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PHYSICO-CHEMICAL STUDIES ON PROTEINS

The Effect of Salts on the Casein-Sodium Hydroxide and Paracasein-Sodium Hydroxide Equilibria*

ALLEN D. ROBINSON, ROSS AIKEN GORTNER AND LEROY S. PALMER**

The nature of the reaction of acids and bases with proteins has been studied by numerous investigators. Conflicting conclusions have been drawn from their work concerning the relative importance of colloidal and chemical forces in these reactions. Gortner[1] sums up the present attitude toward the problem in a statement that there are three schools of thought: One holds to the view that acid- and base-binding by proteins may be explained in terms of strictly chemical forces, another believes that surface energies are involved and a third group maintains that both colloidal and chemical forces play a part. Hoffman and Gortner[2] favor this view. Their work indicates a chemical type of combination between hydrogen ion concentrations of pH 2.5 and pH 10.5. Above or below the limits of this range their evidence indicates an adsorption type of combination.

Adequate reviews of the work in this field have been given by Robertson,[3] Loeb,[4] Hoffman and Gortner,[2] Cohn,[5] and Gortner.[1] More recent contributions are those of Bancroft and Barnett.[6]

Our attention is called at the outset to the number of different methods which have been used to measure the extent of acid- or base-binding by proteins. It is obvious that no single method can of itself tell whether such binding is chemical or colloidal in nature. Such an inference can be made only after giving consideration to the amounts bound under the different sets of conditions. The relatively large number of methods employed over a short span of years is in itself evidence that the problem is far from a complete solution.

Because it was deemed impracticable to separate a protein "salt" from solution in sufficient purity for analysis, as was attempted by Van Slyke and Hart[7] with "calcium caseinate" and Spiro and Pemsel[8] with "sodium caseinate," due to alteration in the "salt" during coagulation, investigators have had recourse to indirect methods whereby a measurement of the amount of acid or alkali bound by a protein could be effected. The protein is treated with acid or base in the quantities and under the conditions determined by the experimenter; and the concentration of acid or alkali remaining "unbound" is determined by one of several methods. F. A. Hoffman[9] measured the catalytic

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effect of the unbound ions on hydrolysis reactions, Sjöqvist[10] determined the change in electrical conductivity, while Bugarszky and Liebermann[11] studied the freezing point depression and made potentiometric measurements of the unbound acid or alkali.

The potentiometric method has been deemed the most reliable and has been employed by most subsequent workers. In such a determination it has been generally assumed that the magnitude of the measurement is in no way influenced by the presence of the protein "salt." In other words, the same amount of unbound acid or base in the same volume of aqueous solution should give exactly the same potentiometric reading. This assumption is of doubtful accuracy. A really satisfactory measurement would be one that would not be interfered with by other substances in solution, or would be one to which corrections could be applied for the effect of the other substances which are present.

It has been definitely shown that the alkali bound by protein increases with rising pH and that the acid bound increases with decreasing pH. Gortner[1] points out that this dependence on pH of the amount of reaction occurring suggests that forces of adsorption are involved in the reaction. But Robertson[3] states that this is no proof that proteins do not obey the law of constant combining proportions, and points out in defense of his claim that the same change occurs among complex and double salts and the salts of polybasic acids or polyacid bases in the domain of inorganic chemistry. We are asked to visualize a molecule with many acid groups, only part of which ionize in lower concentrations of alkali, but more of which ionize in higher concentrations. Accordingly we have a greater amount of alkali-binding in these higher concentrations because there are more acid groups in a reactive state. A similar explanation is offered for the effect of a lowered pH on the acid-binding of proteins. Loeb[4] emphasizes that at the same pH a protein will bind equivalent amounts of the different acids or alkalis. One might expect that at an extremely high or low pH, where all the acid or basic groups are ionized, the amount of alkali or acid bound would approach a constant value. Such is not the case. If we are to accept the explanations of Robertson and Loeb, we must consider each protein molecule as having an indefinite number of potential acidic or basic groups differing almost insensibly from each other in their dissociation constants.

Attempts have been made to correlate the binding with the chemical composition of the protein. Greenberg and Schmidt,[12] using Hitchcock's[13] data, have shown that the amount of acid bound by gelatin is essentially equal to the sum of the free amino nitrogen plus the amino group of arginine. Cohn and Berggren[14] calculate that the casein molecule contains from nineteen to twenty-eight free acid groups, and that casein combines with no more base than is required to neutralize them. Cohn[5] points out that the more diamino acids a protein contains the more acid it will bind, whereas the more dibasic acids it contains the more alkali it will bind. All this is suggestive of chemical combination, but it does not provide definite proof that adsorption does not play a rôle. Furthermore these investigators worked within a relatively narrow range of pH. With alterations in the systems decided changes in the amounts of acid or base bound might be revealed.

Evidence in favor of an adsorption reaction is seen in the relation between the amounts of alkali or acid bound as related to the original concentration. When graphed such data yield what appears to be an adsorption curve. This has been shown by Tolman and Stearn[15] using fibrin and hydrochloric acid, Herzog and Adler[16] using hide powder, Procter[17] using gelatin, Tolman and Bracewell[18] using fibrin and alkalies, and Izaguirre[19] using the data of Lloyd and Mays[20] on hydrochloric acid and gelatin. Weber[21] did not find this to be true for fibrin and acids.

Van Slyke and Hart[7] and Van Slyke and Van Slyke[22] pointed out that casein binds more acid at lower temperatures than at higher ones. That is, the binding has a negative temperature coefficient. This is not typical of chemical reactions, but is typical of adsorption. The data of Fischer and Hooker[23] with casein reveal the same fact. Weber did not find the reaction between fibrin and hydrochloric acid to have a negative temperature coefficient. Hoffman and Gortner[2] found a marked negative temperature coefficient of the acid- or alkali-binding at the higher concentrations of acid and alkali than are represented by pH 2.5 and pH 10.5. Within this range the amount of binding was influenced by the chemical composition of the protein; outside the range all proteins showed the same binding capacity, irrespective of their chemical composition. Indeed, when the original concentration was 0.500 normal "there is more alkali bound . . . than can be accounted for by chemical combination assuming that there is an available carboxyl group for each nitrogen atom, an assumption far in excess of possibility." This would mean that within the range pH 2.5 – pH 10.5 the acid and alkali added are neutralized by the amino and carboxyl groups. At pH 2.5 or 10.5 all of these have reacted, and any further reaction must be due to adsorption on the protein micelles. Thomas and Mayer[24] found that if acid were added to gelatin the interferometer readings increased in a straight line ratio until a "stoichiometric" point was reached at which the rate of increase became larger but remained a straight line function. This might be interpreted as confirmatory evidence for the theory of Hoffman and Gortner.

Bancroft and Barnett[6] have made phase rule studies of the proteins. Known amounts of gaseous ammonia or hydrogen chloride were added to dry proteins and the partial pressure of the gas at equilibrium was measured. The pressure-concentration curves for these gases with solid acids or bases showed clearly whether or not definite chemical compounds were formed. A stoichiometric reaction was shown by the appearance of a flat in the curve during which time the solid acid or base was reacting with the gas to form a chemical compound. When applied to proteins it appeared that casein, arachin, zein, fibrin and gliadin adsorb ammonia readily with no evidence of the formation of any chemical compound. Casein, arachin, fibrin, gliadin and edestin did form definite compounds with hydrogen chloride. Zein did not form a chemical compound with hydrogen chloride. The graphs for those proteins which did form definite chemical compounds indicate that they subsequently adsorb more gas than was necessary for the formation of initial chemical compounds.

The Problem

A new method of attack in the problem of acid and alkali binding is suggested by the work of Kolthoff and Bosch[25] on the influence of neutral salts on acid-base equilibria. By determining potentiometrically the pH of successive dilutions of equimolar mixtures of a weak acid and one of its salts they were able to calculate the dissociation constant of the acid, using the Debye-Hückel equation. On the addition of neutral salts to one of the dilutions, changes in pH were noted which were shown to be due to an increase in the activity coefficient of the undissociated acid. The application of this method to protein study is based on the hypothesis that a protein is a weak acid. However the calculations of Kolthoff and Bosch involved the degree of basicity of the acid, its molecular weight and its average ionic size. None of these values are known with any degree of certainty for proteins. So the thermodynamic study as applied to weak acids presents difficulties when applied to proteins. It should be possible however to make similar investigations using a protein as a weak acid, and to judge from the observations recorded whether it behaves as a true electrolyte, or whether it reacts in a manner that can be explained only on the assumption that colloidal behavior is involved.

Both casein and paracasein were chosen for this investigation since we desired to ascertain whether a study of this kind would reveal any deep-seated difference in the chemical nature of the two proteins. Doubts that there is any such difference had already been expressed by Richardson and Palmer.[26]

Experimental

Reagents.—Paracasein was prepared from skimmed milk according to the method of Van Slyke and Baker[27] and Van Slyke[28] for casein. Previous to the addition of acid the calcium was precipitated by the addition[29] of 0.5 cc. saturated potassium oxalate for every 100 cc. of milk and the precipitate removed by supercentrifuging. The milk was heated to 40°C. and rennet was added. The milk was kept at this temperature for a length of time determined by the time required for the formation of a firm curd when rennet in the same concentration was added to some of the milk from which the calcium had not been removed. Precipitation with acid and solution in alkali for purification then followed the procedure of Van Slyke and Baker.

The protein so prepared analyzed as follows: 5.88% moisture, 0.072% ash, 14.80% nitrogen, 0.863% phosphorus, and 0.621% sulfur. The composition on a moisture-free basis was: ash 0.076%, nitrogen 15.73%, phosphorus 0.91%, sulfur 0.66%. This agrees well with analyses of casein and paracasein reported by Bosworth,[30] Geake,[31] Hammarsten,[32] Lehman and Hempel,[33] and Van Slyke and Bosworth.[34]

Other protein preparations used included one of paracasein used by Richardson and Palmer[26] with an ash content of 0.04%. A sample of casein used by

Hoffman and Gortner[2] was also available. It had an ash content of 0.34%, most of which was porcelain dust derived from grinding the material in a porcelain ball mill. A sample of isoelectric gelatin, having an ash content of 0.13%, was also used.

Pure alanine was used for comparative purposes. The neutral inorganic salts were of "analytical" grade and were ground to a powder, dried for five or six hours at 100°C. and kept in a desiccator. Their aqueous solutions were tested for neutrality with indicators. Only the potassium iodide was not as pure as desired, apparently containing traces of potassium carbonate. The sodium hydroxide solutions used were prepared carbonate-free. Freshly redistilled water collected so as to be free from carbon dioxide was always used.

Apparatus and Methods.—The amount of alkali bound by the protein was determined potentiometrically and is expressed as gram equivalents bound per gram of protein. Measurements were made with a L. and N. Type K potentiometer, using a high resistance galvanometer, readings being made to a tenth of a millivolt. Bailey electrodes and a normal calomel half-cell were used. Appropriate corrections were made for any determinations which were run at temperatures other than 25.0°. All potentiometric readings were calculated to pH values, taking into account appropriate temperature corrections. The values for K_w were likewise corrected for temperature variations, a value of 0.2828 at 25° being used for the value of the calomel cell. The set-up was tested by the use of sodium hydroxide-succinic acid buffers. A series of these is reproduced in Table II as indicative of what may be expected in a system where only chemical combination is taking place.

The protein was made up in 50 cc. volumes of the required degree of alkalinity and salt concentration. Where large enough concentrations of protein were being used, these were weighed into 100 cc. Erlenmeyer flasks, and 0.1 normal carbonate-free base, aliquots of the salt solution, and conductivity water were added to bring the final volume to 50 cc. When the concentration of protein desired was too small to permit of direct weighing without introducing large errors, a stock solution was made in sodium hydroxide of a suitable concentration and aliquots were taken to be diluted subsequently to the desired volume. Stock salt solutions of 1.0, 0.1, 0.01, and 0.001 normality were prepared. When extremely dilute solutions of protein were required, a volume of 300 cc. was used.

The protein dissolved rather readily in solutions at pH 9.0 or 12.0. Difficulty was experienced in securing solution of the protein at a pH near the neutral point. For this work a stock solution of protein in weak alkali was prepared and shaken in a mechanical shaker for twenty-four hours. The final pH of this solution was less than 7.0. In all experiments where the pH of the system exceeded 7.0, the E.M.F. readings were always made within ten hours after the protein was wetted with alkali. According to Cohn and Berggren[14] no appreciable amount of caseose is split off from casein in that time.

