normal boiling points. In conjunction with this, it was thought worth while to compare single-walled and vacuum-jacketed boiling vessels to afford substantial ground for the criticism of some previous determinations. The apparatus, recently described by Cottrell<sup>2</sup> for measuring the boiling points of aqueous solutions was used with entire success at  $-33^{\circ}$ .

## Apparatus

The majority of the measurements were made in a vacuum-jacketed vessel<sup>3</sup> of the dimensions shown in Fig. 1.<sup>4</sup> Current for heating the coil of platinum wire in the bottom of the tube was obtained from a 110 volt circuit, and regulated by means of a variable six lamp resistance. The side tube, B, was used for introduction of liquid. A small coil condenser was sealed to D, although in the measurements to be described, additional liquid was added if necessary to compensate for that evaporated as the substances used were inexpensive. The double-walled

<sup>1</sup> Jour. Phys. Chem., 26, 358 (1922).

<sup>2</sup> Jour. Am. Chem. Soc., 41, 721 (1919).

<sup>3</sup> Gibbs: Ibid., 27, 851 (1905).

<sup>4</sup> The terminals of the heating coil may be attached to lead-in wires passing through the large stopper, as described by Beckmann: Zeit. anorg. Chem., 55, 371(1907). This would permit the use of a plain Dewar tube. The coil should be large enough so that the maximum energy expenditure will not overheat the wire and cause local dissociation of the liquid.

portion was silvered, with the exception of a vertical streak on either side, through which the thermometer was read. The tube contained carefully cleaned garnets to a depth of about five centimeters to insure even boiling and minimize superheating. The thermometer was inserted through a cork closing the top.

A few determinations were made to show the reliability to be expected from single-walled tubes, and to show the effect of accomplishing boiling by radiation and conduction of heat from the air.

The single-walled vessel was similar to the one described, except that the vacuum jacket and side tubes were omitted. It was 22 cm in length and 3.5 cm in diameter. Near the hole for the thermometer in the stopper was a smaller opening for the introduction of liquid, this serving also to establish atmospheric pressure within. Internal and external radiation screens were used during some of the measurements, and garnets were placed in the bottom of the tubes.

The form of Cottrell apparatus used is shown with dimensions in Fig. 2. It consisted of a long tube one cm internal diameter, with two six mm pumping tubes sealed on as shown. The ends of the latter were widened into funnels to aid in catching bubbles of vapor. The thermometer, which was held by a stopper fitting an enlargement at the top, cleared the sides of

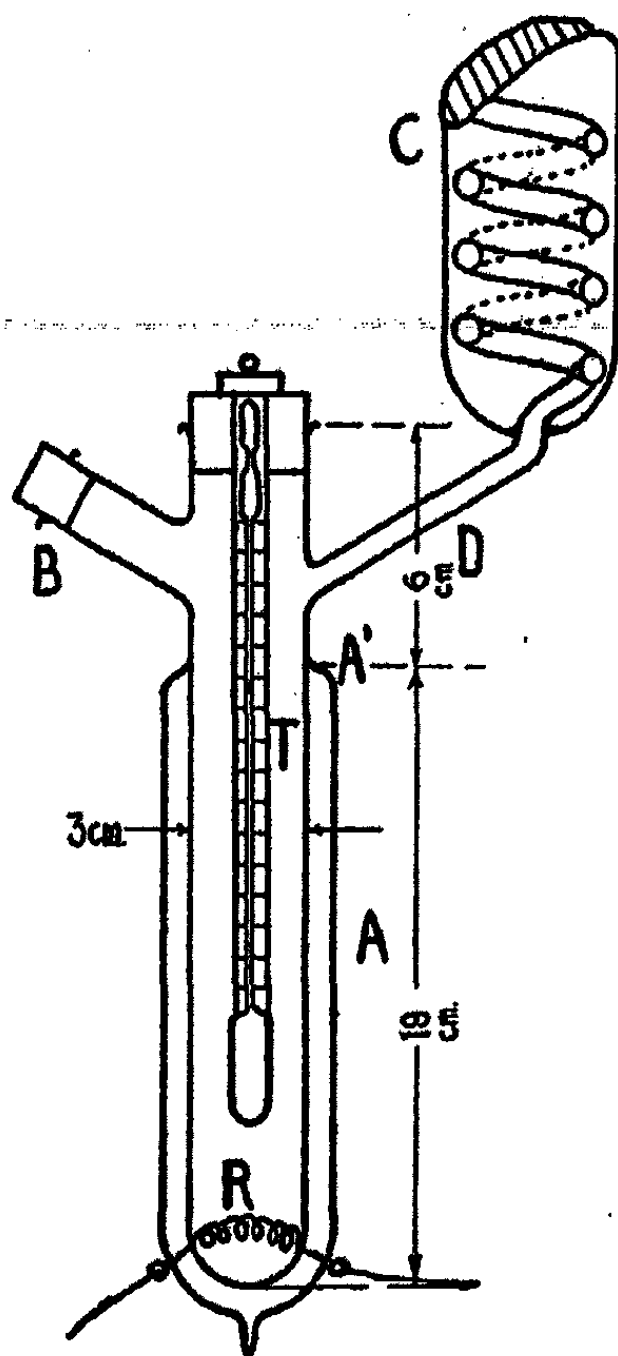


Fig. 1  
Apparatus used for Boiling Point Determinations

the large tube by 0.6 mm. This latter was of sufficient length to extend below the bottom of the thermometer bulb, forming a protective screen around it. A small hole opposite and above the upper pumping tube aided the operation.

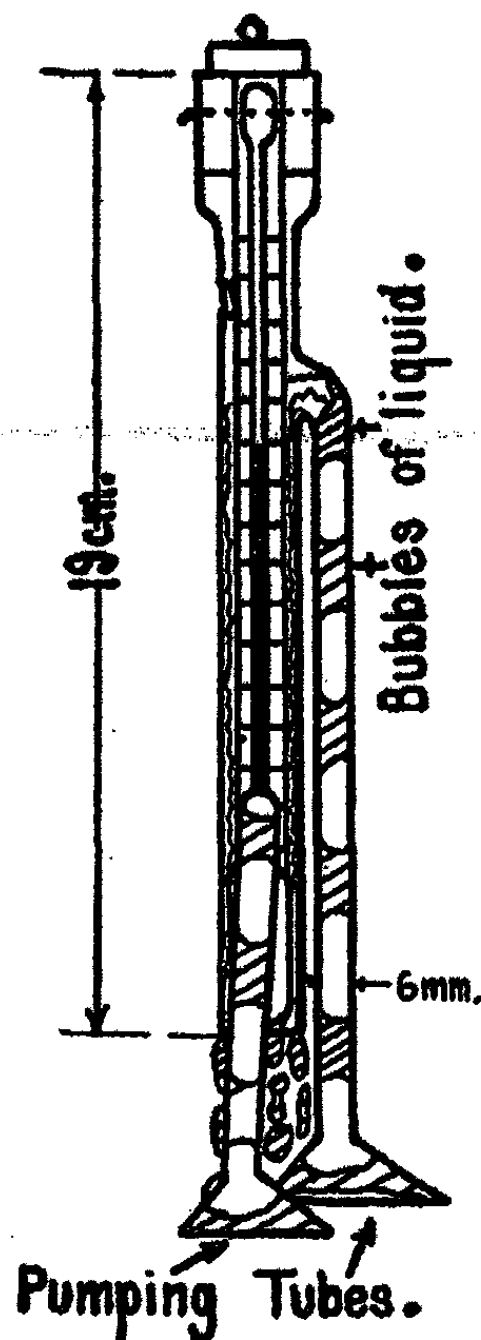


Fig. 2  
Cottrell Tube

Fig. 2  
Cottrell Tube

cates give the following corrections (rounded to the nearest 0.1°).

Temperature	No. 21713	No. 21714
-25°	no correction	0.1° high
-35°	"	0.4° high
-45°	"	0.3° high

<sup>1</sup> Loc. cit.

The action is similar to that of the air-lift pump. Alternate bubbles of vapor and liquid are formed in the small tubes, and rise, as the average density of this mixture is less than that of the liquid. Liquid flows over both the thermometer and the inside of the glass casing. Provision must be made for rapid rates of pumping in low temperature work such as this.

#### Thermometry and Barometry

The siphon barometer used was in perfect agreement with the manometer of the vapor pressure apparatus described in a preceding paper.<sup>1</sup> All barometer readings were made with a cathetometer. The observed barometric height was corrected to 0° for the expansion of the mercury and of the brass cathetometer scale. The two toluene thermometers used in measurements of the boiling point of ammonia were calibrated in 1905 by the Physikalische technische Reichsanstalt. The accompanying certificates

No. 21713 and No. 21714 were duplicates, and were graduated in fifths of a degree from  $-20^{\circ}$  to  $-50^{\circ}$  in a length of 20 cm. Temperatures were read, as a rule, with the telescope of the cathetometer. The toluene thermometers were kept in the liquid whose boiling point was to be measured from one-half to two hours before use, unless otherwise noted.

Mercury thermometer No. 1, used in the determinations of the boiling point of sulfur dioxide, was calibrated near  $-10^{\circ}$  by comparison with a resistance thermometer in a constant temperature bath.<sup>1</sup>

Temperature read	Resistance, ohms	True temp.	Correction
$-7.00^{\circ}$	9.133	$-7.0^{\circ}$	0.0°
$-9.90^{\circ}$	9.039	$-9.9^{\circ}$	0.0°
$-11.02^{\circ}$	9.001	$-11.0^{\circ}$	0.0°

No. 1 was 30 cm long and was graduated from  $+50^{\circ}$  to  $-12^{\circ}$  in fifths of a degree.

Toluene thermometers No. 21731 and No. 2 were used in the measurements on nitrous oxide. The former, 37.5 cm long, was graduated in degrees from  $+50^{\circ}$  to  $-100^{\circ}$ . The divisions were large,  $10^{\circ}$  equaling 13 mm. The calibrations given on the accompanying P. T. R. certificate are:

$+20^{\circ}$ ,  $0^{\circ}$ ,  $-60^{\circ}$ ,  $-79^{\circ}$  no error;  $-20^{\circ}$ ,  $0.2^{\circ}$  high;  $-40^{\circ}$ ,  $0.6^{\circ}$  high.

The corrections are rounded to the nearest  $0.2^{\circ}$ . It is to be regretted that calibrations were not made at lower temperatures. The correction at  $-90^{\circ}$  is assumed to be zero.

No. 2 was narrower than No. 21731, but otherwise nearly the same; it was compared with the platinum resistance thermometer at ten temperatures between  $-68^{\circ}$  and  $-91^{\circ}$ , and the calibrations, with two exceptions, fall on a smooth curve. The greatest deviation of check calibrations is  $0.2^{\circ}$  at  $-78^{\circ}$ . The correction to be added to the thermometer reading at  $-90^{\circ}$  is  $+1.3^{\circ}$ .