Calculations of the amount of alkali bound were made according to the equations of Cohn and Berggren:[14]

$$\text{pH} + \text{pOH} = \text{Log}\ (1/K_w)$$

$$\frac{(\text{OH}^-)}{(\text{NaOH})} = \gamma$$

$$\text{pOH}^- = \log\ [1/(\text{NaOH})\gamma] = \text{pNaOH} + \text{p}\gamma$$

$$\text{or pNaOH} = \text{pOH} - \text{p}\gamma.$$

and since pNaOH = log 1/(NaOH) the concentration of the uncombined NaOH is readily calculated. The pH was determined from potentiometric measurements. Log $1/K_w$, the solubility product of water was obtained from Clark's[35] tables. Values for pγ were taken from Lewis and Randall,[36] using the average values given for γ for Na^+ and OH^-, and obtaining certain values by interpolation from the plotted curves. A table of such values is reproduced by Gortner.[1] From pNaOH the concentration of free sodium hydroxide can be obtained. This subtracted from the original concentration gives the amount "bound" by the protein present.

Certain assumptions are necessary in employing this method of calculation, and we are employing the same assumptions which were made by Cohn and Berggren,[14] in order that our data may be directly compared with theirs. The values for γ were determined from electromotive force measurements in which the activity of the sodium hydroxide was affected by sodium chloride present. In our investigations protein "salts" were present. We therefore assume* for purposes of calculation (1) that the protein and sodium hydroxide react in stoichiometric proportions, (2) that the so-formed protein salt is completely dissociated, (3) γNa^+ of Na^+ + proteinate$^-$ = γNa^+ of $Na^+ + Cl^-$, (4) therefore, γ proteinate$^-$ = γCl^-, (5) there is no adsorption of Na^+ or of NaOH on the micelles, and no effect of the ionic micelles on the γ of Na^+.

In previous investigations[2,37] it was assumed that the magnitude of the measurement was in no way influenced by the presence of the protein "salt." We now "assume" that the magnitude of its effect is the same as that of the sodium chloride in the concentration in which it was present in the measurements of the value of γ. A comparison of this method of calculation with that of Palmer and Richardson[37] and Hoffman and Gortner[2] using their data shows that the two methods agree closely in the lower ranges of alkali con-concentration, but differ in the higher ranges. At first this difference shows itself in the present calculations giving a slightly *lower* binding capacity figure, but as the alkali concentration is increased still more the lower values are given by the method of calculation used by Hoffman and Gortner and Palmer and Richardson. We cannot draw hard and fast conclusions from these observations save that differences are noted, particularly at higher

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* In order that there may be no misunderstanding it is emphasized that these assumptions are made "for purposes of calculation" and for comparison with Cohn's data. I personally believe that no one of these assumptions is strictly correct. R. A. Gortner.

concentrations of alkali. Opinions may well differ as to which method of calculation is the more nearly correct. Both present obvious inadequacies.

The Effect of pH on the Alkali-binding Capacity of Casein and Paracasein.—It was desired to determine how the amount of alkali bound per gram of paracasein varied with the pH of the equilibrium mixture. Accordingly solutions were prepared in which the concentrations of protein and sodium hydroxide were varied so as to give a series covering a fairly wide range of alkalinity. Measurements and calculations were made as described. The results are recorded in Table I. Data on casein are included for comparison.

Similar determinations were made of the binding of sodium hydroxide by succinic acid. In Table II these results are detailed. The object of these series of measurements was to afford an opportunity to compare the binding by the proteins with the binding by an acid of known constitution, it being known in the latter case that the binding was strictly stoichiometrical.

Two things of significance are noted immediately. In the first place, the amount of alkali bound by succinic acid is essentially a constant. That is, throughout a wide range of hydroxyl ion concentration, succinic acid reacts in the same proportion with sodium hydroxide. This is to be expected as

TABLE I

Comparison of the Alkali-binding Capacity of Casein and Paracasein at Various Degrees of Alkalinity

		Casein*		Paracasein*	
Sodium Hydroxide	Protein	Equilibrium pH	Equivalents of Alkali bound per gm. Protein $\times 10^6$	Equilibrium pH	Equivalents of Alkali bound per gm. Protein $\times 10^6$
Normality	gms. per liter				
0.001	1.0			8.833	99.15
0.006	6.0			9.397	99.44
0.020	10.0	11.230	169.0	11.213	174.68
0.040	20.0	11.411	180.9	11.371	181.89
0.060	30.0	11.487	184.5	11.413	185.8
0.050	20.0	11.863	195.3	11.863	193.0
0.075	30.0	12.003	198.4	11.959	201.4
0.100	40.0	12.083	202.5	12.056	203.4
0.060	20.0	12.118	200.5	12.091	198.6
0.040	10.0	12.125	202.8	12.102	205.1
0.050	10.0	12.289	208.3	12.260	204.5
0.075	20.0	12.335	208.6	12.325	206.0
0.100	.30.0	12.369	210.9	12.356	209.6
0.060	10.0	12.407	212.7	12.393	209.7
0.075	10.0	12.531	227.6	12.503	219.7
0.100	20.0	12.536	230.2	12.544	213.6
0.100	10.0	12.667	253.6	12.669	236.7

* Detns. by A. D. R. (1929).

it is conceded that the reaction is strictly stoichiometrical. The amount of alkali bound by the proteins, however, *increases with increasing alkalinity of solution.* This is characteristic of the behavior of proteins. As pointed out previously it has been explained both on the assumption that colloidal forces are entering into the reaction, and that there is an increase in the number of acid groups available for chemical reaction.

The second fact to be noted in our data is that, under similar conditions of concentration and pH, casein and paracasein are very similar in their base-binding capacity. This is contrary to the generally accepted view. In fact the essential difference between the two proteins has always been stated to be the difference in their base-binding capacity. Yet two different workers,

Table II

The Alkali-binding Capacity of Succinic Acid at Various Degrees of Alkalinity, Temperature 25°

(Series A and Series B determined by different individuals—R.A.G. and A.D.R.—a year apart and using different solutions and different potentiometric equipment)

	Sodium Hydroxide	Succinic Acid per Liter*	Equilibrium pH	Equivalents of Alkali bound per gram of Succinic Acid** $\times 10^5$
	Normality	Grams		
Series A	0.020	1.1804	7.195	169.43
	0.040	2.3608	8.189	169.42
	0.050	2.3608	11.816	170.25
	0.075	3.5412	12.034	164.88
	0.100	4.7216	12.066	173.12
	0.040	1.1804	12.290	170.41
	0.050	1.1804	12.295	173.59
	0.075	2.3608	12.347	172.65
	0.100	3.5412	12.394	172.54
	0.100	2.3608	12.537	172.14
	0.100	1.1804	12.670	172.65
Series B	0.040	2.3608	10.166	168.51
	0.050	2.3608	11.810	167.38
	0.075	3.5412	12.021	166.21
	0.100	4.7216	12.059	173.69
	0.040	1.1804	12.115	175.53
	0.050	1.1804	12.295	173.59
	0.075	2.3608	12.347	172.65
	0.100	3.5412	12.407	173.86
	0.100	2.3608	12.557	183.70

* These quantities of succinic acid were chosen so that the "alkali bound" would be in the same range as that "bound" in the casein-paracasein series.

** Theory 169.43 × 10^{-5}

(R. A. G. and A. D. R.), working a year apart, but working in a parallel manner, secure almost identical values for the two proteins. We shall have occasion to refer to this later.

The Effect of Neutral Salts on the Amount of Alkali bound by Casein and Paracasein.—The main object of this study was to test the effect of the addition of various quantities of neutral salts to the protein sodium hydroxide systems. Measurements were made at four varying ranges on the pH scale, the amounts of protein and base being selected so as to obtain this degree of acidity or alkalinity. The salts used with both proteins were potassium chloride, potassium bromide, and potassium iodide. Some data are reported for the casein—NaOH systems where sodium chloride and lithium chloride were used. Rather unsatisfactory results were obtained with the potassium iodide experiments, due probably to the small amount of potassium carbonate contained in the supposedly pure salt. Therefore where figures on potassium iodide are given, it should be recognized that they are recorded merely for purposes of comparison with the effects of the other salts.

The systems were prepared by diluting a sodium hydroxide-paracasein solution with the proper amount of water and stock solutions of neutral salts so as to bring the final solution to the proper concentration. In this manner values were obtained at about pH 12, pH 9, pH 6, and pH 5.

The data for the salt effect at the highest pH are given in Table III. Data on the effect of dilution of the protein-base system of the same relative concentration as used in the "salt effect" studies are included, it being deemed desirable to have this available for purposes of calculation. Table III includes as well dilution data for a casein-sodium hydroxide system of the same concentration and the effect of potassium chloride and sodium chloride on such a casein system.

Certain features appear outstanding in these data. The effect of the three salts on the paracasein-sodium hydroxide system at this range of pH is practically identical. It is true that potassium iodide seems to exert a slightly different magnitude of effect than the others, but this is due probably to impurities in the salt as pointed out above. There does not appear to be a significant lyotropic series for the anions. Whether any significance should be attached to the fact that when the data are plotted the curves resemble those of the adsorption type, we shall leave until later to decide.

It would appear then that either there are unjustifiable assumptions in the method of calculation which was employed, or else that in some manner the presence of a neutral salt increases the base-combining capacity of a protein. Different neutral salts with a common univalent cation and different monovalent anions exert essentially equal effects in increasing this capacity. At a pH of approximately 12 it becomes noticeable in salt solutions as dilute as 0.0025 normal. Salt solutions weaker than this exert no appreciable

TABLE III

Dilution and Salt Effect Data for Casein- and Paracasein-Sodium Hydroxide Systems at pH 11 to pH 12.5

Salt Normality	Concentration of Protein	Sodium Hydroxide	Paracasein		Casein				
			pH	Equivalents* of Alkali bound per gm. Protein × 10⁵	pH	Equivalents* of Alkali bound per gm. Protein × 10⁵	Temperature	pH	Equivalents** of Alkali bound per gm. Protein × 10⁵
	gm. per liter	Normality					°C.		
None	20	0.100	—	—	—	—	25	12.579	202.2
”	15	0.075	12.407	227.5	12.429	213.0	25	12.465	200.9
”	12	0.060	12.330	218.3	12.351	204.7	25	12.386	193.0
”	10	0.050	12.282	204.5	12.300	200.8	25	12.313	191.7
”	8	0.040	12.163	209.0	12.184	205.6	25	12.230	186.0
”	4	0.020	11.875	209.2	11.920	190.0	25	11.952	179.5
”	2	0.010	11.553	232.1	11.619	188.5	25	11.682	167.4
”	1	0.005	11.345	179.0	11.391	170.4	25	11.418	149.1
”	0.3333	0.00167	10.901	168.1	10.944	136.0	25	10.979	126.6
0.5000 N KCl	10	0.05	12.176	256.5	12.184	241.2		—	—
0.2500 ” ”	10	0.05	12.209	247.4	12.195	234.8		—	—
0.1000 ” ”	10	0.05	12.203	240.9	12.189	228.0		—	—
0.0500 ” ”	10	0.05	12.231	234.3	12.200	221.1		—	—
0.0250 ” ”	10	0.05	12.201	231.2	12.227	216.2		—	—
0.0100 ” ”	10	0.05	12.212	224.3	12.208	215.6		—	—
0.0050 ” ”	10	0.05	12.214	221.5	12.195	212.9		—	—
0.0025 ” ”	10	0.05	12.278	203.9	12.197	211.6		—	—
0.0010 ” ”	10	0.05	12.277	204.2	12.224	205.2		—	—

* Detns. by A. D. R. (1929).

** Detns. by R. A. G. (1928).

TABLE III (continued)

Dilution and Salt Effect Data for Casein- and Paracasein-Sodium Hydroxide Systems at pH 11 to pH 12.5

Salt Normality	Concentration of Protein	Sodium Hydroxide	Paracasein		Casein				
			pH	Equivalents* of Alkali bound per gm. Protein × 10^5	pH	Equivalents* of Alkali bound per gm. Protein × 10^5	Temperature	pH	Equivalents** of Alkali bound per gm. Protein × 10^5
0.5000 N KBr	10	0.05	12.126	264.8	—	—		—	—
0.2500 " "	10	0.05	12.154	249.1	—	—		—	—
0.1000 " "	10	0.05	12.162	244.5	—	—		—	—
0.0500 " "	10	0.05	12.177	236.0	—	—		—	—
0.0250 " "	10	0.05	12.219	219.5	—	—		—	—
0.0100 " "	10	0.05	12.224	216.2	—	—		—	—
0.0050 " "	10	0.05	12.235	208.9	—	—		—	—
0.0025 " "	10	0.05	12.135	217.9	—	—		—	—
0.0010 " "	10	0.05	12.244	204.5	—	—		—	—
0.5000 N KI	10	0.05	12.092	282.5	—	—		—	—
0.2500 " "	10	0.05	12.133	261.0	—	—		—	—
0.1000 " "	10	0.05	12.184	230.8	—	—		—	—
0.0500 " "	10	0.05	12.200	220.7	—	—		—	—
0.0250 " "	10	0.05	12.212	213.1	—	—		—	—
0.0100 " "	10	0.05	12.215	210.9	—	—		—	—
0.0050 " "	10	0.05	12.235	197.3	—	—		—	—
0.0025 " "	10	0.05	12.241	205.3	—	—		—	—
0.0010 " "	10	0.05	12.228	202.5	—	—		—	—
0.5000 N NaCl	10	0.05	—	—	—	—	25	12.168	222.2
0.2500 " "	10	0.05	—	—	—	—	25	12.213	211.6
0.1000 " "	10	0.05	—	—	—	—	25	12.255	200.8
0.0500 " "	10	0.05	—	—	—	—	25	12.282	199.4
0.0250 " "	10	0.05	—	—	—	—	25	12.294	197.3
0.0100 " "	10	0.05	—	—	—	—	25	12.306	193.1

* Detns. by A. D. R. (1929).
** Detns. by R. A. G. (1928).

TABLE IV

Dilution and Salt Effect Data for Casein- and Paracasein-Sodium Hydroxide Systems at pH 8 to 9.6

Salt Normality		Concentration of Protein	Sodium Hydroxide	Paracasein*				Casein		
				pH	Equivalents of Alkali bound per gm. Protein × 10⁵	pH	Equivalents* of Alkali bound per gm. Protein × 10⁵	Temperature	pH	Equivalents** of Alkali bound per gm. Protein × 10⁵
		gm. per liter	Normality					°C.		
None		20.0	0.02	—	—	—	—	25	9.588	99.78
"		10.0	0.0100	—	—	—	—	25	9.607	99.44
"		7.5	0.0075	9.370	99.57	9.578	98.98	—	—	—
"		6.0	0.0060	9.397	99.44	9.574	98.75	—	—	—
"		5.0	0.0050	9.349	99.40	9.582	98.54	25	9.627	99.86
"		4.0	0.0040	9.298	99.34	9.550	98.31	—	—	—
"		2.0	0.0020	9.014	99.32	9.460	97.30	—	—	—
"		1.0	0.0010	8.833	99.15	9.300	96.40	—	—	—
"		0.5	0.0005	8.487	99.21	8.982	96.48	28	8.838	97.74
"		0.167	0.000167	7.653	99.67	8.183	98.34	29	8.149	98.50
0.500	N KCl	10	0.010	—	—	—	—	25	9.268	99.65
0.500	" "	5	0.005	8.723	99.85	9.206	99.45	25	9.228	99.37
0.250	" "	10	0.010	—	—	—	—	25	9.281	99.67
0.250	" "	5	0.005	8.766	99.83	9.223	99.43	25	9.230	99.41
0.100	" "	10	—	—	—	—	—	25	9.338	99.65
0.100	" "	5	0.005	8.839	99.80	9.256	99.39	25	9.298	99.36
0.0500	" "	5	0.005	8.927	99.75	9.309	99.30	29	9.060	99.52
0.0250	" "	5	0.005	9.016	99.70	9.396	99.15	29	9.140	99.45
0.0100	" "	5	0.005	9.123	99.62	9.476	98.98	29	9.221	99.35
0.0050	" "	5	0.005	9.176	99.56	9.532	98.84		—	—
0.00250	" "	5	0.005	9.272	99.46	9.555	98.78		—	—
0.00100	" "	5	0.005	9.250	99.44	9.571	98.73		—	—
0.00050	" "	5	0.005	9.286	99.41	—	—		—	—
0.00025	" "	5	0.005	9.275	99.41	—	—		—	—

* Detns. by A. D. R. (1929).

** Detns. by R. A. G. (1928).

TABLE IV (continued)

Dilution and Salt Effect Data for Casein- and Paracasein-Sodium Hydroxide Systems at pH 8 to 9.6

Salt Normality	Concentration of Protein	Sodium Hydroxide	Paracasein*		Casein				
			pH	Equivalents of Alkali bound per gm. Protein × 10^5	pH	Equivalents* of Alkali bound per gm. Protein × 10^5	Temperature	pH	Equivalents** of Alkali bound per gm. Protein × 10^5
0.500 N KBr	5	0.005	8.653	99.88	—	—	25	9.218	99.39
0.250 " "	5	0.005	8.762	99.85	—	—	25	9.232	99.41
0.100 " "	5	0.005	8.820	99.82	—	—	25	9.278	99.40
0.050 " "	5	0.005	8.973	99.75	—	—	—	—	—
0.025 " "	5	0.005	9.049	99.70	—	—	—	—	—
0.010 " "	5	0.005	9.133	99.64	—	—	—	—	—
0.0050 " "	5	0.005	9.218	99.54	—	—	—	—	—
0.0025 " "	5	0.005	9.264	99.51	—	—	—	—	—
0.0010 " "	5	0.005	9.311	99.43	—	—	—	—	—
0.0005 " "	5	0.005	9.279	99.40	—	—	—	—	—
0.500 N KI	5	0.005	8.972	99.84	—	—	25	9.252	99.33
0.250 " "	5	0.005	8.800	99.83	—	—	25	9.202	99.45
0.100 " "	5	0.005	8.825	99.82	—	—	25	9.272	99.39
0.050 " "	5	0.005	8.912	99.73	—	—	—	—	—
0.025 " "	5	0.005	9.019	99.67	—	—	—	—	—
0.010 " "	5	0.005	9.162	99.62	—	—	—	—	—
0.005 " "	5	0.005	9.227	99.55	—	—	—	—	—
0.0025 " "	5	0.005	9.206	99.49	—	—	—	—	—
0.0010 " "	5	0.005	9.267	99.42	—	—	—	—	—
0.0005 " "	5	0.005	9.276	99.41	—	—	—	—	—

* Detns. by A. D. R. (1929).

** Detns. by R. A. G. (1928).

TABLE IV (continued)

Dilution and Salt Effect Data for Casein- and Paracasein-Sodium Hydroxide Systems at pH 8 to 9.6

Salt Normality	Concentration of Protein	Sodium Hydroxide	Paracasein*		Casein				
			pH	Equivalents of Alkali bound per gm. Protein × 10^5	pH	Equivalents* of Alkali bound per gm. Protein × 10^5	Temperature	pH	Equivalents** of Alkali bound per gm. Protein × 10^6
0.500 N NaCl	10	0.010	—	—	—	—	25	9.224	99.69
0.500 " "	5	0.005	—	—	—	—	25	9.090	99.54
0.250 " "	10	0.010	—	—	—	—	25	9.260	99.68
0.250 " "	5	0.005	—	—	—	—	25	9.159	99.50
0.100 " "	10	0.010	—	—	—	—	25	9.324	99.66
0.100 " "	5	0.005	—	—	—	—	25	9.211	99.48
0.050 " "	5	0.005	—	—	—	—	29	9.045	99.54
0.025 " "	5	0.005	—	—	—	—	29	9.144	99.44
0.010 " "	5	0.005	—	—	—	—	29	9.236	99.35
0.500 N LiCl	10	0.010	—	—	—	—	25	9.195	99.73
0.500 " "	5	0.005	—	—	—	—	25	9.163	99.51
0.250 " "	10	0.010	—	—	—	—	25	9.234	99.71
0.250 " "	5	0.005	—	—	—	—	25	9.171	99.51
0.100 " "	10	0.010	—	—	—	—	25	9.317	99.67
0.100 " "	5	0.005	—	—	—	—	25	9.207	99.49

* Detns. by A. D. R. (1929).
** Detns. by R. A. G. (1928).

effect on the base-binding capacity of paracasein. From our study we would designate 0.001 normality to be the "fading out" point of the salt effect.*

Table IV shows the salt effect on the paracasein-sodium hydroxide and casein-sodium hydroxide systems at approximately pH 9. It includes dilution data as well. Here we have results very similar to those observed at the higher pH. The addition of neutral salts increases the base-binding capacity of paracasein, and the order of the increase appears superficially to resemble the typical adsorption curve. As before, the three salts seem to exert equal effects. The fading out point of the salt effect however is at a normality of 0.00025 to 0.0005 as compared with 0.001 at the higher pH. Salt concentrations which appear to have no effect on paracasein at pH 12 will cause it to bind more alkali at pH 9.**

In general the casein results agree with those for the paracasein systems. The actual figures are not the same, though nearly so. The amount of alkali bound by the paracasein is in general slightly greater than that bound by casein. While the fading out point was not determined for casein-sodium hydroxide systems, it would appear to be similar to that for paracasein.

Table V gives the dilution and salt effect data for casein and paracasein systems at a pH of approximately 6. It will be noted that whereas in previous dilution studies, dilution *lowered* the pH of a solution, in this case it *raised* it. This is due of course to the fact that while we have alkali present, it is not present in sufficient quantity to overcome the acidity of the protein. We are merely making an acid solution less acid by dilution.

The salt effect is similar to that in the previous series. The fading out point is reached at a salt concentration of 0.0001 normality, lower than in any of the previous studies. That is, the lower the pH, or perhaps the more nearly "neutral" the solution is, the more effect do small quantities of neutral salts produce.

For purposes of comparison similar studies were made on an amino acid-sodium hydroxide system, alanine being the amino acid used. The dilution and salt effect data are reproduced in Table VI. Measurements were also made of the salt effect of a neutral salt containing a divalent cation, calcium chloride. It was impossible to use this salt in paracasein studies, due to the formation of a curd of "calcium paracaseinate." Like the proteins, alanine binds more alkali in the presence of a neutral salt. The calcium chloride

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* In most of the data which are reported for casein, the salt solutions were not sufficiently dilute to prevent a shift in the pH of the casein-NaOH system. A distinct "salt effect" persists at a salt concentration of 0.01 N and this "salt effect" fades out only as we approach 0.0010 N salt concentration. There is, therefore a greater "salt effect" in these casein-NaOH systems than Kolthoff and Bosch[25] found in their acid-base equilibria studies. However, the data which we do present is adequate to demonstrate that the paracasein-NaOH system is essentially identical in its behavior in this respect to the casein-NaOH system.

** Admittedly the excess "binding" due to the presence of the salt appears to be very small numerically; thus the values are 99.85×10^{-6} equivalents in the presence of 0.5 N KCl and 98.54×10^{-6} equivalents in the salt-free system. These extremes, however, represent a range in equilibrium pH values of 8.723 and 9.349 respectively, and accordingly represent readily measurable differences. There is no question but that these systems show a pronounced "salt effect."

TABLE V

Dilution and Salt Effect Data for Casein and Paracasein-Sodium Hydroxide Systems at pH 6 to 7

			Paracasein*			Casein**	
Salt Normality	Concentration of Protein	Sodium Hydroxide	pH	Equivalents of Alkali bound per gm. × 10⁵	Temperature	pH	Equivalents of Alkali bound per gm. × 10⁵
	gm. per liter	Normality			°C.		
None	10.0	0.0050	—	—	27	6.657	49.9993
"	7.5	0.00375	6.601	49.9993	—	—	—
"	6.0	0.00300	6.622	49.9991	—	—	—
"	5.0	0.00250	6.630	49.9988	27	6.703	49.9984
"	4.0	0.00200	6.658	49.9984	—	—	—
"	2.0	0.00100	6.713	49.9965	—	—	—
"	1.0	0.00050	6.768	49.9925	—	—	—
"	0.5	0.00025	6.743	49.9858	27	6.836	49.9793
"	0.167	0.0000833	6.825	49.8492	27	7.235	49.8415
0.50000 N KCl	5	0.0025	5.865	49.99981	27	6.080	49.99957
0.25000 " "	5	0.0025	5.930	49.99978	27	6.131	49.99948
0.10000 " "	5	0.0025	6.064	49.99970	27	6.238	49.99935
0.05000 " "	5	0.0025	6.166	49.99961	—	—	—
0.02500 " "	5	0.0025	6.273	49.99951	—	—	—
0.01000 " "	5	0.0025	6.399	49.99931	—	—	—
0.00500 " "	5	0.0025	6.479	49.99917	—	—	—
0.00250 " "	5	0.0025	6.540	49.99905	—	—	—
0.00100 " "	5	0.0025	6.581	49.99896	—	—	—
0.00050 " "	5	0.0025	6.562	49.99887	—	—	—
0.00025 " "	5	0.0025	6.571	49.99885	—	—	—
0.00010 " "	5	0.0025	6.587	49.99881	—	—	—

* Data of A. D. R. (1929).