<sup>1</sup> See Jour. Phys. Chem., 26, 362 (1922) for calibration of resistance thermometer.

In using the thermometers, it was found desirable to examine the stem capillaries carefully for toluene before recording any data.

#### Corrections Applied to Thermometer Readings

In determinations of boiling points at low temperatures, it is desirable to keep the liquid thread in the capillary of the thermometer, as well as the bulb, at the temperature to be determined, to avoid uncertain corrections for exposed stem. This introduces an error, as the average pressure on the thermometer bulb is greater than atmospheric by the height of liquid above its center. In all measurements of this kind, a correction has accordingly been applied to the barometric pressure, taking the density of liquid ammonia at  $-33.4^\circ$  to be  $0.68^1$  and of nitrous oxide to be  $1.23^2$  at  $-90^\circ$ . This correction is somewhat uncertain, as the liquid and vapor phases are not necessarily in equilibrium throughout the tube.

All boiling points were reduced to correspond to a mercury column of 760 mm at  $0^\circ$ . From the vapor pressure determinations previously described, it was found that the pressure changed 3.6 mm for ammonia, and 3.5 mm for sulfur dioxide per tenth of a degree change in temperature near the normal boiling points. The correction applied per mm difference between the observed barometric pressure and 760 mm was then  $0.028^\circ$  for ammonia, and  $0.029^\circ$  for sulfur dioxide. The boiling point of nitrous oxide changes  $2^\circ$  for every 0.1 atmosphere difference in pressure<sup>2</sup> near the normal boiling point. The latter correction, only approximate, is sufficiently accurate.

#### The Boiling Point of Ammonia

##### Preparation of the Ammonia:

A small cylinder containing sodium was filled with commercial liquid ammonia, and allowed to stand for some weeks to ensure complete removal of moisture. Ammonia from this

<sup>1</sup> Fitzgerald: *Jour. Phys. Chem.*, 16, 654 (1912).

<sup>2</sup> *Sitzungsber. Akad. Wiss., Berlin*, 1904, 1198.

supply was distilled into a steel vessel of 500 cc capacity. A portion of this was distilled into a second similar vessel, from which it was distilled as needed into a closed glass tube for transfer to the boiling point apparatus (Fig. 3). Connections between the glass tube of this container and the lead tube leading from the steel vessel were made with sealing wax. The ammonia, purified by three distillations, was introduced into the boiling apparatus, A, through the side tube, B. The "nozzle" A of the container was inserted through a hole in the stopper closing B and the tube rotated until ammonia was blown past the stopcock. In this manner, a sample could be introduced into the apparatus without coming in contact with and absorbing moisture from the air. The end of the condensing coil was attached to a drying tube.

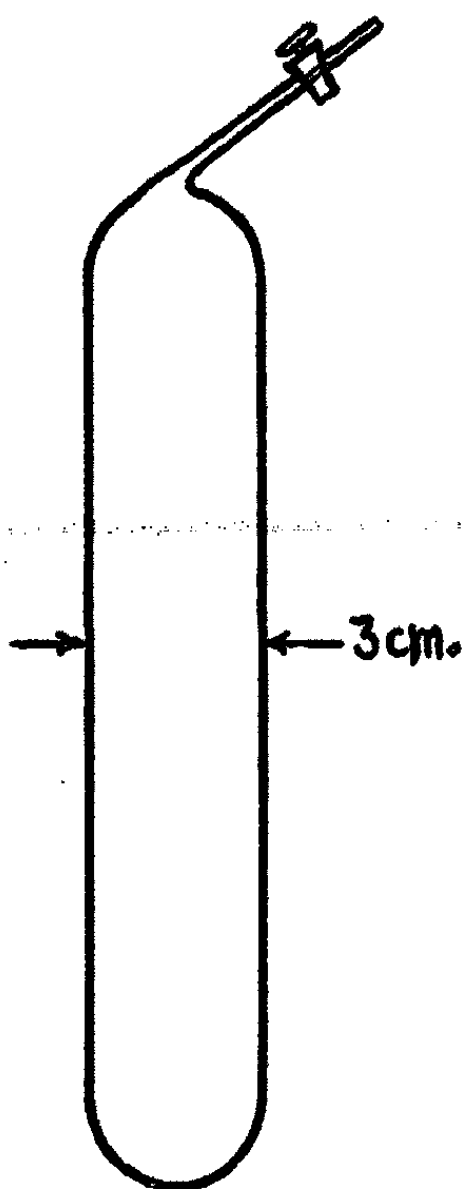


Fig. 3

#### Measurements of the Boiling Point

1. *With Complete Immersion of Stem and Bulb.*—The average height of ammonia necessary to keep the toluene thread in the stem cooled was 10.3 cm. To correct for this excess pressure,  $0.14^\circ$  was subtracted from the final result, reduced to 760 mm [ $10.3 \times 0.68 \times 0.028/13.6 = 0.14$ ].

These readings, as well as the ones yet to be described, were taken at five to ten minute intervals. Omitting the first result, where one would expect the liquid to be superheated, the average of the corrected readings is  $-33.23^\circ$ . The barometric pressure was 762.6 mm at  $0^\circ$ . The boiling point, corrected to 760 mm, is  $-33.30^\circ$ , but the ammonia is boiling under an

additional head of 10.3 cm of ammonia ( $= 10.3 \times 0.68/13.6$  or 5.2 mm mercury). The true normal boiling point is accordingly  $-33.44^\circ$ .

Current, amps. <sup>1</sup>	0	0.5	1.0	1.5	2.0
Energy, watts <sup>1</sup> approx.	0	0.1	0.4	0.8	1.4
21714, readings	$-32.82^\circ$	$-32.89^\circ$	$-32.89^\circ$	$-32.90^\circ$	$-32.90^\circ$
Temp., corrected	$-33.16^\circ$	$-33.23^\circ$	$-33.23^\circ$	$-33.24^\circ$	$-33.24^\circ$
Current, amps.	2.0	3.0			
Energy, watts	1.4	3.2			
21714, readings	$-32.86^\circ$	$-32.88^\circ$			
Temp., corrected	$-33.20^\circ$	$-33.22^\circ$			

It was noticed that as the ammonia boiled away exposing increasing lengths of stem, the temperature changed very little, until a considerable amount had evaporated. This perhaps occurred because the temperature rise due to increasing uncooled steam was counteracted somewhat at first by the fall due to decreasing height of liquid. The latter amounts to a lowering of the pressure. This same phenomenon was noticed by Gibbs.<sup>2</sup>

2. *With Cottrell Tube and Vacuum-jacketed Vessel.*—

(a) Average pressure (mean of three readings) 756.5 mm at  $24^\circ$ . Average boiling point (21713)  $-33.54^\circ$  (mean of seven readings taken in the course of an hour). Temperature variation,  $0.10^\circ$ . Currents, 0–4 amperes [0–5.6 watts] the boiling point, corrected to 760 mm, is  $-33.36^\circ$ .

In this and following experiments with the Cottrell tube, a few garnets were placed in the vessel to aid the formation of bubbles. (b) In this instance, the temperature variation was  $0.04^\circ$ . The following data were recorded:

<sup>1</sup> The lamps used took 0.55, 0.53, 0.50, 1.0 and 1.8 amperes current. Approximately, the first three took half an ampere, the fourth one ampere, and the fifth two amperes. The energy expenditures were found by calculation, knowing the current taken by the coil and its resistance (0.35 ohm under the experimental conditions).

<sup>2</sup> Loc. cit.

Current (approx.)	2	3	3	3.5	4
Energy, watts (approx.)	1.4	3.2	3.2	4.3	5.6
Temp. observed 21713	-33.55°	-33.58°	-33.59°	-33.57°	-33.56°
Temp., corrected	same				

Corrected barometric pressure (0°) 754.2 mm.  
Boiling point, corrected to 760 mm -33.41°.

The pumping was in all cases excellent. The use of the Cottrell tube eliminates the necessity of correction for the depth of immersion of the thermometer.

(c) Ammonia was distilled directly from the stock cylinder containing sodium into the glass container, from which it was transferred to the boiling vessel.

Amps.	Approx. energy, watts	P. T. R. 21714 readings	Temperature corrected
2	1.4	-33.38°	-33.72°
4	5.6	-33.40°	-33.74°

Barometric pressure 749.1 mm (corr.).  
Boiling point, corrected to 760 mm. -33.43°.

3. *With Single-walled and with Air-jacketed, Double-walled Vessels.*—(a) The energy was obtained from a small multiple cell storage battery. The maximum energy expenditure in the coil under the experimental conditions (five cells connected) probably lies between 1.5 and 2.5 watts. Adjustable internal

Cells connected	0	4	4	4	5
21714, readings	-32.50°	-32.70°	-32.66°	-32.07°	-32.80°
Temperature, corrected	-32.86°	-33.06°	-33.02°	-33.06°	-33.16°
Cells connected	5	5	0	0	
21714, readings	-32.80°	-32.75°	-32.60°	-32.64°	
Temperature, corrected	-33.16°	-33.11°	-32.96°	-33.00°	

Barometer, corrected, 754.2 mm.  
Average height of ammonia above the center of thermometer bulb, 11.6 cm.



and external radiation screens were used, but no definite conclusions could be drawn from the results as to their effect.

Omitting the results with zero current, which are obviously not reliable, the average boiling point at 754.2 mm. is  $-33.10^\circ$ . However, the ammonia is boiling under an additional pressure due to 11.6 cm of liquid (equivalent to 5.8 mm of mercury). The boiling point corrected to 760 mm is then  $-33.10^\circ$ .

The boiling in all cases was vigorous. It is evident that with zero current the liquid is considerably superheated, although boiling. The lowering of the boiling point observed with the first applications of energy through the coil is very noticeable.

(b) The terminals of the heating coil<sup>1</sup> were attached through a variable lamp resistance to a 110 volt circuit. The Cottrell tube was used, and this, together with the larger expenditure of energy lowered the average boiling point found in (a)  $0.2^\circ$ .

Amps. (approx.)	2	3.5	3.5	2
21714, readings	$-33.41^\circ$	$-33.45^\circ$	$-33.46^\circ$	$-33.44^\circ$
Temperature, corrected	$-33.41^\circ$	$-33.45^\circ$	$-33.46^\circ$	$-33.44^\circ$

Barometer, 753.6 mm at  $0^\circ$ .

Boiling point, corrected to 760 mm  $-33.26^\circ$ .

The Cottrell tube does not entirely prevent superheating under these conditions.

(c) This determination was run concurrently with one in the vacuum-jacketed vessel (2, b). The two samples of ammonia were distilled in succession from the small steel cylinder, and so were as nearly identical as possible. The single-walled tube was used with an inner platinum radiation screen. No. 21783 indicated an average temperature of  $-33.23^\circ$  at a pressure of 754.2 mm (corr.). The average depth of immersion was 7.5 cm. The boiling point, corrected to 760 mm is  $-33.17^\circ$ . The results obtained by boiling the ammonia in an air-jacketed (double-walled) tube with no internal application of energy were unsatisfactory, in spite of the use of garnets. The

<sup>1</sup> Resistance not determined, but not far from 0.4 ohm.

boiling, although good, was not as vigorous as with the single-walled tube. With thermometer 21713 the normal boiling point was found to be  $-33.10^{\circ}$ . The Cottrell tube lowered this to  $-33.19$ . Its effect in promoting equilibrium between liquid and vapor phases is readily seen.

TABLE 1

Remarks	Normal boiling points observed	Mean
<i>Single-walled boiling tube:</i>		
(A) No internal supply of energy	$-32.94^{\circ}$	$-32.94^{\circ}$
(B) Energy supplied internally	$-33.10^{\circ}$ , $-33.17^{\circ}$	$-33.14^{\circ}$
(C) With Cottrell tube and internal supply of energy	$-33.26^{\circ}$	$-33.26^{\circ}$
<i>Air-jacketed (double-walled) tube:</i>		
(A) No internal supply of energy	$-33.10^{\circ}$	$-33.10^{\circ}$
(B) Same, but with Cottrell tube	$-33.19^{\circ}$	$-33.19^{\circ}$
<i>Silvered Vacuum-jacketed Vessel:</i>		
Energy supplied internally	$-33.44^{\circ}$	$-33.44^{\circ}$
Same, but with Cottrell tube	$-33.41^{\circ}$ , $-33.36^{\circ}$ , $-33.43^{\circ}$	$-33.40^{\circ}$

The average of the four latter reliable values obtained with the vacuum-jacketed tube is  $-33.41^{\circ} \pm 0.1^{\circ}$ .

### Sulfur Dioxide

*Preparation.*—Sulfur dioxide obtained from a small cylinder of the commercial liquid, was passed successively through wash bottles containing concentrated sulfuric acid, water, through calcium chloride and phosphorus pentoxide tubes, and was finally condensed in a glass bulb provided with a siphon. Introduction into the vacuum-jacketed boiling tube was carried out as described.

### Measurements of the Boiling Point

(a) With Cottrell tube, unsilvered vacuum-jacketed vessel.

Amps.	Approx. energy, watts	No. 1, readings	Temperature corrected
2	1.4	$-10.10^\circ$	$-10.10^\circ$
3.5	4.3	$-10.10^\circ$	$-10.10^\circ$

Barometer, corr., 757.7 mm.

Boiling point, corrected to 760 mm,  $-10.02^\circ$ .

(b) Vacuum-jacketed vessel, without Cottrell Tube.

No corrections were made for depth of immersion, but this was probably small, for the  $-10^\circ$  division was close to the bulb. The normal boiling points obtained were  $-10.03^\circ$  and  $-10.01^\circ$ , the maximum temperature variation being  $0.02^\circ$  and  $0.03^\circ$  during the two series.

### Nitrous Oxide

Nitrous oxide from a cylinder of the commercial liquid was

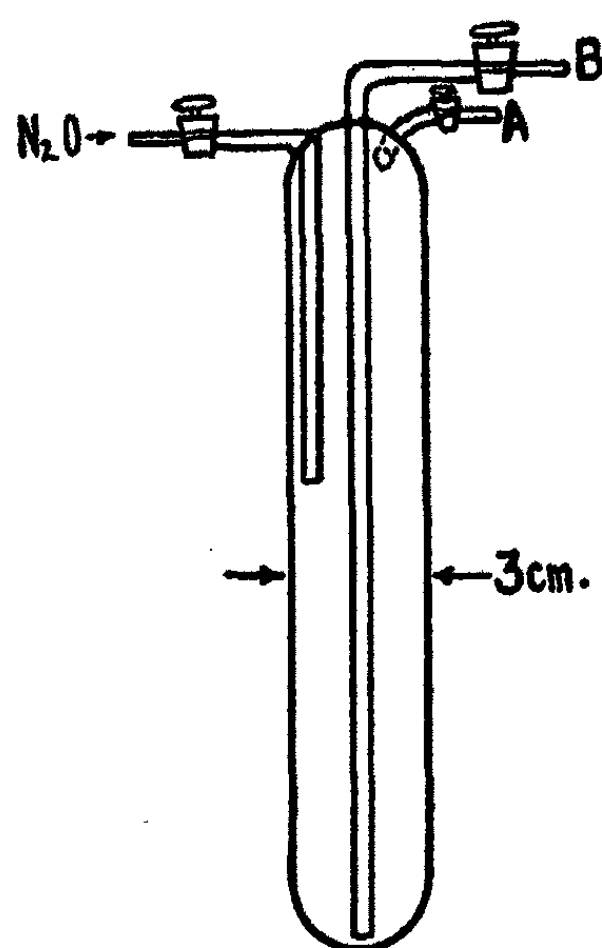


Fig. 4

passed through a 75 cm soda lime tube, two phosphorus pentoxide tubes, and a tightly packed glass wool filter before condensation in the apparatus illustrated (Fig. 4). As liquid air was used to condense the nitrous oxide, it was necessary to attach a soda lime tube to A to prevent entrance of moisture or carbon dioxide from the atmosphere. When the solid was melted the condensation tube was inverted, and liquid blown through B into the boiling vessel. The usual precautions were observed.

No.	Amps.	Approx. energy, watts	Depth of immersion of bulb, cm.	No. 21731	No. 2	Temperature corrected
1	0	0	0		-72.5°	-71.7°
2	0	0	7.5	-89.4°		-89.4°
3	2	1.4	7.0	-89.4°		-89.4°
4	4	5.6	6.0	-89.4°		-89.4°
5	2	1.4	4.5	-89.4°		-89.4°
6	2	1.4	5.0		-90.7°	-89.4°
7	4	5.6	4.6		-90.7°	-89.4°
8	4	5.6	4.3		-90.7°	-89.4°

Barometric pressure 756.2 mm (two observations).

The readings were taken during one and three quarter hours.

In No. 1, the thermometer bulb was just touching the surface of the liquid. The intense superheating of the vapor is evident. The Cottrell tube of the size used was entirely unsuited for determinations at such low temperatures, although with larger boiling vessels and larger Cottrell tubes, there is no reason why accurate results should not be obtained. The nitrous oxide was boiling gently with zero current. In Nos. 5. and 8 there was about 10° exposed stem, and so these have not been considered. The pressure under which boiling occurred is 762.1 mm (thermometer 21731) and 760.4 mm (thermometer 2), adding to the barometric pressure that due to the column of liquid above the thermometer bulb. The normal boiling point is then -89.5° (thermometer No. 21731) or -89.4° (thermometer No. 2).

#### Discussion of Results and Comparison with Work of Other Investigators

The following determinations of the boiling point of ammonia have been made:

Observer	Date	Temp.	Pressure	Remarks
Guyton <sup>1</sup>		—48.75°	700 app.	Condensation temperature
Bunsen <sup>2</sup>	1839	—33.7°	749.3	Static vapor pressure measurements
Faraday <sup>3</sup>	1844	—49° app.	700 app.	Static vapor pressure measurements
Loir and Drion <sup>4</sup>	1860	—35.7°	760	In an open vessel
Regnault <sup>5</sup>	1862	—38.1°	752	In an open vessel
Regnault <sup>6</sup>	1862	—32.6°	760	Manometric
Joannis <sup>7</sup>	1893	—38.2°	764	
Ladenburg <sup>8</sup>		—35.0°	760	
Dickerson <sup>9</sup>		—33.0°	760	
Lange <sup>10</sup>		—33.7°	760	
Pictet <sup>11</sup>		—33.0°	760	Manometric
De Fore-rand <sup>12</sup>	1903	—32.5°	760	In an open vessel
Gibbs <sup>13</sup>	1905	—33.46°	760	Vacuum-jacketed vessel
Brill <sup>14</sup>	1906	—33.0° —33.1°	760	Manometric and direct
Davies <sup>15</sup>	1906	—33.5°	760	Manometric
Burrell and Robert-son <sup>16</sup>	1915	—34.6°	760	Manometric
Keyes and Brown-lee <sup>17</sup>	1918	—33.52° —33.21°	760	Manometric and direct
Bureau of Stand-ards <sup>18</sup>	1921	—33.35°	760	Manometric and direct
Postma <sup>19</sup>	1920	—33.35°	760	Vapor pressure measurement
Bergs-trom <sup>20</sup>	1919	—33.4°	760	Manometric and direct
Stock and Hen-ning <sup>21</sup>	1921	—33.35°	760	Manometric

(For footnotes see next page.)

It is impossible to obtain the true boiling point of a liquid in an open vessel. The author has in this manner obtained temperatures below  $-40^{\circ}$  with ammonia.

It has been experimentally shown in this paper that high results are obtained with single-walled tubes, even with internal application of energy and with garnets to insure more even boiling. The variation of the observed boiling point with heat supplied is marked. The Cottrell tube may advantageously be used in determinations of boiling points in vacuum jacketed vessels at least as low as  $-33.4^{\circ}$ . With the exceptions of the measurements of the Bureau of Standards, of Gibbs, and of Keyes and Brownlee (?), most of the direct determinations referred to were evidently made in single-walled vessels. In a number of cases no mention is made of the type of apparatus used.

The measurements of Gibbs were made with a silvered vacuum-jacketed tube, such as described in this article. Some of the toluene thermometers he used were also used in this investigation. No mention is made of emergent stem, although it is stated that corrections were not made for the

<sup>1</sup> Ann. Chim, 29, 290.

<sup>2</sup> Pogg. Ann., 46, 97 (1839).

<sup>3</sup> Ann. Chim. Phys., (3) 15, 227.

<sup>4</sup> Bull. Soc. chim. Paris, 1860, 184.

<sup>5</sup> Jahresber. über Fort. Chem., 1863, 70.

<sup>6</sup> Mém. de l'Acad., 26, 535 (1862).

<sup>7</sup> Comptes rendus, 115, 820 (1893).

<sup>8</sup> Quoted in "Verflüssigtes Ammoniak als Lösungsmittel," J. Bronn, Berlin (1905).

<sup>9</sup> Probably quoted Pictet.

<sup>10</sup> Probably quoted Bunsen.

<sup>11</sup> Arch. Genève, 13, 212.

<sup>12</sup> Ann. Chim. Phys., [7] 28, 537 (1903).

<sup>13</sup> Loc. cit.