** Data of R. A. G. (1928).

TABLE V (continued)

Dilution and Salt Effect Data for Casein and Paracasein-Sodium Hydroxide Systems at pH 6 to 7

Salt Normality	Concentration of Protein	Sodium Hydroxide	Paracasein* pH	Paracasein* Equivalents of Alkali bound per gm. × 10^5	Temperature	Casein** pH	Casein** Equivalents of Alkali bound per gm. × 10^5
0.50000 N KBr	5	0.0025	5.843	49.99979	—	—	—
0.25000 " "	5	0.0025	5.912	49.99977	—	—	—
0.10000 " "	5	0.0025	6.043	49.99969	—	—	—
0.05000 " "	5	0.0025	6.145	49.99960	—	—	—
0.02500 " "	5	0.0025	6.242	49.99950	—	—	—
0.01000 " "	5	0.0025	6.351	49.99936	—	—	—
0.00500 " "	5	0.0025	6.438	49.99922	—	—	—
0.00250 " "	5	0.0025	6.497	49.99911	—	—	—
0.00100 " "	5	0.0025	6.551	49.99903	—	—	—
0.00050 " "	5	0.0025	6.571	49.99889	—	—	—
0.00025 " "	5	0.0025	6.600	49.99887	—	—	—
0.00010 " "	5	0.0025	6.600	49.99882	—	—	—
0.10000 N KI	5	0.0025	6.038	49.99969	—	—	—
0.05000 " "	5	0.0025	6.146	49.99960	—	—	—
0.02500 " "	5	0.0025	6.234	49.99951	—	—	—
0.01000 " "	5	0.0025	6.369	49.99936	—	—	—
0.00500 " "	5	0.0025	6.442	49.99924	—	—	—
0.00250 " "	5	0.0025	6.513	49.99914	—	—	—
0.500 N NaCl	5	0.0025	—	—	27	6.006	49.9996
0.250 " "	5	0.0025	—	—	27	6.086	49.9995
0.100 " "	5	0.0025	—	—	27	6.220	49.9994
0.500 N LiCl	5	0.0025	—	—	27	6.074	49.9995
0.250 " "	5	0.0025	—	—	27	6.130	49.9995
0.100 " "	5	0.0025	—	—	27	6.208	49.9994

* Data of A. D. R. (1929).

** Data of R. A. G. (1928).

effect exceeded that of potassium chloride. It is probable that the salt of a divalent cation has a greater effect on the alkali-binding capacity of a protein than has the salt of a monovalent cation, both salts having a common anion. It will further be noted that the theoretical equivalents of NaOH were bound only when essentially equivalent amounts of the amino acid and the alkali were present.

TABLE VI

Dilution and Salt Effect Data for Alanine-Sodium Hydroxide System at pH 9.2 to 10

Salt Normality	Alanine	Sodium Hydroxide	pH	Equivalents of Alkali bound per Mole of Alanine* $\times 10^3$
	Normality	Normality		
None	0.0200	0.0100	9.775	495.5
"	0.0150	0.0075	9.791	494.2
"	0.0120	0.0060	9.785	491.2
"	0.0100	0.0050	9.767	491.5
"	0.0080	0.0040	9.767	489.5
"	0.0040	0.0020	9.788	480.5
"	0.0020	0.0010	9.747	466.3
"	0.0010	0.0005	9.659	445.3
"	0.0003	0.00016	9.203	439.1
0.5000 N KCl	0.01	0.005	9.670	493.2
0.2500 " "	0.01	0.005	9.677	493.4
0.1000 " "	0.01	0.005	9.699	493.0
0.0500 " "	0.01	0.005	9.703	492.7
0.0250 " "	0.01	0.005	9.721	492.7
0.0100 " "	0.01	0.005	9.750	492.1
0.0050 " "	0.01	0.005	9.767	492.2
0.0025 " "	0.01	0.005	9.763	491.9
0.0010 " "	0.01	0.005	9.763	491.9
0.5000 N $CaCl_2$	0.01	0.005	9.376	496.4
0.2500 " "	0.01	0.005	9.496	495.5
0.1000 " "	0.01	0.005	9.571	494.6

* Theory = 449.08×10^{-3}.

Studies were made of the effect of salts on protein-water systems. Any results obtained in these could not be reported in terms of the effect on the alkali-binding capacity of the protein. But increase in base-binding capacity is accompanied by a lowering of the pH of the system. Casein-water, paracasein-water, gelatin-water, and alanine-water systems were treated with varying amounts of potassium chloride and the effect upon the pH of the system determined. These results are recorded in Tables VII and VIII.

TABLE VII

The Effect of KCl on the pH of Protein-in-H_2O Systems

Concentration of Protein in Gm. per liter	KCl	Casein	Paracasein	Gelatin
	Normality	pH	pH	pH
2	0.5000	4.910	4.884	5.070
2	0.2500	4.931	4.917	5.014
2	0.1000	4.986	4.960	5.018
2	0.0500	5.003	4.976	5.088
2	0.0250	5.040	4.984	5.074
2	0.0100	4.959	5.035	4.923
2	0.0050	4.978	5.115	4.926
2	0.0025	4.999	5.180	4.962
2	0.0010		5.217	4.910
2	0.0005			4.955
2	0.0000	5.137	5.356	5.003
40	0.0000	4.738	5.104	
40	0.0100	4.832	4.978	

TABLE VIII

Effect of KCl on the pH of an Alanine-in-H_2O Solution

Conc. Alanine = 0.2 moles per liter

KCl Normality	pH	KCl Normality	pH
0.500	6.635	0.025	6.730
0.250	6.668	0.010	6.710
0.100	6.697	0.000	6.800
0.050	6.721		

The addition of increasing amounts of potassium chloride lowers the pH of the alanine in water solution. This effect is similar to the salt effect on the protein-base system. A similar effect is indicated for the casein-water and paracasein-water systems, though all data are not in harmony with this generalization. Values which do not fall in line with the general trend are due probably to experimental errors of measurement. On repeating these studies a similar series of data was obtained, but with values of slightly different magnitude. It will be observed that the casein and paracasein impart different pH values of the water systems, that for paracasein being the higher. The magnitude of the salt effect seems to be of the same order for both proteins.

It seems impossible to draw any conclusions from the gelatin studies. There is no apparent relationship between salt concentration and direction or magnitude of change in pH.

Discussion

Base-binding Capacity.—The difference in base-binding capacity of casein and paracasein and of succinic acid has already been discussed at some length. The amount of alkali bound by casein and paracasein was found to increase with the equilibrium pH, whereas the amount bound by succinic acid was constant over a wide pH range. This would indicate that other factors than a stoichiometrical combination were acting—possibly an adsorption type of reaction between protein and alkali being added to a stoichiometrical binding. If this were due to increased ionization of the protein as an acid at higher pH values we might reasonably expect to find a point at which the protein ceases to bind larger quantities of alkali. That is, all the carboxyl groups would have reacted, and there would be no further salt formation between the protein and the alkali. From this point on, the amount of alkali bound per gram of protein would be the same, irrespective of the pH of the solution. This constant value was not reached, even though the systems were studied at pH 12.7. It would appear doubtful then if those who believe the reaction to be strictly stoichiometrical are justified in their stand. No amount of hypothetical argument will alter the fact that the curve for the alkali-binding of a protein over a changing pH range does not resemble the one for the alkali-binding of an organic acid of known constitution and which dissolves to form a true solution.

The Dilution Series.—The dilution data for the various systems are of interest. It is impossible to make use of them to calculate dissociation constants, as Kolthoff did, for reasons which have been previously stated. His first step was to determine the pH at infinite dilution, using the Debye-Hückel equation:

$$-\log f_1 = 0.5\sqrt{\mu}$$

where μ is the concentration. The value 0.5 may be employed if we are dealing with a monobasic acid, as acetic acid. For a dibasic acid, 1.5 would be used; for a tribasic one, 2.5; etc. Assuming paracasein does dissociate as an acid, we may let its degree of basicity be equal to x + 1. Then the equation would become

$$-\log f_1 = (x + 0.5)\sqrt{\mu}$$

Assuming that the dilutions were carried far enough, then the values for the greater dilutions, substituted in the above equation should yield values from which we might express the pH at infinite dilution in terms of the basicity of paracasein, or

$$pH^{\infty} = pH + (x + 0.5)\sqrt{\mu}$$

Thus from the dilution data for paracasein in Table III,

$$pH^{\infty} = 11.553 + (x + 0.5)\sqrt{0.01}$$
$$pH^{\infty} = 11.345 + (x + 0.5)\sqrt{0.005}$$

using these as simultaneous equations and solving for x, we find that x = −7.6, or the degree of basicity = −6.6. Similar calculations from other series of the dilution data yield values for x + 1 as follows:

	Paracasein	Casein
Table III	− 6.6	− 7.4
Table IV	−34.1	−31.3
Table V	− 3.7	

In each case, the degree of basicity of the acid (paracasein or casein), has a negative value. This is a necessary consequence since the two terms of the expression for pH" are smaller in one case than in the other. That is, a decreasing pH is accompanied by a decreasing value under the square root sign. These expressions then can be equal only if x is negative. Whereas we might expect more satisfactory results for alanine, we find it responding to our calculations after the manner of the proteins to give a degree of basicity of −8.3. Alanine is known to be monobasic. It would accordingly appear that this method of calculation cannot be applied to amphoteric electrolytes.

From the dilution data we are led to draw two conclusions. First, our studies do not lend themselves to ready theoretical mathematical interpretation. This may be due to the fact that there is not the constant proportion between the reacting substances that we expect in a strictly stoichiometrical reaction, or it may be due to effects other than stoichiometrical combination. In fact, this lack of definiteness suggests strongly that classical chemical effects are not responsible for the whole of the reaction. It has been pointed out by Randall and his coworkers[38,39] that thermodynamic method cannot be applied in heterogeneous systems. These observations throw doubt on the question of applying thermodynamic equilibrium calculations to our data.

Secondly, we have seen that the proteins "bind" different amounts of alkali, the amount which is bound depending both upon the concentration of the protein and the concentration of the alkali. This confirms other findings.

The Effect of Salts on the Reaction between Proteins and Sodium Hydroxide.—The presence of salts, such as KCl, KBr and KI, increase the ability of the protein to "bind" sodium hydroxide and when the equivalents of alkali bound per gram of protein are plotted against the normality of the salt solution, the resulting curves approximate parabolas and indicate that adsorption may be involved in the increase. In order to test this possibility, the logarithms of salt normality were plotted against the logarithms of alkali bound per gram of protein. A representative curve is shown in Fig. 1. In this figure (paracasein-NaOH-KCl at pH 12), it is seen that the curve approximates a straight line, except for extremely small values of salt concentration. Accordingly it would appear that at this pH the increase in the alkali binding is probably due to adsorption.