<sup>14</sup> Ann. Phys., [4] 21, 170 (1906).

<sup>15</sup> Proc. Roy. Soc., 78, 28, 42.

<sup>16</sup> Jour. Am. Chem. Soc., 37, 2482 (1915).

<sup>17</sup> Ibid., 40, 39 (1918).

<sup>18</sup> Ibid., 42, 206.

<sup>19</sup> Rec. Trav. chim. Pays-Bas., 39, 515 (1920).

<sup>20</sup> Loc. cit.

<sup>21</sup> Zeit. Physik, 4, 226 (1921).

depth of immersion of the thermometer. The average of all measurements is  $-33.46^\circ$  (six readings). The maximum temperature variation is  $0.21^\circ$ . The Cottrell tube gives more consistent results, for the variation among the three described in this paper was only  $0.07^\circ$ .

Keyes and Brownlee found the normal boiling point by manometric means to be  $-33.25^\circ$  and by direct determinations to be  $-33.21^\circ$  (most probable value). The boiling point was observed to be a function of the heating current, and ranged from  $-33.13^\circ$  with zero current, to  $-33.70^\circ$  with four amperes. The actual energy expenditures are uncertain. The temperature was measured with a calibrated Beckmann thermometer.

The vapor pressure measurements of the Bureau of Standards are referred to in a preceding paper.<sup>1</sup> The normal boiling point determined by manometric means is  $-33.354^\circ$ . In addition, seventeen observations were made of the boiling point, using a method analogous to the ordinary determination of steam points. The mean boiling point at 760 mm. was found to be  $-33.341^\circ$  and the individual values are in agreement to within a few hundredths of a degree. This method would undoubtedly give more accurate results than the determination in a small vacuum-jacketed tube but possesses the disadvantage of requiring an external bath to cool the apparatus.

Henning and Stock by manometric means found the normal boiling point to be  $-33.35^\circ$ . Postma, in the course of an investigation of the system ammonia-water likewise obtained this value.

Other results are discussed in a previous paper.<sup>2</sup>

#### Sulfur Dioxide

The following determinations of the boiling point of sulfur dioxide have been made:

---

<sup>1</sup> Loc. cit.

<sup>2</sup> Loc. cit.

Name	Date	Boiling point	Pressure, mm.	Remarks
Bunsen <sup>1</sup>	1839	-10.5°	744	Manometric?
Drion <sup>2</sup>		about -8°	760	
Andréeff <sup>3</sup>		-10.3°	741	
Andréeff <sup>3</sup>		-9.9°	754	
Faraday <sup>4</sup>		about -10°	760	
Blümcke <sup>5</sup>	1888	-10°	760	Manometric
Régault <sup>6</sup>	1863	-10.08°	760	Manometric
Pictet <sup>7</sup>		-10.0°	760	Manometric
Gibbs <sup>8</sup>	1905	-10.09°	760	Direct
Burrell and Robertson <sup>9</sup>	1915	-11.0°	760	Manometric
Henning and Stock <sup>10</sup>	1921	-9.99°	760	Manometric
Bergstrom <sup>11</sup>	1919	-10.05°	760	Manometric
		-10.02°	760	Direct

Gibbs used the same apparatus as the author. With the exception of Drion and Burrell and Robertson, the normal boiling points given in the preceding table are all very close to -10.0°.

#### Nitrous Oxide

The following measurements of the boiling point have been described:

- <sup>1</sup> Pogg. Ann., 46, 97.
- <sup>2</sup> Ann. Chim. Phys., (3) 56, 5.
- <sup>3</sup> Ann. Chim. Pharm., 110, 1.
- <sup>4</sup> Phil. Trans., 135, 1, 155.
- <sup>5</sup> Wied. Ann., 34, 10.
- <sup>6</sup> Mém. de l'Acad., 1863, 535.
- <sup>7</sup> Arch. de Genève, 13, 212.
- <sup>8</sup> Loc. cit.
- <sup>9</sup> Jour. Am. Chem. Soc., 37, 2691 (1915)
- <sup>10</sup> Loc. cit.
- <sup>11</sup> Loc. cit.



Observer	Date	Temperature	Pressure, mm.	Remarks
Faraday <sup>1</sup>	1845	-87.2°	760	Alcohol thermometers manometric
Regnault <sup>2</sup>	1863	-87.9°	767.3	Hydrogen thermometer
Cailletet <sup>3</sup>	1893	-92°	760	Manometric
Ramsay and Shields <sup>4</sup>		-89.8°	760	Direct, in Dewar tube vessel
Wills <sup>5</sup>	1874	-92°	760	Direct
Grunmach <sup>6</sup>	1904	-89.4°	741.1	
Cailletet and Colardeau <sup>7</sup>	1888	-88.8°	760	
		-88.7°		
		-88.9°		
Burrell <sup>8</sup>	1915	-88.7°	760	Direct?
Bergstrom	1919	-89.5°	760	Manometric Direct

Faraday and Wills used alcohol thermometers calibrated above 0° and graduated in equal divisions below without calibration. The results are incorrect, as the apparent coefficient of alcohol in glass is not constant. Wills states that "the boiling point (normal) usually said to be -88°, is, according to my experiments -92°, but I would give more credence to the lower figure."

Cailletet and Colardeau, aside from the mention of the use of a long Dewar tube vessel, say nothing of their apparatus. A thermocouple, used in another part of their investigation, was in practically perfect agreement with the hydrogen and resistance thermometers. The thermocouple was calibrated at +100.0°, and at the normal boiling point of methyl chloride,

<sup>1</sup> Phil. Trans., 135, 1, 155.

<sup>2</sup> Ann. Chim. Phys., [3] 26, 259.

<sup>3</sup> Arch. de Genève, 66, 16.

<sup>4</sup> Jour. Chem. Soc., 63, 835.

<sup>5</sup> Ibid., 27, 21 (1874).

<sup>6</sup> Sitzungsber Akad. Wiss., Berlin., 1904, 1198.

<sup>7</sup> Comptes rendus, 106, 1493 (1888).

<sup>8</sup> Jour. Am. Chem. Soc., 37, 2691 (1915).

which he assumed to be  $-23.4^{\circ}$ . Gibbs<sup>1</sup> and Regnault<sup>2</sup> found this to be  $-24.09^{\circ}$  and  $-23.73^{\circ}$ , respectively.

Ramsay and Shields made three direct determinations upon fairly large quantities of nitrous oxide contained in a Dewar tube vessel. A hydrogen thermometer was immersed in the liquid, and rapid boiling was maintained during the observations to avoid superheating. It is not clear whether this was accomplished by internal application of energy or not.

Grünmach made a direct determination in a Dewar tube container, using a pentane thermometer calibrated by the Physikalische Technische Reichsanstalt. The description is meager.

Burrell and Robertson's results may be subject to an error similar to the one noticed in the case of ammonia and sulfur dioxide. His results when plotted by the method of Ramsay and Young give a fair straight line (for the solid). His triple point (approximately  $-90.6^{\circ}$ ) is twelve degrees higher than the freezing point found by Ramsay and Shields ( $-102.3^{\circ}$ ).

#### Summary

(1) A comparison was made of single-walled and vacuum-jacketed boiling vessels. A modification of the apparatus described by Cottrell for the determination of the boiling points of aqueous solutions was used during part of the work.

(2) It was found that (a) The boiling point of ammonia, determined in a single-walled vessel, is about  $0.2^{\circ}$  high, even with internal application of energy. The Cottrell tube will partially lessen this error. (b) Boiling points may be determined accurately in a vacuum-jacketed vessel, probably as low as  $-90^{\circ}$ . A correction should be applied for the depth of immersion of the thermometer bulb. There should be no uncooled stem. The Cottrell apparatus can be used successfully at temperatures at least as low as  $-33.4^{\circ}$ . There is no reason why, with suitable apparatus, it could not be used at much lower temperatures. Better equilibrium between vapor and liquid is

<sup>1</sup> Loc. cit.

<sup>2</sup> *Mém. de l'Acad.*, 1863, 535.

obtained, and uncertain temperature corrections are eliminated. A smaller quantity of liquid is generally required.

(3) The following boiling points were determined:

Ammonia  $-33.41^{\circ} \pm 0.1^{\circ}$ . Sulfur dioxide  $-10.02^{\circ} \pm 0.1^{\circ}$ . Nitrous oxide  $-89.5^{\circ} \pm 0.2^{\circ}$ .

In conclusion, the writer wishes to express his thanks to Professor Franklin, at whose suggestion, and under whose direction this work was undertaken.

*Stanford Univ.*  
*Calif.*

## NEW BOOKS

**Chemical Principles.** By Arthur A. Noyes and Miles S. Sherrill. Revised edition. 22 X 15 cm.; pp. xviii + 310. New York: The Macmillan Co., 1922. Price: \$4.00.—In the preface the authors state that "the purpose of the course is to give students an intimate knowledge of fundamental chemical principles and a training in logical, scientific thinking, such as will enable them to attack effectively the practical problems arising in their subsequent educational or professional work in any of the branches of chemistry or related sciences. Descriptive text-books of physical chemistry afford a general survey of chemical laws and theories which may suffice for the purposes of students who are not preparing for a professional career on the educational, research, or industrial sides of chemistry, but they do not give that intensive training which is essential for pursuing successfully more specialized courses of scientific study or for applying chemical principles to industrial problems. No one regards a course of lectures on the principles of mathematics as a suitable method of giving beginners the ability to handle that science, and with scarcely more reason can descriptive courses on physical chemistry be expected to afford a working knowledge of chemical principles in their quantitative aspects. Only by constantly applying the principles to concrete problems will the student acquire such a knowledge and the power to use it in new cases. The course of instruction, as carried out by the authors, consists of class-room exercises, mainly of the recitation type, given to sections of twenty to thirty students.

The book is divided into three parts. The first deals with the atomic, molecular, and ionic theories and the properties of substances directly related to these theories. The headings of the chapters are: the composition of substances and the atomic theory; the molal properties of gases and the molecular and kinetic theories; the molal properties of solutions and the molecular theory; the atomic properties of solid substances; the electrolytic behavior of solutions and the ionic theory. The second part is devoted to the rate and equilibrium of chemical changes from mass action and phase view-points, the sub-headings being: the rate of chemical changes; the equilibrium of chemical changes at constant temperature; the equilibrium of chemical systems in relation to the phases present. In the third part the authors discuss the energy effects attending chemical changes, and the equilibrium of chemical changes in relation to these effects. The chapters in this section are entitled: the production of heat by chemical changes; the production of work by isothermal chemical changes in relation to their equilibrium conditions; the production of work from isothermal changes by electrochemical processes; the effect of temperature on the work producible by isothermal chemical changes and on their equilibrium conditions; systemization of free-energy values.