Paracasein-NaOH-salts at pH 9 and paracasein-NaOH-salts at pH 6 did not yield straight lines, but rather sigmoid curves with a greater curvature

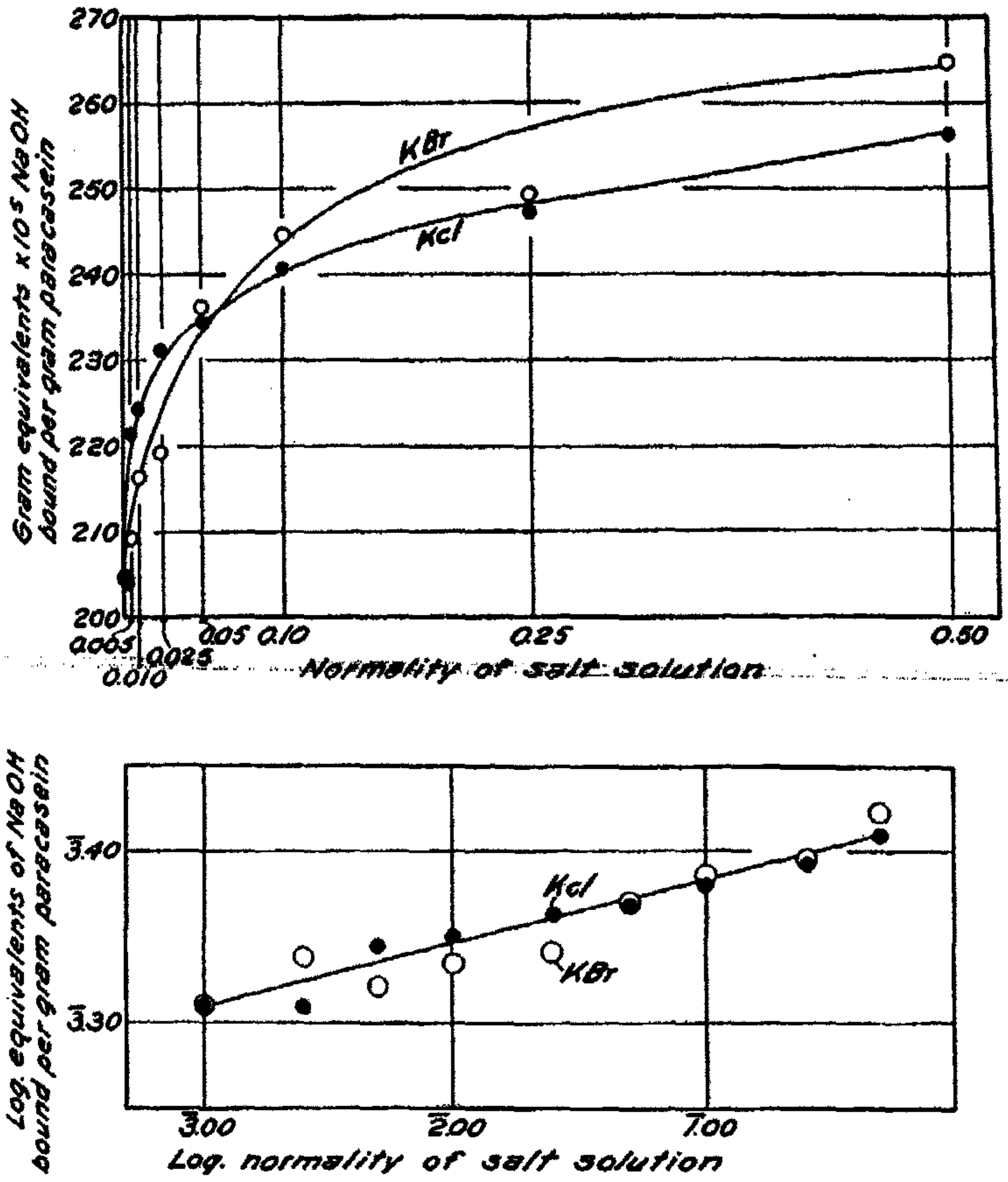


FIG. 1

Showing the effect of various concentrations of KCl and KBr on the alkali binding of paracasein at approximately pH 12.

at pH 6 than at pH 9. It would thus appear that there is less of an adsorption effect at pH 6 than at pH 9 and less at pH 9 than at pH 12. We believe that there is certainly some adsorption at pH 9, and possibly some at pH 6.

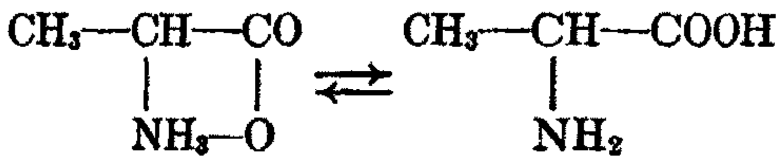
These findings appear to substantiate the findings of Hoffman and Gortner.[2] Adsorption is primarily concerned in the extra binding at pH 12, while more nearly classical chemical forces were involved at pH 9 and pH 6, more so in the latter than in the former. If the effect of added salts is to increase the activity of the undissociated molecule, as Kolthoff and Bosch found for certain acids, then the above is simple of explanation. The increased activity may result in increased power of adsorption and increased opening up of active groups. In the lower pH ranges where complete stoichiometrical binding has not occurred, there is further increase in the active groups followed by chemical reactions. Above pH 10.5, where the stoichiometrical binding is completed, the increased activity results in adsorption although some adsorption may occur below pH 10.5.

At lower pH values a shift in the equilibrium pH is observed with a lower salt concentration than at a higher pH. Kolthoff and Bosch[25] found that the salt effect in relatively simple acid-base systems disappeared at much higher concentrations of salt than those which we have found to show a decided effect in the casein- and paracasein-NaOH systems. Kolthoff,* after reviewing our data, comments on this fact as follows: "The striking effect of small amounts of neutral salts on the pH of the caseinate solutions shows definitely that they do not behave like simple acid-base systems of the classical type."

It should furthermore be emphasized that there is no definite lyotropic series for the anions Cl, Br and I in the "salt effect." Whether there is one for cations we did not determine. It is probable that a divalent cation would produce a greater effect than does a monovalent one.

This "salt effect" in a protein-NaOH system offers a logical explanation for the divergence which Hoffman and Gortner[40] found in a comparison of the "titration curve" and the "back titration curve" of a protein-NaOH-HCl system. They observed that when proteins were electrometrically titrated with sodium hydroxide (or calcium hydroxide) and then the mixture was back-titrated with equivalent amounts of hydrochloric acid, the "back-titration curve" invariably was different from the original titration curve, being shifted toward lower pH values. Due to the presence of the "salt effect" which we have noted, it is a necessary consequence that the second curve did not coincide with the initial one. Accordingly, the interpretation of pH measurements made in protein systems containing even small quantities of neutral inorganic salts is complicated by the concomitant "salt effect."

No explanation is offered for the increased reactivity of alanine with sodium hydroxide in the presence of salts. It can hardly be explained by an increase in the dissociation of alanine or by a shift of the internal salt equilibrium to the right:



$$\begin{array}{l} \mathrm{CH_3{-}CH{-}CO} \\ \qquad | \qquad\ \ | \\ \ \ \mathrm{NH_3{-}O} \end{array} \rightleftarrows \begin{array}{l} \mathrm{CH_3{-}CH{-}COOH} \\ \qquad\ \ | \\ \qquad \mathrm{NH_2} \end{array}$$

Either the assumptions upon which our calculations are based are at fault, or else the amino group is in some unknown manner entering into the reaction. It cannot be through the formation of carbamino salts, since every precaution was taken to avoid the presence of carbon dioxide.

In the tables, data have been reported which were obtained from single preparations of casein and paracasein. That other preparations yield essentially identical data was proven by working with two other preparations of casein which have been used for physico-chemical studies in our laboratories. One of these samples was that used by Richardson and Palmer.[26] We also tested their sample of paracasein and secured values which were within experimental error of those which we report.

Therefore, as our contribution to the casein-paracasein problem, we must conclude that technic such as we have used shows little if any difference

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* Private communication.

in these two proteins. Both bind approximately the same amounts of sodium hydroxide and both show essentially the same salt effect. If however we compare the dilution data for the two proteins as presented in Table III, we find that somewhat more alkali is bound by paracasein than by casein at similar concentrations of protein and alkali, or at the same pH. This is in harmony with the generally accepted notion of the reaction of the two proteins. Yet it is contrary to the findings presented in Table I. In general the systems reported in Table I were much more concentrated than were those reported in Table III. As a matter of fact only two of the systems had identical concentrations in both series, and the concentration of the system unquestionably affects the amount of base which is "bound" even though the ratio of protein:NaOH may be identical.

Summary and Conclusions

1. The amount of sodium hydroxide "bound" by casein and paracasein increased with the equilibrium pH. This suggests that adsorption may play a part in the reaction.

2. In similar studies succinic acid "bound" a constant amount of sodium hydroxide over an increasing pH range.

3. At pH 12.2 adsorption was probably the factor causing increased combination. At pH 9.0 and pH 6.0, binding by acidic groups appears to largely account for the results obtained.

4. The amount of sodium hydroxide "bound" by casein and paracasein is increased by the presence of potassium chloride, potassium bromide, or potassium iodide.

5. The addition of neutral salts causes a shift in the equilibrium pH of a casein-NaOH or a paracasein-NaOH system toward a lower pH value. This "salt effect" is much more pronounced in these protein-base systems than has been reported to be the case for simpler acid-base systems. Concentrations of neutral salts, as low as 0.001 N in some instances, produced a measurable pH shift.

6. The magnitude of the salt effect is essentially the same for potassium chloride, potassium bromide and potassium iodide. This "salt effect" exhibits no marked lyotropic series for these anions. These protein-NaOH systems are more sensitive to the addition of salts at a pH closer to their isoelectric points than at one further away.

7. This "salt effect" must be taken into consideration in the interpretation of the electrometric titration curves of proteins. If one titrates proteins electrometrically with either acid or alkali and then back-titrates the resulting system, the back-titration curve, due to the salt effect, will not coincide with the original titration curve. If a protein solution contains even small quantities of neutral inorganic salts, the equilibrium pH which is attained on the addition of a definite quantity of acid or alkali will be different from that which would be attained in the absence of the neutral inorganic salts.

8. In the pH ranges studied, and with the methods employed, casein and paracasein react essentially alike. The paracasein, in some instances, appears to bind slightly more alkali than does casein. Both respond in the same manner to the addition of salts.

9. This study affords evidence that a strictly classical thermodynamical treatment of the data of protein systems does not indicate a "maximum binding capacity" of NaOH by either casein or paracasein, such as is a necessary consequence of a stoichiometrical salt-formation, uncomplicated by adsorption reactions. The amount of sodium hydroxide which is bound by either casein or paracasein increases with increasing equilibrium hydrogen ion concentration in spite of attempts to apply assumptions of a strictly stoichiometrical combination to the calculation of the data.

Literature Cited

[1] R. A. Gortner: "Outlines of Biochemistry" (1929).
[2] W. F. Hoffman and R. A. Gortner: Colloid Symposium Monograph, **2**, 209-368 (1925).
[3] T. B. Robertson: "The Physical Chemistry of the Proteins" (1918).
[4] J. Loeb: "Proteins and the Theory of Colloid Behavior" (1922).
[5] E. J. Cohn: Physiol. Reviews, **5**, 349-437 (1925).
[6] W. D. Bancroft and C. E. Barnett: J. Phys. Chem., **34**, 449-98, 753-98, 1217-53 (1930).
[7] L. L. Van Slyke and E. B. Hart: Am. Chem. J., **33**, 461-96 (1905).
[8] K. Spiro and W. Pemsel: Z. physiol. Chem., **26**, 233-71 (1898).
[9] F. A. Hoffman: Z. klin. Med., **10**, 793-6 (1889).
[10] J. Sjöqvist: Skand. Arch. Physiol., **5**, 277-375; **6**, 255-61 (1895).
[11] S. Bugarszky and L. Liebermann: Pflüger's Arch., **72**, 51-74 (1898).
[12] D. M. Greenberg and C. L. A. Schmidt: Proc. Soc. Expt. Biol. Med., **21**, 281-4 (1924).
[13] D. I. Hitchcock: J. Gen. Physiol., **6**, 95-104 (1923).
[14] E. J. Cohn and R. E. L. Berggren: J. Gen. Physiol., **7**, 45-79 (1924-25).
[15] R. E. Tolman and A. E. Stearn: J. Am. Chem. Soc., **40**, 264-72 (1918).
[16] R. O. Herzog and J. Adler: Kolloid-Z., **2**, Supplement, III-XI, March 1908.
[17] H. R. Procter: J. Chem. Soc., **105**, 313-27 (1914).
[18] R. C. Tolman and R. S. Bracewell: J. Am. Chem. Soc., **41**, 1503-10 (1919).
[19] R. de Izaguirre: Kolloid-Z., **32**, 47-51 (1923).
[20] D. J. Lloyd and C. Mayes: Proc. Roy. Soc., **93B**, 69-85 (1922).
[21] J. Weber: Z. physiol. Chem., **172**, 1-37 (1927).
[22] L. L. Van Slyke and D. D. Van Slyke: Am. Chem. J., **38**, 383-456 (1907).
[23] M. L. Fischer and M. O. Hooker: Kolloidchem. Beihefte, **23**, 200-17 (1926).
[24] A. W. Thomas and C. W. Mayer: Proc. Soc. Expt. Biol. Med., **25**, 667-9 (1928).
[25] I. M. Kolthoff and W. Bosch: Rec. Trav. chim., **46**, 430-8 (1927); **47**, 558-75, 819-25, 826-33, 861-72, 872-82 (1928); **48**, 37-48 (1929).
[26] G. A. Richardson and L. S. Palmer: J. Phys. Chem., **33**, 557-76 (1929).
[27] L. L. Van Slyke and J. C. Baker: J. Biol. Chem., **35**, 127-36 (1918).
[28] L. L. Van Slyke: Chem. Age, **32**, 163-5 (1924).
[29] L. S. Palmer: "Laboratory Experiments in Dairy Chemistry," 41 (1926).
[30] A. W. Bosworth: J. Biol. Chem., **19**, 397-8 (1914).
[31] A. Geake: Biochem. J., **8**, 30-7 (1914).
[32] O. Hammersten: Z. physiol. Chem., **7**, 227-73 (1883).
[33] J. Lehman and W. Hempel: Archiv. ges. Physiol., **56**, 558-78 (1894).
[34] L. L. Van Slyke and A. W. Bosworth: J. Biol. Chem., **14**, 203-6 (1913).
[35] W. M. Clark: "The Determination of Hydrogen Ions," 45 (1928).
[36] G. N. Lewis and M. Randall: "Thermodynamics," 382 (1923).
[37] L. S. Palmer and G. A. Richardson: Colloid Symposium Monograph, **3**, 112-34 (1926).
[38] W. M. Hoskins, M. Randall and C. L. A. Schmidt: J. Biol. Chem., **88**, 215-39 (1930).
[39] M. Randall and J. Y. Cann: Chem. Reviews, **7**, 369-406 (1930).
[40] W. F. Hoffman and R. A. Gortner: J. Phys. Chem., **29**, 769-781 (1925).

SOME REMARKS ON THE USE OF THERMOPILES FOR THE ABSOLUTE MEASUREMENT OF RADIANT ENERGY[*]

BY PHILIP A. LEIGHTON AND WESLEY G. LEIGHTON

Among the instruments which may conveniently be applied to the accurate measurement of radiant energy in absolute terms,[**] the thermopile, used with a sensitive galvanometer,[1] has come into almost universal use. In photochemistry, for example, almost every value of quantum yields which has yet been published depends, directly or indirectly, upon a calibrated thermopile as the instrument for the determination of the absolute amount of energy involved.

The measurement of relative light intensities, itself a matter demanding the most careful technique, is simple compared to the translation of these measurements into absolute units. During the past eight years, the authors have investigated thirteen thermopiles, involving seven distinct types of construction, with regard to their applicability to absolute energy measurements. Some of the results of these studies have been published in connection with the work for which the thermopiles were used, and descriptions of most of the errors involved, together with precautionary measures, have been published by others, but the statements are so widely scattered through the literature that the knowledge seems to be gained by each new worker largely through experience. It therefore seems worth while to publish in one account a description of the observations which have been made and the precautions which have been found necessary in order to obtain reliable results.

1. Remarks on Design and Construction

Much of the work on the design and construction of line and surface thermopiles suitable for absolute energy measurements has been carried out by W. W. Coblentz,[2] who gives detailed directions for their construction. The absolute thermopile of Coblentz and Emerson merits more attention than it has received. The construction of line and surface thermopiles has also been described by Johansen,[3] Voege,[4] Moll,[5] and others.[6] Single junction thermo-

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[*] Contribution from the Chemistry Laboratories of Stanford University and of Pomona College.

[**] The term "energy" as here used refers to energy per unit time. We believe this is preferable to the use of the term "intensity" since energy per unit area is usually not considered.

[1] G. S. Forbes: J. Phys. Chem., **32**, 489-90 (1928)

[2] Coblentz: Bur. Standards Bull., **4**, 391 (1908); **12**, 503 (1916); **9**, 7 (1913); **11**, 131 (1914); Bur. Standards Sci. Papers, **17**, 187 (1921); J. Opt. Soc. America, **5**, 259 (1921); **7**, 439 (1923).

Coblentz and Emerson: Bur. Standards Bull., **11**, 157 (1914); **12**, 505 (1916).

[3] Johansen: Ann. Physik, (4) **33**, 517 (1910).

[4] Voege: Physik. Z., **21**, 288 (1920); **22**, 119 (1921).

[5] Moll: Proc. Phys. Soc. London, **35**, 257 (1923).

[6] Weigert: "Optische Methoden der Chemie," 295 (1927).

couples of high sensitivity but with small sensitive surface are described by Moll and Burger,[7] Brackett and McAlister,[8] and Petit and Nicholson.[9] A single thermocouple adapted to absolute energy measurements has recently been employed by Beckmann and Dickinson.[10]

The majority of these instruments have been designed with cases which may be evacuated. Evacuation is found to increase the sensitivity from two to twelve times over that at atmospheric pressure. In case a vacuum thermocouple or thermopile is used, care must be taken that the pressure is very low (less than 10^{-4} mm.) or that it is constant, since in the pressure range between 10 mm. and 10^{-3} mm. the sensitivity changes rapidly with pressure.[9] The sensitivity is also a function of the nature of the enclosed gas. Using a surface thermopile, we have found the sensitivity in an atmosphere of hydrogen is less than half of that in air, pressure being atmospheric in both cases, and even at a pressure of 10^{-4} mm., the sensitivity in hydrogen is slightly less than that in air. The question of the position of the slit with respect to the radiation receivers must be considered in the design of vacuum thermopiles for absolute energy measurements, and is discussed in section 5.

If the beam to be measured is of uniform energy distribution, and if it is of suitable dimensions, a surface thermopile offers the simplest means for absolute energy measurement. Variations in sensitivity over the surface make certain precautions necessary, which are discussed under section 6.

If the beam of light may be focused to a spot not more than 5 mm. in diameter, a single thermocouple of the Beckmann and Dickinson type,[6] with a single receiver large enough to include the entire beam, may be employed.

For beams of varying size and intensity distribution, a line thermopile of the many-junction type, operated by the methods described in this paper, provides a satisfactory means of absolute energy measurement.

In the case of line thermopiles, an integration process, as described in section 7, must be carried out in order to obtain absolute energy values. To simplify this process, it is important that the length of the sensitive portion of the pile be equal to or slightly greater than that of one dimension of the beam—preferably the dimension showing the most uniform distribution of intensity.

The integration process may be further simplified by using radiation receivers as wide as is compatible with uniform sensitivity over their surface.

We have experimented with several types of construction with this end in view. The construction shown in Fig. 1 enables one to use receivers up to 3 or 4 mm. wide without loss in uniform sensitivity. The junctions are of silver and bismuth wire, 0.05 mm. and 0.1 mm. diameter, respectively, the receivers of tin foil, about 0.02 mm. in thickness. The center receivers are each 3 to 4 mm. wide by 2 mm. high. the balancing receivers on the dark junctions are exactly half the area of the center receivers.

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[7] Moll and Burger: Z. Physik, 32, 575 (1925); Moll: Physica, 6, 233 (1926).

[8] Brackett and McAlister: Rev. Sci. Instruments, 1, 181 (1930).

[9] Petit and Nicholson: Astrophys. 56, 295 (1922); 68, 279 (1928); Petit: Carnegie Inst. Wash., Year Book, 140 (1929).

[10] Beckmann and Dickinson: J. Am. Chem. Soc., 52, 126 (1930).

Welding and mounting are accomplished after the directions of Coblentz.[11] A silver, then a bismuth wire of the proper lengths are welded in two places to each center receiver (Fig. 1, b). Then two pieces of foil of half size are welded to the silver wire, about 1 cm. from each edge of the center receiver. Next these individual junctions are mounted, by means of the extending silver wires, on an ivory or bakelite block, as described by Coblentz. The final welding of adjacent junctions may be accomplished by carefully setting a glass plate mounted on a firm base, of just the size of the opening in the block, directly behind and in contact with the junctions. The bismuth wires from one junction are then welded to the silver wires of the next junction, care being taken that the weld is in the center of each small piece of foil previously attached to the silver.

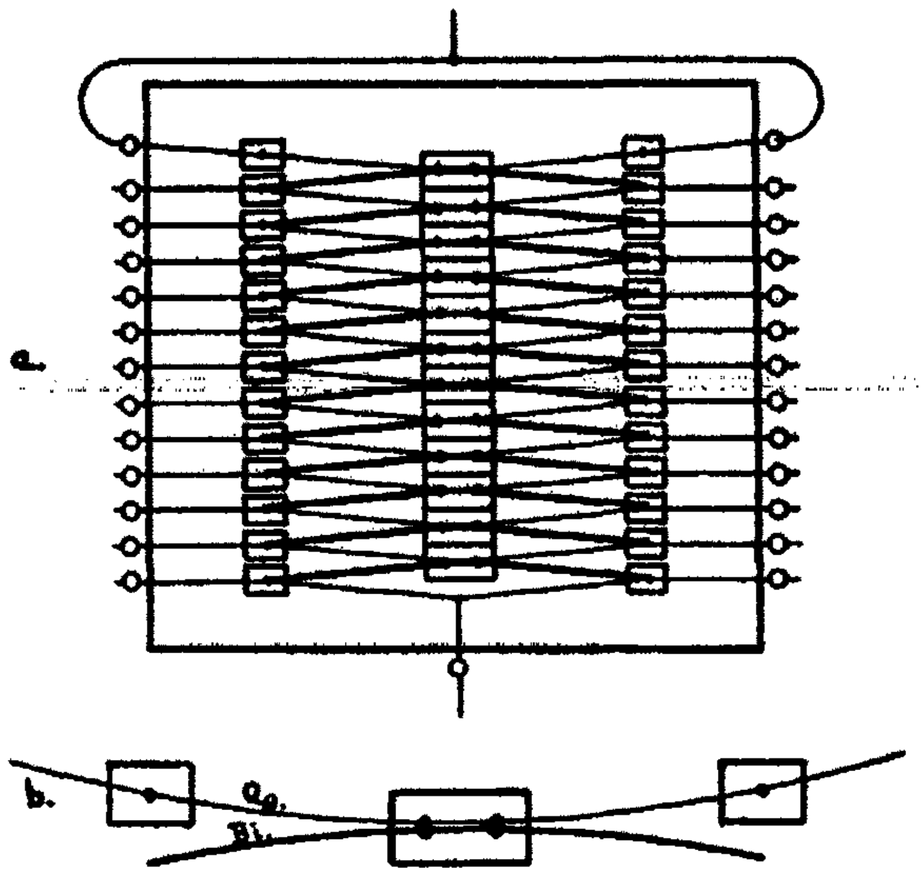

Fig. 1
Construction of Thermopile with Wide Radiation Receivers.

Daniels[12] has designed and constructed thermopiles with receivers of silver foil, sufficiently heavy so that their width may be extended to 10 mm. while still retaining a uniform sensitivity over their surface. The heavier receiver extends the period of response of the thermopile, which allows time for a fairly uniform temperature to be attained throughout the receiver, no matter what part of it is exposed. It is necessary to use these piles in a thermostat.

In the case of line thermopiles, as will be shown in section 5, it is absolutely essential to choose an instrument which is or may be fitted with a slit narrower than and very close to the radiation receivers. For this reason some types of commercial line thermopiles are not to be recommended for absolute energy measurements.

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[11] Coblentz: Bur. Standards Bull., 9, 15 (1913).

[12] F. Daniels: private communication.

2. Avoidance of Errors due to Drift

A thermopile-galvanometer combination which is sufficiently sensitive to measure beams of monochromatic light of average intensity is naturally very responsive to small changes in temperature, air currents, and similar disturbances. On a bismuth silver thermopile with 20 junctions and a galvanometer of sensitivity 15 mm/μv, a difference of 10^{-4} degree between hot and cold junctions should produce a deflection of approximately 1 cm. on a scale 5 meters distant from the galvanometer.

These disturbances result most commonly in a slow drift of the "zero point" of the galvanometer. The drift may be greatly reduced or avoided entirely by evacuating or thermostating the thermopile. There is, however, usually an additional drift produced on exposure to light, due to conduction along the wires to the cold junctions, Peltier effect, etc., so that even when a pile is completely protected, after exposure to light it requires some time to return to the original zero.