There are some points which the reviewer would like to see changed in the next edition. On p. 57 and elsewhere the authors give the modified Raoult's law and do not give the van't Hoff formula, although the latter is the theoretical one. It is very much of a question whether one is justified in saying, p. 58, that "fundamentally, Raoult's law expresses the tendency of the solvent to

escape from the solution, and it should therefore be independent of the equation of state of the vapor." In the diagram on p. 76 for the distribution of a solute between two non-miscible liquids, the two liquids have apparently the same density. The proof is unsound because the system is not theoretically in equilibrium. On p. 84 is the statement that "certain animal membranes, such as parchment or bladder, are permeable for water, but not for certain solutes of high molecular weight (the so-called colloids)." Parchment is not an animal membrane, colloids are not solutes, and they do not necessarily have high molecular weights. It should have been stated, on p. 176, that the diagram of sulphur ignores the existence of a second liquid modification in the melt. Another illustration should have been taken or some reference should have been made to the work of Alexander Smith.

The influence of Nernst shows itself in the remarks on the phase rule, pp. 181, 203. "The phase rule furnishes a basis for the classification of different types of equilibrium. It also enables the number of phases that can exist under specified conditions to be predicted. The usefulness of the phase rule itself is, however, often exaggerated. . . . The preceding problems illustrate the characteristic differences between the conclusions to be drawn from the phase rule and from the mass-action law. The phase rule is qualitative, its application presupposes no special knowledge beyond that of the number of components and phases, and it is applicable without any limitation of concentration. The mass-action law is quantitative, its application presupposes knowledge of the molecular species present, and, if numerical values are to be computed, also of their dissociation-constants; and it is applicable in exact form only to solutions or gases at small concentrations."

There seems to be a feeling that the phase rule and the mass law are antagonistic in some mysterious way, whereas the phase rule gives the broad, general, qualitative classification, while the mass law supplements this by giving the quantitative relations in and between the phases. If one knows where the railroad tracks are (phase rule), one can predict with absolute accuracy where the trains will run, and, in the case of a single-track road, one can point out the only places where trains going in the opposite direction can pass; but one cannot, unless one is a Sherlock Holmes, tell the number of trains per day or the speed at which they travel. If one has the latest time-table (mass law) one knows a lot of quantitative data, such as the time of arrival and departure of trains, the equipment, etc. One can also deduce the mean speed (reaction velocity), the length of run made by the dining car, etc. If the locomotive cannot make steam owing to cold weather and therefore behaves like an imperfect gas, the time-table does not hold. The time-table, like the mass law, only holds accurately under favorable conditions. Nobody ever discusses the relative merits of tracks and time-tables and it is not clear to the reviewer why the kindred problem of phase rule and mass law should have such a fatal fascination for some people.

On p. 218 is the statement that "the heat of dilution of substances in solution is also important; for it enables the heat of formation of a solution of one concentration to be calculated from that of a solution of another concentration, and thus enables heats of reaction to be calculated at different concentrations." This seems rather an anthropomorphic view-point. A reference to the change

of the calculated osmotic pressure with the heat of dilution would have been helpful to the student.

On p. 13 the volume of one mol of a perfect gas at 20° and one atmosphere is given as approximately twenty-four liters, presumably a misprint for 22.4.

The reviewer has gone into what seem to him to be slips in considerable detail because the standing of the senior author is such that many of these statements might well be accepted by the student solely on his authority, a very unscientific proceeding. One of the penalties of greatness is that it becomes increasingly necessary to watch one's step.

As would be expected, the book is written very clearly. The question of electrolytic dissociation is a case in point, pp. 124, 125, 153, 169-172. The problems have been selected judiciously, and anybody, who works through them, will acquire a great ability in doing numerical calculations. Whether this will help the student in "applying chemical principles to industrial problems" is quite another matter. The reviewer doubts whether many industrial problems can be solved by means of quantitative calculations. He doubts whether the quantitative theory of dilute aqueous solutions is applicable in anything more than an occasional case. The reviewer wonders whether short qualitative problems in research would not be better for the students than this intensive drill. If that is out of the question, the reviewer would prefer an advanced course of lectures, laying special stress on the shortcomings in our present theories. The proof of the pudding is always in the eating and this book seems to have stood the test. Everybody must be grateful to the authors for putting squarely before us one solution of the educational problem, whether we are willing to accept it as the best solution or not.

Wilder D. Bancroft

**Molecular Diffraction of Light.** By C. V. Raman. 22 X 14 cm.; pp. x + 103. Calcutta: Calcutta University Press, 1922.—This small volume takes up "the general theory of the molecular scattering of light in all refractive media, including in a comprehensive survey the cases of gases, vapours, liquids, crystals, and amorphous solids." The chapters are entitled: fundamental principles; scattering of light by gases; atmospheric scattering and twilight phenomena, molecular scattering in liquids; the colour of the sea and the albedo of the earth; scattering of light in crystals; scattering of light in amorphous solids; the Doppler effect in molecular scattering; molecular diffraction and the quantum theory of light.

When accounting for the blue of the sky by the scattering of light by the molecules of the air Rayleigh postulated that the phases of the waves scattered laterally by the individual molecules are absolutely at random, so that their energy effects are additive. "The foregoing discussion makes two points clear. The validity of the principle of random phase depends on the conditions being such that the compressibility of the medium is given with sufficient accuracy by Boyle's law. Secondly, the ultimate justification of the principle rests on the complete non-uniformity in the spatial distribution of the molecules in so far as very small volume elements are concerned. As we shall see later on, it is precisely these factors, namely, the compressibility of the medium and the non-conformity of the spatial distribution of the molecules, which enter into the general theory of light-scattering developed according to the principles laid down by

Einstein and Smoluchowski, and which, as has been pointed out by these writers, in the case of gases obeying Boyle's law leads to results substantially identical with those obtained from Rayleigh's formula. It is important therefore to notice that in respect of gases at any rate, the special theory developed by Rayleigh and the more general theory of Einstein and Smoluchowski rest on exactly the same logical bases and differ only in the detailed mode of calculation of the intensity of the light scattered," p. 12.

The scattering of light in saturated ether vapor instead of in air is directly proportional to the square of the refractivity of the ether, p. 48.

In the first paper on the subject, Lord Rayleigh emphasized the fact that his theory of molecular scattering is not applicable to the case of highly condensed media such as dense vapours, liquids, and solids because the molecules in them possess only a greatly restricted freedom of movement and their distribution cannot therefore be regarded as a simple random arrangement. Actually Strutt has found that liquid ether scatters a great deal less light than the vapor in proportion to the relative densities.

The author considers that the blue color of water is due chiefly to light scattered by diffraction, "the selective absorption of the water only helping to make it a fuller hue," p. 75.

On p. 95 the author states: "In the year 1905, Einstein put forward the hypothesis that the energy of a beam of light is not distributed continuously in space but that it consists of a finite number of localized indivisible energy-bundles or "quanta" capable of being absorbed or emitted only as wholes. The theory had some notable successes to its credit, especially the prediction of the photoelectric equation and the explanation of the phenomena of ionization of gases by X-rays. Nevertheless it has been felt that very serious difficulties stand in the way of its acceptance. Maxwell's electro-magnetic theory conceives the energy of light as distributed in a continuous manner through space and offers a satisfactory explanation of whole groups of phenomena, the mere existence of some of which, especially those classed under the heading of interference and diffraction, seems very difficult to reconcile with the hypothesis of light-quanta. The tendency has therefore been to regard the propagation of light in space as determined by Maxwell's equations, but that these equations for some reason or other fail when we have to deal with the emission or absorption of energy from atoms or molecules. The discontinuity is thus conceived to be limited to the act of emission or the act of absorption or of both. Historically, the quantum hypothesis had its origin in the derivation of Planck's radiation formula, and an assumption that the discontinuity occurs only in emission is apparently sufficient for that limited purpose. Hence, though Planck's hypothesis of quantum emission, reinforced as it has been by the success of Bohr's theory of line-spectra, has passed into general acceptance, Einstein's idea of light-quanta has apparently been regarded as unnecessarily revolutionary in character. This feeling has perhaps been strengthened by the considerable degree of success which has attended the use of the "correspondence-principle" recently introduced by Bohr in which an attempt is made to effect a reconciliation, limited though it be, between Maxwell's theory and the quantum theory of emission of light.

"If, however, we view the matter from a purely philosophic standpoint, Einstein's original conception of the discontinuous nature of light itself has much



to recommend it. It fits in with the assumed discontinuous character of the emission and absorption of energy as part of a consistent and homogeneous theory, whereas the idea that emission and absorption are discontinuous while the propagation of light itself is continuous belongs to the class which Poincaré has described as "hybrid hypotheses." Such hybrid hypotheses may serve temporarily as useful planks to bridge gaps in existing knowledge, but there is little doubt that they must ultimately make way for a more consistent system of thought. Historically, Maxwell's theory is the embodiment of the belief of nineteenth-century physicists in the validity of Newtonian dynamics as applied to physical phenomena in their ultimate analysis, and especially as applied to phenomena occurring in the medium which was postulated as pervading all space. The belief in the validity of Newtonian dynamics as applied to the ultimate particles of matter has however received a rude shock from the success of the quantum theory as applied to the theory of specific heats, and there seems no particular reason why we should necessarily cling to Newtonian dynamics in constructing the mathematical framework of field-equations which form the kernel of Maxwell's theory. Rather, to be consistent, it is necessary that the field-equations should be modified so as to introduce the concept of the quantum of action. In other words, the electrical and magnetic circuits should be conceived not as continuously distributed in the field but as discrete units each representing a quantum of action, and possessing an independent existence, somewhat in the manner of vortex-rings in a perfect fluid. Interference and diffraction phenomena may then be conceived of as arising from the approach or separation, i. e., crinkling of the mean "lines of flow" of energy in the field.

"Bohr's theory has made the idea familiar that the emission or absorption of light from the atom or the expulsion of an electron involves something in the nature of a catastrophic change in the atom itself. If, therefore, we wish to look for some experimental support for Einstein's conception that light itself consists of quantum units, we must consider those optical phenomena in which obviously no such catastrophic change in the atoms or molecules is involved. The molecular diffraction or scattering of light is obviously such a phenomenon, which stands in the most intimate relationship with the general theory of the propagation, reflection, refraction and dispersion of light. If we found that the phenomena of molecular scattering of light are completely and satisfactorily explained on the basis of the classical electromagnetic theory, the case against Einstein's conception would be enormously strengthened. If, on the other hand we find that the classical theory based on the idea of continuous wave-propagation breaks down and fails to explain the observed facts, we should naturally feel called upon to revise our ideas regarding the nature of light itself."

*Wilder D. Bancroft*

*Study Questions in Elementary Organic Chemistry. By Alexander Lowy and Thomas B. Downey. 23 X 15 cm; pp. vi + 91. New York: D. Van Nostrand Company, 1921. Price: \$1.00.*—In the preface the authors say that "the study questions contained in this pamphlet are used in connection with the elementary organic chemistry course given at the University of Pittsburgh to students in the Schools of Chemistry, Medicine, Engineering, Mines, College, and Education. This method has proven successful in our own institution in



aiding the students to master the subject matter more thoroughly; and, with this object in view, we offer the pamphlet for the benefit of students in other institutions."

When the reviewer was an undergraduate, the professor of mathematics handed out a long list of questions on calculus and told us that the examination questions would be taken from that list. "Study questions" seems to be a euphemism for "examination questions." The questions are grouped under the following headings: introductory part; saturated paraffins; olefines; diolefines; general questions on paraffin hydrocarbons; halogen derivatives of hydrocarbons; monatomic alcohols; polyatomic and unsaturated alcohols; ethers; aldehydes and ketones; monobasic acids; polybasic acids; salts; acid anhydrides; esters of inorganic and organic acids, fats, oils, and waxes; acyl halides; acid amides; halogen substitution products of acids; hydroxy-acids; amino-acids; aldehyde acids and ketone-acids; carbohydrates; amines; nitro and nitroso compounds; cyanogen compounds; alkyl cyanides, alkyl isocyanides, cyanic acid, and related compounds; sulphur, phosphorus, and arsenic compounds; organo-metallic compounds; uric acid group; introductory questions on cyclic compounds; aromatic hydrocarbons; halogen derivatives of aromatic hydrocarbons; sulfonic acids; nitro compounds; amines and other reduction products of nitro compounds; diazo compounds; aromatic alcohols, phenols and ethers; aldehydes; ketones; quinones; acids; derivatives of benzene with two or more unlike groups; dyes; the terpenes and camphors; heterocyclic compounds; alkaloids; proteins.

Wilder D. Bancroft

*La théorie einsteinienne de la gravitation; essai de vulgarisation de la théorie.* By Gustav Mie. Translated by J. Rossignol. 19 × 12 cm.; pp. xi + 118. Paris: J. Hermann, 1922. Price: 4.50 francs.—Perhaps the most interesting thing about this volume at the present time is that it is an authorized translation from the German. In the summary, p. 103, the author says: "Throughout this book I have taken the view-point of the physicist, who makes observations and measurements. It was not possible to indicate the mathematical depths of the theory because mathematics has its own language just as music does. Listening to the description of a symphony will not carry us into the heart of the music even though an extraordinary musician describes it to us. It is necessary to hear the symphony itself. The more carefully one listens to the music, the better one grasps its developments and the more deeply the spirit of the work sinks in. Similarly one does not seize the real spirit of a mathematical theory unless one plunges into the mathematical details. . . . ."

"Whoever analyzes carefully the theory of Einstein can scarcely avoid a peculiar impression. Behind the universe which we detect by physical methods, and which we can only describe in terms of rigid and stern laws, we seem to get a glimpse of a fine and delicate gauze of mathematical ideas, which have their own laws and which, up to a certain point, are independent of our human contacts. I have tried to show that the new developments of physics cause us to recognize everywhere a profound principle of unity which we call the ether. The physics of the ether forms the basis of all the apparently complicated phenomena and lets us perceive, through this complication, a mathematically marvelous clearness and harmony."

Wilder D. Bancroft





## NAME INDEX

### To Papers

Adams, E. Q.,	The rôle of hydrogen- and hydroxyl-ion diffusion in nerve and muscle action . . .	639
Alsgaard, P. C.,	Electrolytic production of sodium perborate,	137
Bancroft, Wilder D.,	Mordants. I, II, III, . . .	447, 501, 736
Bergstrom, F. W.,	The vapor pressure of sulfur dioxide and ammonia, . . .	358
Bergstrom, F. W.,	The boiling points of ammonia, sulfur dioxide and nitrous oxide, . . .	876
Bhatnagar, S. S.,	The water-proofing efficiency of some bi- and trivalent salts of higher fatty acids and their adsorption by the fibres of paper, . . .	61
Bogue, R. H.,	Hydrogen-ion concentration and the properties of the emulsion colloids . . .	801
Briggs, T. R. and A. W. Bull,	The physical chemistry of dyeing . . .	845
Brown, O. W.,	See Henke and Brown . . .	324, 631
Brown, O. W. and C. O. Henke,	Catalytic preparation of aniline. I, II, . . .	161, 272
Brown, O. W. and C. O. Henke,	Catalytic action of copper, . . .	715
Brown, O. W., S. V. Cook and J. C. Warner,	Effect of grinding upon the apparent density of lead oxides, . . .	477
Bull, A. W.,	See Briggs and Bull, . . .	845
Clark, N. A.,	The rate of formation and the yield of yeast in wort, . . .	42
Cook, S. V.,	See Brown, Cook and Warner . . .	477
Cooke, Martha C.,	See Tower and Cooke, . . .	728
Craig, W. A.,	See Hicks and Craig, . . .	563
Dhar, N. R.,	See Ganguly and Dhar . . .	701, 836
Elder, R. B.,	Note on the measurement of surface tension, . . .	558
Ferguson, J. B.,	The melting interval of certain under-cooled liquids with a note on the use of liquid air as a refrigerant . . .	549
Ferguson, J. B.,	The melting and freezing point of sodium chloride, . . .	626
Ganguly, P. B. and N. R. Dhar,	Coagulation of manganese dioxide sol by different electrolytes, . . .	701
Ganguly, P. B. and N. R. Dhar,	Adsorption of ions by freshly-precipitated manganese dioxide . . .	836
Getman, F. H.,	A spectrophotometric study of solutions of cupric chloride, . . .	217

- Getman, F. H., A study of the absorption of light by solutions of cupric lithium chloride, . . . 377
- Gordon, Neil E. and E. E. Reid, The solubility of liquids in liquids . . . 773
- Gortner, R. A., See Sharp and Gortner, . . . 101
- Henke, C. O., See Brown and Henke, . . . 161, 272, 715
- Henke, C. O. and O. W. Brown, Catalytic preparation of azobenzene and aniline. I, II, . . . 324, 631
- Hicks, J. F. G. with W. A. Craig, Relations in fused salt media. II, . . . 563
- Holmes, E. O., Jr. and W. A. Patrick, The action of ultra-violet light on gels, 25
- Huggins, M. L., Electronic structures of atoms . . . 601
- Huggins, M. L., Boron hydrides, . . . 833
- Hughes, W. E., Studies on the electro-deposition of lead from Mathers' perchlorate bath. I, . . . 316
- Joshi, S. S., See Sanyal and Joshi, . . . 481
- Kenrick, F. B., The scattering of light: note on Wolski's paper on optically empty liquids. II, 72
- Lehrman, S., See Martin and Lehrman, . . . 75
- Lenher, V., G. B. L. Smith and G. G. Town, The vapor pressure of selenium oxychloride, 156
- Martin, W. H., The relation between light-absorption and light-scattering for liquids, . . . 471
- Martin, W. H. and S. Lehrman, The scattering of light by dust-free liquids, 75
- Miller, L. B., See Pearce and Miller, . . . 1
- Milligan, L. H., The mechanism of the dehydration of crystalline aluminum hydroxide and of the adsorption of water by the resulting alumina, . . . 247
- Neuhausen, B. S., The solubility of gases in liquids, . . . 553
- Paddon, W. W., The effect of light on fibres dyed with a mixture of chrysaniline and fuchsine, 288
- Paddon, W. W., Dyeing of deaminated wool, . . . 384
- Paddon, W. W., The mordanting of wool with potash alum, 790
- Patrick, W. A., See Holmes and Patrick, . . . 25
- Pearce, J. N. and L. B. Miller, Some colloidal properties of pleistocene clays and their bearing on the chemical theory of the formation of gumbotil, . . . 1
- Rabinovich, A. T., On the conductivity of the latent image, 577
- Reid, E. E., See Gordon and Reid, . . . 773
- Reitstötter, Josef, See Westgren and Reitstötter, . . . 537
- Robinson, W. O., The absorption of water by soil colloids, 647
- Sanyal, R. P. and S. S. Joshi, The formation of a water-in-oil type emulsion by the concentration of the oil phase, 481

- Sharp, P. F. and R. A. Gortner,  
 Physico-chemical studies of strong and weak  
 flours, . . . . . 101
- Smith, G. B. L.,  
 See Lenher, Smith and Town, . . . . . 156
- Smith, H. W.,  
 The nature of secondary valence. V, VI, 256, 349
- Thompson, J. G.,  
 The preliminary study of zirkite ore, . . . . 812
- Tower, O. F. and Martha C. Cooke,  
 On the preparation of colloidal solutions of  
 nickel and cobalt hydroxides and some  
 other compounds of these metals . . . . 728
- Town, G. G.,  
 See Lenher, Smith and Town, . . . . . 156
- Warner, J. C.,  
 See Brown, Cook and Warner, . . . . . 477
- Weiser, H. B.,  
 Hydrous oxides. III, IV, . . . . . 401, 654
- Westgren, Arne, and Josef Reitstötter,  
 On the coagulation of colloids, . . . . . 537
- Wismer, K. L.,  
 The pressure-volume relation of superheated  
 liquids, . . . . . 301
- Witt, J. C.,  
 The oxidation of oxalic acid in the absence of  
 other acids, . . . . . 435
- Witzemann, E. J.,  
 The transition from crystalloid to colloid  
 properties within homologous series, . . . 201