The errors due to both types of drift may largely be avoided by what has been termed the "ballistic" or "swinging equilibrium" method of reading.[13] This differs from the method of reading with a ballistic galvanometer, in that a condition of swinging equilibrium is established by proper manipulation of a shutter between the light source and the thermopile. The shutter is first opened, then at the instant the mirror reaches a maximum deflection it is closed, the instant a minimum is reached it is again opened, and so on. With a thermopile of the Coblentz type these alternate maxima and minima will be reached within the period of the average d'Arsonval galvanometer—say three to five seconds. After allowing one or two complete swings in order to attain maximum amplitude, readings of maxima and minima are taken, then the average of two successive minima is subtracted from the intermediate maximum.

As shown by the accompanying actually recorded example, a considerable drift during the course of a set of readings has little effect on the actual deflection as obtained by this method.

Min.	Av.	Max.	Def.
34.8			
	35.0	54.3	19.3
35.2			
	35.5	54.6	19.1
35.8			
	36.0	55.2	19.2
36.2			
	36.35	55.5	19.15
36.5			
	36.6	55.8	19.2
36.7			
		Av. =	19.19

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[13] P. A. Leighton and G. S. Forbes: J. Am. Chem. Soc., 51, 3551 (1929).

Ordinarily, about one minute is required to obtain a set of readings of five maxima and six minima, giving five values of the deflection, which may be averaged to give a very reproducible figure.

The foregoing method cannot be applied to thermopiles with periods longer than the period of the galvanometer. With such thermopiles it is necessary for the galvanometer to come to rest both for the maximum and minimum reading, and thermostating of the pile is essential to accuracy.

With a low resistance d'Arsonval galvanometer (such as Leeds and Northrup Type HS 2285x, C. D. R. 5Ω, I.R. 18Ω, period 7 sec. and sensitivity 15.3 mm./μv.), easily readable swing maxima and minima are obtained when the thermopile resistance or external resistance is greater than the critical damping resistance, ratios of as high as six fold having been found satisfactory. The precautions required by the variation in sensitivity at different positions of the galvanometer mirror (section 8) could be avoided by using the galvanometer as a null instrument, but the effect of drift in the thermopile E.M.F., we believe, can be eliminated more simply by observing deflections at swinging equilibrium. Moreover, if the light-flux being measured is itself subject to fluctuations during the course of a swing, the resulting deflection will tend to represent the integrated intensity during the short exposure.

3. Calibration

If the thermopile is calibrated by means of standard carbon lamps, as furnished by the Bureau of Standards, two sources of error (assuming that the absolute intensity of the radiation reaching the thermopile window from the standard lamp is accurately known) are to be considered. These sources of error arise from the conditions that:

1. The thermopile is usually calibrated in radiation of one wave length and used for another.

2. The thermopile may be calibrated for one range of galvanometer deflections and used for another.

The calibration in one wave length and use in another involves the question of non-selectivity of the absorbing surface. A carefully prepared platinum-black, lamp black,[14] or bismuth black[15] surface may safely be assumed as non-selective in absorption throughout the ordinary range of ultra-violet, visible, and near infra-red radiations. Such a surface will reflect a small amount, about 0.5 to 1.5% of the incident radiation,[14] and variation in the amount of this reflection with wave length will produce some error, but the error will in general be of the second order and may be neglected. On the other hand, we have found some commercial thermopiles to give values as much as 20% too high when calibrated in the visible and infra-red of the carbon lamp and used for λ 2500Å or shorter in the ultra-violet. If the radiation receivers are not apparently perfectly black to the eye, they should be re-blackened. In most cases smoking with a sperm candle will suffice.[14]

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[14] Coblentz: Bur. Standards Bull., **9**, 283 (1913); **11**, 98 (1914); **12**, 510, 522 (1916).

[15] A. H. Pfund: Rev. Sci. Instruments, **1**, 397 (1930).

Calibration in one wave length and use in another also involves a correction for changes in absorption and reflection of the thermopile window with wave length. On account of this change with wave length, the window will reflect and absorb different amounts of the standard lamp radiation for each current input.

The transmission of the thermopile window should therefore be measured not only for every wave length for which it is to be used, but also for every current input of the standard lamp radiation. In the case of the standard lamp radiation, these measurements of window transmission should not be made with a thermopile which is already protected with another window, but on an uncovered thermopile. Very careful shielding to avoid drift due to air currents will be necessary when the window is removed.

We have calculated the reflection and absorption losses to be expected for a crystal quartz window 1 mm. thick, when placed in the radiation from a standard carbon lamp burning at the four different current inputs at which it was calibrated. These calculations were made as follows:

1. The color temperature was estimated from measurements of the brightness temperature as made by an optical pyrometer. From this the spectral energy distribution of the radiation from the carbon filament was calculated from the radiation laws.

2. This spectral energy distribution was corrected for absorption by the glass bulb, using the data of Coblentz.[16]

3. The reflection of quartz, using Fresnel's law, and the absorption of 1 mm. of quartz, using Coblentz' data, were calculated for a series of points in the wave length region covered by the standard lamp.

4. The net loss was calculated from the losses at each wave length and the spectral energy distribution of the radiation.

A set of these calculations, for a carbon lamp burning at 1000°K, and the final results for four temperatures in the range usually covered by these lamps, are given in Tables I and II.

TABLE I

Standard Carbon Lamp at 1000° K

Radiation region μ	Total radiation below 4.0 μ	Transmitted by glass wall of lamp	Resulting radiation transmitted through glass	Amount reflected by quartz window	Amount absorbed by quartz window	Amount of *total* radiation reflected	Amount of total radiation absorbed
4.0–3.5	21%	4.3%	1.7%	7.5%	5%	0.13%	0.08%
3.5–3.0	23	27	12	7.8	2.0	0.93	.24
3.0–2.5	24	71	33	8.15	0.8	2.69	.27
2.5–2.0	17	85	26	8.4	0.5	2.18	.13
2.0–1.5	11	89	19	8.6	0.2	1.63	.04
1.5–1.0	4	90	7	8.8	—	0.61	—
1.0–0.5	0.6	90	1	9.0	—	0.09	—
	100%		100%			8.26%	0.76%

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[16] Coblentz: Bur. Standards Bull., 9, 116 (1913).

TABLE II

Reflection and Absorption Losses by 1 mm. Quartz Window in Radiation from Carbon Filament Lamp in Glass

Carbon Filament Temperature	Quartz Window 1 mm. thick		
	Reflects	Absorbs	Total Loss
1000° K	8.26%	0.76%	8.97%
1200	8.34	0.69	8.97
1400	8.44	0.56	8.96
1600	8.61	0.36	8.94

It is worthy of note that the changes in reflection and absorption with different current inputs are in opposite directions and almost exactly balance. Accordingly, for a good quartz window of 1 mm. thickness the transmission factor may be taken as a constant for carbon lamp radiation, regardless of current input. Most quartz windows will closely approximate the results given in Table II, but for the greatest accuracy the transmission should be directly determined for each window which is to be used. For example, as compared with our calculated value of 8.96%, Coblentz[17] gives 8.5%; we have found a range of values from 8.3% to 9.1%; while Beckman and Dickinson[18] give 9.4% for a window of unspecified thickness.

In the visible and ultra-violet region, down to 2000Å, only the reflection correction need be considered for crystal quartz. If the same window be used in calibration and in measurement, the correction to be applied is the ratio of

$$\frac{\text{Fraction of standard lamp radiation transmitted}}{\text{Fraction of radiation to be measured transmitted}}$$

The observed galvanometer deflection or energy calculated therefrom should be multiplied by this correction, the values of which for the principal lines of the mercury arc are given in Table III. A series of observed values for an average window are also included.

TABLE III

Quartz Window

Reflection Losses and Corrections for Mercury Arc Lines

Wave Length Å	Quartz Window Reflects		Thermopile Correction Factor (calculated values)
	Calculated	Observed	
Std. lamp radiation	8.96%	9.0	—
5770	9.2	9.2	1.003
4350	9.5	9.4	1.006
3663	9.7	9.5	1.008
3130	10.2	10.3	1.014
2654	10.5	11.5	1.017
2537	10.9	12.0	1.022

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[17] Coblentz: Bur. Standards Sci. Papers, 237 and 401.

[18] Beckman and Dickinson: loc. cit.

At shorter wave lengths, the observed values usually become higher than the calculated values. This illustrates again the importance of measuring the transmission directly for each window at every wave length used.

The second source of error to be considered in calibration arises from the fact that the thermopile may be calibrated over one range of galvanometer deflections and used over another. Our experience has shown that in very few cases is it safe to assume a linear relationship between incident energy and deflection produced, over any great range of deflections. Each thermopile-galvanometer combination shows a different set of characteristics and must be calibrated over the entire range in which it is to be used. As an illustration, Table IV shows the number of ergs per centimeter of deflection for a series of energies for two typical thermopiles.

TABLE IV

Variations in Sensitivity with Size of Deflection

Cms. Deflection Scale Dist. 5 meters	Total Energy on Pile, Ergs		Ergs per Cm. Deflection	
	Pile No. 1 Surface 24.15 mm^2	Pile No. 2 Surface 314 mm^2	Pile No. 1	Pile No. 2
2	30	182	15.0	91.0
4	*59*	358	14.7	89.9
7	*101*	619	14.4	88.4
10	*144*	*874*	14.4	87.4
15	216	*1290*	14.4	86.0
25	363	*2090*	14.5	83.6
40	585	3280	14.6	82.0
60	888	4900	14.8	81.7
100	1498	8170	15.0	81.7
150	2265	12300	15.1	82.0
200	3045	16450	15.2	82.2

Pile No. 1, a line thermopile of the Coblentz type, shows a fairly uniform sensitivity for the range 7 to 25 centimeters, with a decrease in sensitivity at very small deflections, and a fairly uniform decrease at larger deflections. Pile No. 2, a commercial surface thermopile, shows a very definite increase in sensitivity with deflection up to about 60 cms., followed by a slight decrease in sensitivity for deflections above 100 cms. In each case the energies in the range covered by the standard lamps are in italics.

We have employed three methods for extending the calibration over any desired range.[19] All avoid any assumptions regarding distance. The first method is made possible by the fact that several energy outputs are known for a given standard lamp, and is based on the conclusion that regardless of distance these known energies should bear constant ratios to each other.

The pile is first calibrated with the lamp at the standard distance. If calibration for larger energies is desired, the pile is moved toward the lamp

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[19] Forbes: loc. cit., p. 490.

until the deflection obtained with the lowest current input is approximately doubled. From the calibration in the first position and the observed deflection, the energy now falling on the pile with this lowest current input may be calculated. Each energy value of the lamp is now multiplied by the factor,

$$\frac{\text{Energy flux with lowest current at new distance}}{\text{Energy flux with lowest current at standard distance}}$$

This gives the energy flux from the standard lamp for the higher current inputs at the new distance, and by comparing with the deflections produced the calibration is extended. This process may be repeated as many times as necessary. If two points on the new setting overlap the old setting each time, the accuracy is much increased.

The second method consists of setting up two lamps (not standards) alongside each other, with a shield in between and a shutter in front of each. The current in the lamps is so adjusted that either one alone gives a deflection in the range covered by the standard lamps. The energy flux from each lamp is thus calculated. Next the deflection produced when both shutters are opened simultaneously is measured, in which case the energy flux on the pile is the sum of the two single values. This process may be repeated with larger current inputs until any desired range is covered.

A third method which we have tried for extrapolating the calibration curve beyond the range of the standard makes use of a monochromatic source of constant intensity, as follows:

(1) Select a glass filter which transmits between 20 and 80% of light of the wave length available. With the source at such a distance that the incident and transmitted intensities, I_0 and I, fall within the range covered by the standard lamp, determine $I/I_0 = K$.

(2) Move the source to a position at which the new transmitted intensity, I', is approximately equal to I_0 of the first position. Observe deflections produced by I' and I'_0. As the absolute value of I' may be read from the curve already established, I'_0 follows as

$$I'_0 = I' \cdot (1/K),$$

where the only assumption is that $I/I_0 = K$ is independent of intensity. The calibration curve, relating deflection to absolute intensity, is thus extended to I'_0. Further repetitions at increasingly greater intensities will obviously serve to extrapolate the curve as far as is required.

At five times the maximum intensity available from a standard lamp this method agreed with the other methods to within 1%.