## NAME INDEX

### *To New Books*

Bennett, H. G.,	Animal Proteins, . . . . .	295
Bingham, Eugene C.,	Fluidity and Plasticity, . . . . .	794
Burton, E. F.,	The Physical Properties of Colloidal Solutions, . . . . .	496
Chamot, E. M.,	Elementary Chemical Microscopy, . . . . .	400
Doelter, C.,	Handbuch der Mineralchemie, Vol. 2, Part III, . . . . .	499
Döring, Th.,	Analytische Chemie, . . . . .	200
Fischer, M. H.,	Soaps and Proteins, . . . . .	299
Foerster, Fritz,	Elektrochemie wässriger Lösungen, . . . . .	493
Fries, Amos A. and C. J. West,	Chemical Warfare, . . . . .	89
Gibbs, J. Willard,	L'équilibre des substances hétérogènes, . . . . .	700
Hackh, I. W. D.,	Chemical Reactions and Their Equations, . . . . .	700
Harrow, Benjamin,	Contemporary Science, . . . . .	91
Hatschek, Emil,	An Introduction to the Physics and Chemistry of Colloids, . . . . .	600
Hatschek, Emil,	Laboratory Manual of Elementary Colloid Chemistry, . . . . .	696
Houben, J.,	Die Methoden der organischen Chemie, . . . . .	198
Howe, J. L.,	Inorganic Chemistry for Schools and Colleges, . . . . .	494
Kaye, G. W. C. and T. H. Laby,	Tables of Physical and Chemical Constants, . . . . .	498
Lehmann, O.,	Flüssige Kristalle und ihr scheinbares Leben, . . . . .	300
Loeb, Jacques,	Proteins and the Theory of Colloidal Behavior, . . . . .	687
Loring, F. H.,	Atomic Theories, . . . . .	487
Lowy, Alexander and T. B. Downey,	Study Questions in Elementary Organic Chemistry, . . . . .	899
Luckiesh, M.,	Visual Illusions and Their Applications, . . . . .	699
McCoy, H. N. and Ethel M. Terry,	An Introduction to General Chemistry, . . . . .	100
Mellor, J. W.,	A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. I, II, . . . . .	591, 693
Mercer, J. E.,	Alchemy, its Science and Romance, . . . . .	495
Mie, Gustav,	La théorie einsteinienne de la gravitation, . . . . .	900
Mills, John,	Within the Atom, . . . . .	490
Norris, J. F.,	A Textbook of Inorganic Chemistry for Colleges, . . . . .	94
Noyes, A. A. and M. S. Sherrill,	An Advanced Course of Instruction in Chemical Principles, . . . . .	895

*Name Index*

. 905

Noyes, W. A.,	Organic Chemistry for the Laboratory, . . .	599
Pauli, Wolfgang,	Colloid Chemistry of the Proteins, Part I,	597
Potts, H. E.,	Patents and Chemical Research, . . .	497
Pring, J. N.,	The Electric Furnace, . . .	393
Raman, C. V.,	Molecular Diffraction of Light, . . .	897
Reeve, F. C.,	Elementary Qualitative Analysis of the Metals and Acid Radicals, . . .	391
Richardson, O. W.,	The Emission of Electricity from Hot Bodies, . . .	394
Rickard, T. A.,	Concentration by Flotation, . . .	98
Rougier, Louis,	Philosophy and the New Physics, . . .	798
Russell, E. J.,	Soil Conditions and Plant Growth, . . .	292
Sabin, A. H.,	Red-Lead and How to Use It in Paint, . . .	392
Silberstein, Ludwik,	The Theory of General Relativity and Gravi- tation, . . .	697
Sneed, M. C.,	Qualitative Chemical Analysis, . . .	391
Snell, F. D.,	Colorimetric Analysis, . . .	499
Stewart, A. W.,	Some Physico-Chemical Themes, . . .	594
Taggart, Arthur F.,	A Manual of Flotation Processes, . . .	191
Tammann, Gustav,	Lehrbuch der Metallographie, . . .	197
Trivelli, A. P. H. and S. E. Sheppard,	The Silver Bromide Grain of Photographic Emulsions, . . .	390
Whitmore, F. C.,	Organic Mercury Compounds, . . .	96

## SUBJECT INDEX

*Exclusive of New Books*

Absence of other acids, the oxidation of oxalic acid in the, . . . . .	435
Absorption of light by solutions of cupric lithium chloride, a study of the, . . . . .	377
Absorption of water by soil colloids, the, . . . . .	647
Acid, oxalic, the oxidation of, in the absence of other acids, . . . . .	435
Acids, higher fatty, the water-proofing efficiency of some bi- and trivalent salts of, and their adsorption by the fibres of paper, . . . . .	61
Acids, other, the oxidation of oxalic acid in the absence of, . . . . .	435
Action, catalytic, of copper, . . . . .	715
Action, nerve and muscle, the rôle of hydrogen- and hydroxyl-ion diffusion in, . . . . .	639
Action of ultra-violet light on gels, the, . . . . .	25
Adsorption by the fibres of paper, the water-proofing efficiency of some bi- and trivalent salts of higher fatty acids and their, . . . . .	61
Adsorption of ions by freshly precipitated manganese dioxide, . . . . .	836
Adsorption of water, the mechanism of the dehydration of crystalline aluminum hydroxide and of the, by the resulting alumina, . . . . .	247
Air, liquid, as a refrigerant, note on the use of, . . . . .	549
Alum, potash, the mordanting of wool with, . . . . .	790
Alumina, resulting, the mechanism of the dehydration of crystalline aluminum hydroxide and the adsorption of water by the, . . . . .	247
Aluminum hydroxide, crystalline, the mechanism of the dehydration of, and of the adsorption of water by the resulting alumina, . . . . .	247
Ammonia and sulfur dioxide, the vapor pressure of, . . . . .	258
Aniline and azobenzene, catalytic preparation of, . . . . .	324, 631
Aniline, catalytic preparation of, . . . . .	161, 272, 324, 631
Apparent density, effect of grinding upon the, of lead oxides, . . . . .	477
Atoms, electronic structures of, . . . . .	601
Azobenzene and aniline, catalytic preparation of, . . . . .	324, 631
Bath, Mathers' perchlorate, studies on the electro-deposition of lead from, . . . . .	301
Bearing, some colloidal properties of pleistocene clays and their, on the chemical theory of the formation of gumbotil, . . . . .	1
Bi- and trivalent salts of higher fatty acids, the water-proofing efficiency of some, and their adsorption by the fibres of paper, . . . . .	61
Boiling points of ammonia, sulfur dioxide and nitrous oxide, . . . . .	876
Boron hydrides, . . . . .	833
Catalytic action of copper, . . . . .	715
Catalytic preparation of aniline, . . . . .	161, 272, 324, 631
Catalytic preparation of azobenzene and aniline, . . . . .	324, 631
Certain under-cooled liquids, the melting interval of, with a note on the use of liquid air as a refrigerant, . . . . .	549
Chemical theory of the formation of gumbotil, some colloidal properties of pleistocene clays and their bearing on the, . . . . .	1
Chemistry, physical, of dyeing, the, . . . . .	845
Chloride, cupric, a spectrophotometric study of solutions of, . . . . .	217

*Subject Index*

907

Chloride, cupric lithium, a study of the absorption of light by solutions of,	377
Chloride, sodium, the melting and freezing point of,	626
Chrysaniline and fuchsine, a mixture of, the effect of light on fibres dyed with,	288
Clays, pleistocene, some colloidal properties of, and their bearing on the chemical theory of the formation of gumbotil,	1
Coagulation of colloids, on the,	537
Coagulation of manganese dioxide sol by different electrolytes,	701
Cobalt and nickel hydroxides, on the preparation of colloidal solutions of, and some other compounds of these metals,	728
Colloid properties with homologous series, the transition from crystalloid to,	201
Colloidal properties of pleistocene clays and their bearing on the chemical theory of the formation of gumbotil, some,	1
Colloidal solutions of nickel and cobalt hydroxides and some other compounds of these metals, on the preparation of,	728
Colloids, coagulation of, on the,	537
Colloids, emulsion, the properties of the, hydrogen-ion concentration and,	801
Colloids, soil, the absorption of water by,	647
Compounds of these metals, on the preparation of colloidal solutions of nickel and cobalt hydroxides and some other,	728
Concentration, hydrogen-ion, and the properties of the emulsion colloids,	801
Concentration of the oil phase, the formation of a water-in-oil type emulsion by the,	481
Conductivity of the latent image, on the,	577
Copper, catalytic action of,	715
Crystalline aluminum hydroxide, the mechanism of the dehydration of, and of the adsorption of water by the resulting alumina,	247
Crystalloid to colloid properties within homologous series, the transition from,	201
Cupric chloride, a spectrophotometric study of solutions of,	217
Cupric lithium chloride, a study of the absorption of light by solutions of,	377
Deaminated wool, dyeing of,	384
Dehydration of crystalline aluminum hydroxide, the mechanism of the, and of the adsorption of water by the resulting alumina,	247
Density, apparent, of lead oxides, effect of grinding upon the,	477
Different electrolytes, coagulation of manganese dioxide sol by,	701
Diffusion, the rôle of hydrogen- and hydroxyl-ion, in nerve and muscle action,	639
Dioxide, manganese, freshly-precipitated, adsorption of ions by,	836
Dioxide sol, manganese, coagulation of, by different electrolytes,	701
Dioxide, sulfur and ammonia, the vapor pressure of,	258
Dioxide, sulfur, the boiling points of ammonia, nitrous oxide and,	876
Dust-free liquids, the scattering of light by,	75
Dyed, fibres, with a mixture of chrysaniline and fuchsine, the effect of light on,	288
Dyeing of deaminated wool,	384
Dyeing, the physical chemistry of,	845
Effect of grinding upon the apparent density of lead oxides,	477



Effect of light on fibres dyed with a mixture of chrysaniline and fuchsine, the	288
Efficiency, the water-proofing, of some bi- and trivalent salts of higher fatty acids and their adsorption by the fibres of paper,	61
Electro-deposition of lead from Mathers' perchlorate bath,	316
Electrolytes, different, coagulation of manganese dioxide sol by,	701
Electrolytic production of sodium perborate,	137
Electronic structures of atoms,	601
Empty liquids, optically, note on Wolski's paper on,	72
Emulsion colloids, the properties of the, hydrogen-ion concentration and,	801
Emulsion, water-in-oil type, the formation of a, by the concentration of the oil phase,	481
Fatty acids, higher, the water-proofing efficiency of some bi- and trivalent salts of, and their adsorption by the fibres of paper,	61
Fibres dyed with a mixture of chrysaniline and fuchsine, the effect of light on,	288
Fibres of paper, the water-proofing efficiency of some bi- and trivalent salts of higher fatty acids and their adsorption by the,	61
Flours, strong and weak, physico-chemical studies of,	101
Formation of a water-in-oil emulsion by the concentration of the oil phase,	481
Formation of gumbotil, chemical theory of the, some colloidal properties of pleistocene clays and their bearing on the,	1
Formation, the rate of, and the yield of yeast in wort,	42
Freezing and melting point of sodium chloride,	626
Freshly-precipitated manganese dioxide, adsorption of ions by,	836
Fuchsine, chrysaniline and, the effect of light on fibres dyed with a mixture of,	288
Fused salt media, relations in,	563
Gases in liquids, the solubility of,	553
Gels, the action of ultra-violet light on,	25
Grinding, effect of, upon the apparent density of lead oxides,	477
Gumbotil, chemical theory of the formation of, some colloidal properties of pleistocene clays and their bearing on the,	1
Higher fatty acids, the water-proofing efficiency of some bi- and trivalent salts of, and their adsorption by the fibres of paper,	61
Homologous series, the transition from crystalloid to colloid properties within,	201
Hydrides, boron,	833
Hydrogen- and hydroxyl-ion diffusion in nerve and muscle action, the rôle of,	639
Hydrogen-ion concentration and the properties of the emulsion colloids,	801
Hydrous oxides,	401, 654
Hydroxide, crystalline aluminum, the mechanism of the dehydration of, and of the adsorption of water by the resulting alumina,	247
Hydroxides, cobalt and nickel, on the preparation of colloidal solutions of, and some other compounds of these metals,	728
Hydroxyl- and hydrogen-ion diffusion in nerve and muscle action, the rôle of,	639
Image, latent, on the conductivity of the,	577

Interval, the melting, of certain under-cooled liquids with a note on the use of liquid air as a refrigerant, . . . . .	549
Ions, adsorption of, by freshly precipitated manganese dioxide, . . . . .	836
Ion, hydrogen, concentration, and the properties of the emulsion colloids, . . . . .	801
Latent image, conductivity of, on the, . . . . .	577
Lead oxides, effect of grinding upon the apparent density of, . . . . .	477
Lead, studies on the electro-deposition of, from Mathers' perchlorate bath, . . . . .	316
Light-absorption and light-scattering for liquids, the relation between, . . . . .	471
Light adsorption of, a study of the, by solutions of cupric lithium chloride, . . . . .	377
Light-scattering and light absorption for liquids, the relation between, . . . . .	471
Light, the effect of, on fibres dyed with a mixture of chrysaniline and fuchsine, . . . . .	288
Light, the scattering of, . . . . .	72
Light, the scattering of, by dust-free liquids, . . . . .	75
Light, ultra-violet, on gels, the action of, . . . . .	26
Liquid air as a refrigerant, note on the use of, . . . . .	549
Liquids, certain under-cooled, the melting interval of, with a note on the use of liquid air as a refrigerant, . . . . .	549
Liquids, dust-free, the scattering of light by, . . . . .	75
Liquids in liquids, the solubility of, . . . . .	773
Liquids, light-absorption and light-scattering for, the relation between, . . . . .	471
Liquids, optically empty, note on Wolski's paper on, . . . . .	72
Liquids, the pressure-volume relation of superheated, . . . . .	301
Liquids, the solubility of gases in, . . . . .	553
Lithium chloride, cupric, a study of the absorption of light by solutions of, . . . . .	377
Manganese dioxide, freshly precipitated, adsorption of ions by, . . . . .	836
Manganese dioxide sol, coagulation of, by different electrolytes, . . . . .	701
Mathers' perchlorate bath, studies on the electro-deposition of lead from, . . . . .	316
Measurement of surface tension, note on the, . . . . .	558
Mechanism of the dehydration of crystalline aluminum hydroxide and of the adsorption of water by the resulting alumina, the, . . . . .	247
Media, fused salt, relations in, . . . . .	563
Melting and freezing point of sodium chloride, the, . . . . .	626
Melting interval of certain under-cooled liquids with a note on the use of liquid air as a refrigerant, . . . . .	549
Metals, some other compounds of these, nickel and cobalt hydroxides and, . . . . .	728
Mixture of chrysaniline and fuchsine, the effect of light on fibres dyed with a, . . . . .	288
Mordanting of wool with potash alum, . . . . .	790
Mordants, . . . . .	447, 501, 736
Muscle and nerve action, the rôle of hydrogen- and hydroxyl-ion diffusion in, . . . . .	639
Nature of secondary valence, . . . . .	256, 349
Nerve and muscle action, the rôle of hydrogen- and hydroxyl-ion diffusion in, . . . . .	639
Nickel and cobalt hydroxides, on the preparation of colloidal solutions of, and some other compounds of these metals, . . . . .	728
Nitrous oxide, ammonia and sulfur dioxide, the boiling points of, . . . . .	876
Note on the measurement of surface tension, . . . . .	558
Note on the use of liquid air as a refrigerant, . . . . .	549

Note on Wolski's paper on optically empty liquids, . . . . .	72
Oil phase, concentration of the, the formation of a water-in-oil type emulsion by the, . . . . .	481
Optically empty liquids, note on Wolski's paper on, . . . . .	72
Ore, zirkite, the preliminary study of, . . . . .	812
Oxalic acid in the absence of other acids, the oxidation of, . . . . .	435
Oxidation of oxalic acid in the absence of other acids, the, . . . . .	435
Oxide, nitrous, the boiling points of ammonia, sulfur dioxide, and, . . . . .	876
Oxides, hydrous, . . . . .	401, 654
Oxides, lead, effect of grinding upon the apparent density of, . . . . .	477
Oxychloride, selenium, the vapor pressure of, . . . . .	156
Paper, fibres of, the water-proofing efficiency of some bi- and trivalent salts of higher fatty acids and their adsorption by the, . . . . .	61
Paper, Wolski's, on optically empty liquids, note on, . . . . .	72
Perborate, sodium, electrolytic production of, . . . . .	137
Perchlorate bath, Mathera', studies on the electro-deposition of lead from, . . . . .	316
Phase, oil, concentration of the, the formation of a water-in-oil type emulsion, by the, . . . . .	481
Physical chemistry of dyeing, the, . . . . .	845
Physico-chemical studies of strong and weak flours, . . . . .	101
Pleistocene clays, some colloidal properties of, and their bearing on the chemical theory of the formation of gumbotil, . . . . .	1
Point, the melting and freezing, of sodium chloride, . . . . .	628
Points, boiling, of ammonia, sulfur dioxide and nitrous oxide, the, . . . . .	876
Potash alum, the mordanting of wool with, . . . . .	790
Preliminary study of zirkite ore, the, . . . . .	812
Preparation, catalytic, of aniline, . . . . .	161, 272, 324, 631
Preparation, catalytic, of azobenzene and aniline, . . . . .	324, 631
Preparation of colloidal solutions of nickel and cobalt hydroxides and some other compounds of these metals, on the, . . . . .	728
Pressure, the vapor, of selenium oxychloride, . . . . .	156
Pressure, vapor, of sulfur dioxide and ammonia, . . . . .	358
Pressure-volume relation of superheated liquids, . . . . .	301
Production, electrolytic, of sodium perborate, . . . . .	137
Properties, crystalloid to colloid, the transition from, within homologous series, . . . . .	201
Properties of the emulsion colloids, hydrogen-ion concentration and, . . . . .	801
Properties, some colloidal, of pleistocene clays and their bearing on the chemical theory of the formation of gumbotil, . . . . .	1
Rate of formation and the yield of yeast in wort, the, . . . . .	42
Refrigerant, liquid air as a, note on the use of, . . . . .	549
Relation between light-absorption and light-scattering for liquids, . . . . .	471
Relation, the pressure-volume, of superheated liquids, . . . . .	301
Relations in fused salt media, . . . . .	563
Resulting alumina, the mechanism of the dehydration of crystalline aluminum hydroxide and of the adsorption of water by the, . . . . .	247
Rôle of hydrogen- and hydroxyl-ion diffusion, in nerve and muscle action, . . . . .	630
Salt media, fused, relations in, . . . . .	563

Salts, bi- and trivalent, of higher fatty acids, the water-proofing efficiency of some, . . . . .	61
Scattering of light by dust-free liquids, . . . . .	75
Scattering of light, . . . . .	72
Secondary valence, the nature of the, . . . . .	256, 439
Selenium oxychloride, the vapor pressure of, . . . . .	156
Series, homologous, the transition from crystalloid to colloid properties within, . . . . .	201
Sodium chloride, the melting and freezing point of, . . . . .	628
Sodium perborate, electrolytic production of, . . . . .	137
Soil colloids, the absorption of water by, . . . . .	647
Sol, manganese dioxide, coagulation of, by different electrolytes, . . . . .	701
Solubility of gases in liquids, . . . . .	553
Solubility of liquids in liquids, . . . . .	773
Solutions, colloidal, of nickel and cobalt hydroxides and some other compounds of these metals, on the preparation of, . . . . .	728
Solutions of cupric chloride, a spectrophotometric study of, . . . . .	217
Solutions of cupric lithium chloride, a study of the absorption of light by, . . . . .	377
Spectrophotometric study of solutions of cupric chloride, a, . . . . .	217
Strong and weak flours, physico-chemical studies of, . . . . .	101
Structures of atoms, electronic, . . . . .	601
Studies of the electro-deposition of lead from Mathers' perchlorate bath, . . . . .	318
Studies, physico-chemical, of strong and weak flours, . . . . .	101
Study, a spectrophotometric, of solutions of cupric chloride, . . . . .	217
Study of the absorption of light by solutions of cupric lithium chloride, a, . . . . .	377
Study of zirkite ore, the preliminary, . . . . .	812
Sulfur dioxide and ammonia, the vapor pressure of, . . . . .	358
Sulfur dioxide, nitrous oxide and ammonia, the boiling points of, . . . . .	876
Superheated liquids, the pressure-volume relation of, . . . . .	301
Surface tension, note on the measurement of, . . . . .	558
Tension, surface, note on the measurement of, . . . . .	558
Theory, chemical, of the formation of gumbotil, some colloidal properties of pleistocene clays and their bearing on the, . . . . .	1
Transition from crystalloid to colloid properties within homologous series, . . . . .	201
Trivalent and bivalent salts of higher fatty acids, the water-proofing efficiency of some, and their adsorption by the fibres of paper, . . . . .	61
Type, emulsion, water-in-oil, the formation of a, by the concentration of the oil phase, . . . . .	481
Ultra-violet light on gels, the action of, . . . . .	25
Under-cooled liquids, certain, the melting interval of, with a note on the use of liquid air as a refrigerant, . . . . .	549
Use of liquid air as a refrigerant, note on the, . . . . .	549
Valence, secondary, the nature of, . . . . .	256, 349
Vapor pressure of selenium oxychloride, . . . . .	156
Vapor pressure of sulfur dioxide and ammonia, . . . . .	358
Water, adsorption of, the mechanism of the dehydration of crystalline aluminum hydroxide and of the, by the resulting alumina, . . . . .	247

Water, the absorption of, by soil colloids, . . . . .	647
Water-in-oil type emulsion, the formation of a, by the concentration of the oil phase, . . . . .	481
Water-proofing efficiency of some bi- and trivalent salts of higher fatty acids and their adsorption by the fibres of paper, . . . . .	61
Weak and strong flours, physico-chemical studies of, . . . . .	101
Wolski's paper on optically empty liquids, note on, . . . . .	72
Wool, dyeing of deaminated, . . . . .	384
Wool, the mordanting of, with potash alum, . . . . .	790
Wort, the rate of formation and the yield of yeast in, . . . . .	42
Yeast, the rate of formation and the yield of, in wort, . . . . .	42
Yield of yeast in wort, the rate of formation and the, . . . . .	42
Zirkite ore, the preliminary study of, . . . . .	812