Direct variation of the distance from the pile to the source, with assumption of the inverse square law, for extending the calibration to larger or smaller intensities is limited by the fact that the carbon lamp is not a point source. Trümpler[20] has shown that for linear sources of half length X and pile distance d the inverse square law becomes modified to

$$I_2/I_1 = d_1 (\arctan X/d_2)/d_2 (\arctan X/d_1),$$

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[20] Trümpler: Z. physik. Chem., 90, 385 (1915).

but even this formula cannot be applied with accuracy to carbon lamps. As Table IV shows, an extension of the calibration to very small deflections is also necessary when these are to be used.

The sensitivity of the galvanometer will in many cases vary with the position of the mid-point of the swing. We have found cases where the sensitivity changed by as much as 1% for a displacement of 10 cms. of the mid-point or zero point on a scale 5 meters distant.

It is, therefore, very important that some definite "zero point" or "low point of swing" be chosen on the galvanometer scale, and that all readings, both in calibration and use, be made with the galvanometer so set that the low point of the swing comes close to this predetermined value. Since, when using a constant "low point," the mid-point of the swing will vary with the size of the deflection, the sensitivity will also change with the size of the deflection, and this is undoubtedly a contributory cause to those changes of sensitivity discussed in the preceding paragraphs. This and other questions relative to calibration will be discussed in section 8.

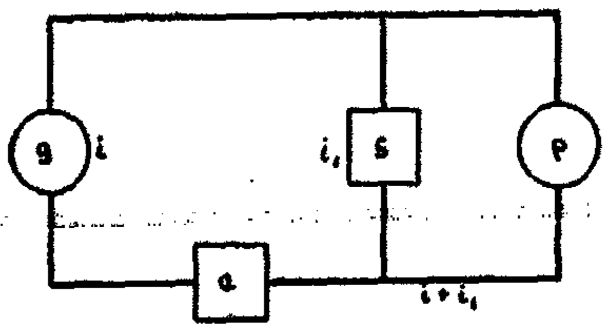

FIG. 2
Wiring Diagram for Shunt and Series Resistances.

4. Auxiliary Resistance Patterns

In case the light intensities to be measured are so high that deflections in excess of the total scale length are produced, it becomes necessary to incorporate in the thermopile-galvanometer circuit a suitable combination of shunt and series resistances.

The conventional scheme of connections is indicated in Fig. 2, where g is the galvanometer resistance, p the thermopile resistance, a the series, and s the shunt resistance. The same type of swing for all resistance patterns employed will be obtained by selecting such combinations of a and s that the resistance external to the galvanometer (i.e., "damping"), remains always the same as it was during the original calibrations. As the latter are usually carried out with the thermopile connected directly to the galvanometer, the desired condition requires an external resistance equal to the thermopile resistance, p. From the law of combination of resistances in parallel, it is obvious that the external resistance must be

$$a + \frac{1}{(1/s) + (1/p)} = \text{external resistance} = p. \qquad (1)$$

Rearranging,

$$a = p^2/(p + s). \qquad (2)$$

The question of extending the calibrations to include the auxiliary resistance patterns was first approached experimentally. As the result of numerous intercomparisons we have found that much labor can be saved by relating the sensitivity with an auxiliary pattern to the original calibration curve by means of the empirical equation

$$(E/E_o)_i = \text{a constant}, \tag{3}$$

where E_o = the intensity required to produce a certain deflection (or galvanometer current, i), with $a = 0$ and $s = \infty$, while E = the intensity required to produce the same deflection with some resistance pattern in which the relation in (2) is maintained. Our experimental results have proved equation (3) to hold independently of the magnitude of the deflection. This indicates that a linear proportionality exists between the thermopile E.M.F., π, and the incident light intensity, E. Thus, equation (3) may be expressed as

$$(\pi/\pi_o)_i = (E/E_o)_i = \text{a constant}. \tag{4}$$

We now proceed to an evaluation of the ratio (π/π_o) in terms of the resistances, Fig. 2. Let i and i_1 be the partial currents through the galvanometer and shunt, respectively. The thermopile current is then $i + i_1$. When $a = 0$ and $s = \infty$, i_1 disappears and, from Ohm's law

$$\pi_o = i(p + g). \tag{5}$$

For any other resistance pattern with which the same galvanometer current, i, is produced by a thermopile E.M.F. = π, it follows from the laws of multiple circuits that

$$\pi = i(a + g) + (i + i_1)p. \tag{6}$$

Similarly,

$$\pi = i_1 s + (i + i_1)p \tag{7}$$

Equating (6) and (7), and solving for i_1,

$$i_1 = i(a + g)/s. \tag{8}$$

Substituting for i_1 in (6),

$$\pi = i(a + g + p + (a + g)p/s). \tag{9}$$

Dividing by (5),

$$(\pi/\pi_o)_i = \frac{as + gs + ps + ap + gp}{s(p + g)}. \tag{10}$$

Substituting the restricting equation $a = p^2/(p + s)$,

$$(\pi/\pi_o)_i = p/s + 1. \tag{11}$$

Substituting for $(\pi/\pi_o)_i$ in terms of (4),

$$(E/E_o)_i = p/s + 1. \tag{12}$$

In this final equation the galvanometer resistance has disappeared, and no function of the deflection appears, so that the constant $(E/E_o)_i$ may be calculated for any proper combination of resistances. As Table V shows, this theoretical expression accurately predicts the experimentally observed energy ratios for a variety of combinations. It thus becomes a very convenient relation to employ when the energies are such that resistance patterns must be used.

TABLE V

Energy Ratios for Various Resistance Patterns

p	s	E/E_0	
		Obs.	Calc.
10.3	7	2.4	2.5
10.3	4	3.7	3.6
36	21	2.76	2.72
36	7	6.3	6.2
31.6	7	5.5	5.5
31.6	11	3.8	3.9
31.6	21	2.5	2.5
28.8	11	3.62	3.62

The fact that this relation (12) holds over a wide range of deflections justifies the assumption made in its derivation that the pile gives a linear ratio of incident energy to E.M.F. produced, and indicates that the decrease in sensitivity always observed at high deflections (Table IV) is a function of the galvanometer and not of the thermopile. This is further indicated by the fact that even an intense beam of radiation falling constantly on the pile does not affect its response when simultaneously used to measure another, much weaker source of radiation, provided that the galvanometer suspension be so turned that the same zero point is obtained for all readings.

5. Effects of Diverging Light

In many cases it is desired to measure the absolute energy of a beam of light all portions of which do not strike the surface of the thermopile at perpendicular incidence. For example, in the laterally diverging beam of light behind a monochromator slit, the edges of the beam may deviate by several degrees from the direction of the central portion.

It is absolutely essential that all of the light which passes through the thermopile slit should fall on the radiation receivers. Light which misses the receivers is a dead loss. To avoid this, it is essential that the slit of the thermopile be placed close to (within 1 mm. of) the sensitive junctions, and that it be slightly narrower than the radiation receivers. With thermopiles in which this is not possible, a laborious correction must be made, and even with this correction no large degree of confidence can be placed in the results. This requirement necessitates some reconstruction in most commercial thermopiles.

The magnitude of the errors involved is shown by the three types of thermopiles indicated in Fig. 3. The upper figures show the relative positions of the radiation receivers, window, and slit in each case. The lower diagrams show the relation between the sensitivity of the pile and the deviation from perpendicular incidence of the incident radiation. No. 1 was a vacuum thermopile, in which the slit was placed outside the vacuum jacket at a distance of 12 mm. from the junctions. This type of thermopile is useless for absolute energy measurements in diverging light. No. 2 was a line thermopile, with a slit of the same width as the receivers placed about 2 mm. in front of them, with the window in between. In this case it is possible to make corrections. No. 3, also a line thermopile, had receivers 3.3 mm. wide, and a slit 3.0 mm. wide (i.e., slightly narrower than the receivers) placed 0.8 mm. in front, with the window on top. With this arrangement no change in sensitivity is produced by divergence up to 5° in either direction from the normal.

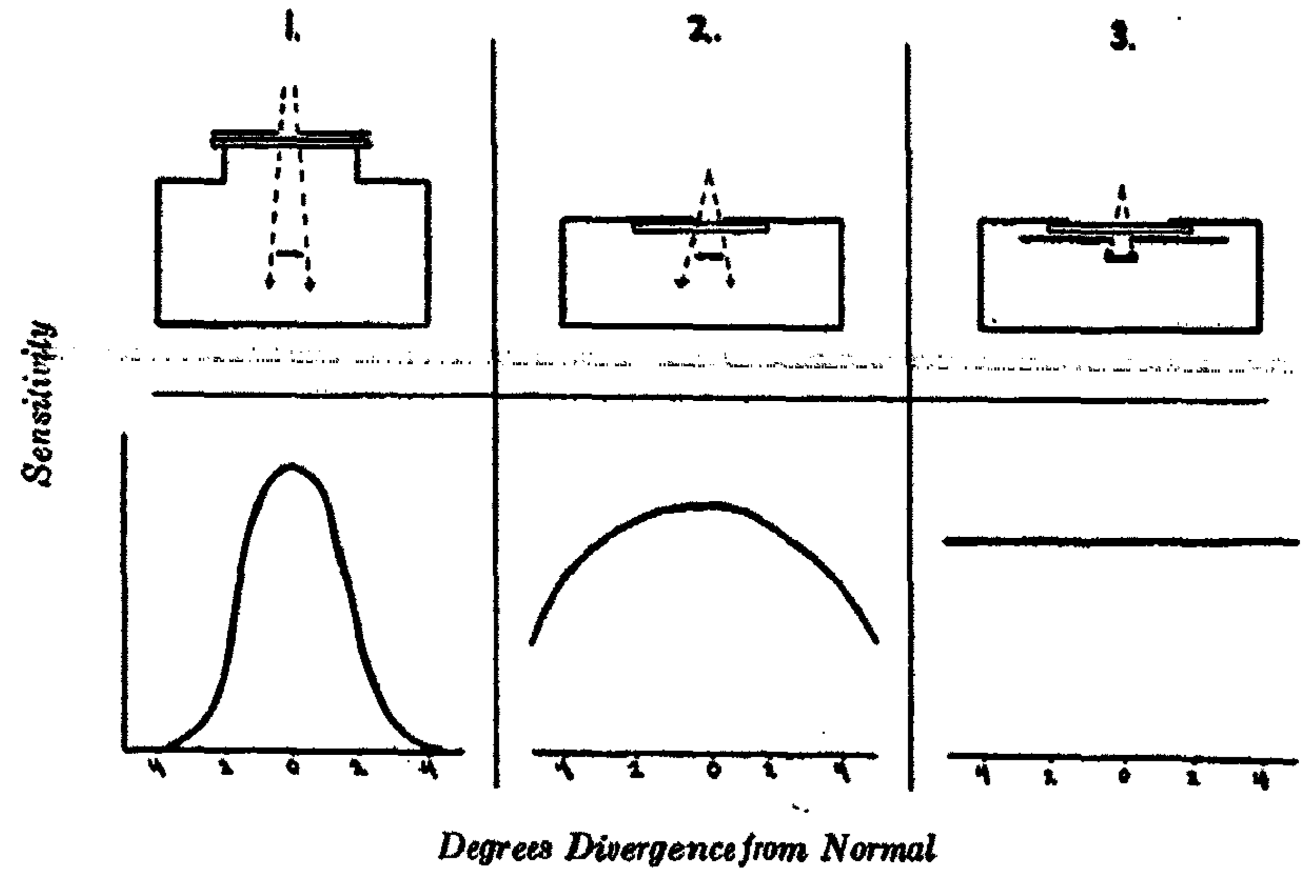

FIG. 3
Effects of Diverging Light on Three Types of Thermopiles.

Although these illustrations all involve line thermopiles, the same considerations exactly apply to surface thermopiles.

6. Surface Variations in Sensitivity

If a spot of light of limited area be moved over the surface of a thermopile, the response produced will be found to vary with the position of the spot, and the smaller the area of this spot, the larger become the variations. Of the thirteen thermopiles which the authors have investigated, not one has proven an exception to this rule.

In the case of line thermopiles of the construction described in section 1, the chief variations to be considered are those along the long axis of the sensitive opening. These may be investigated by mounting an auxiliary slit of adjustable width in front of and at right angles to the thermopile slit, and, placing the thermopile in a uniform beam of light, taking readings at intervals

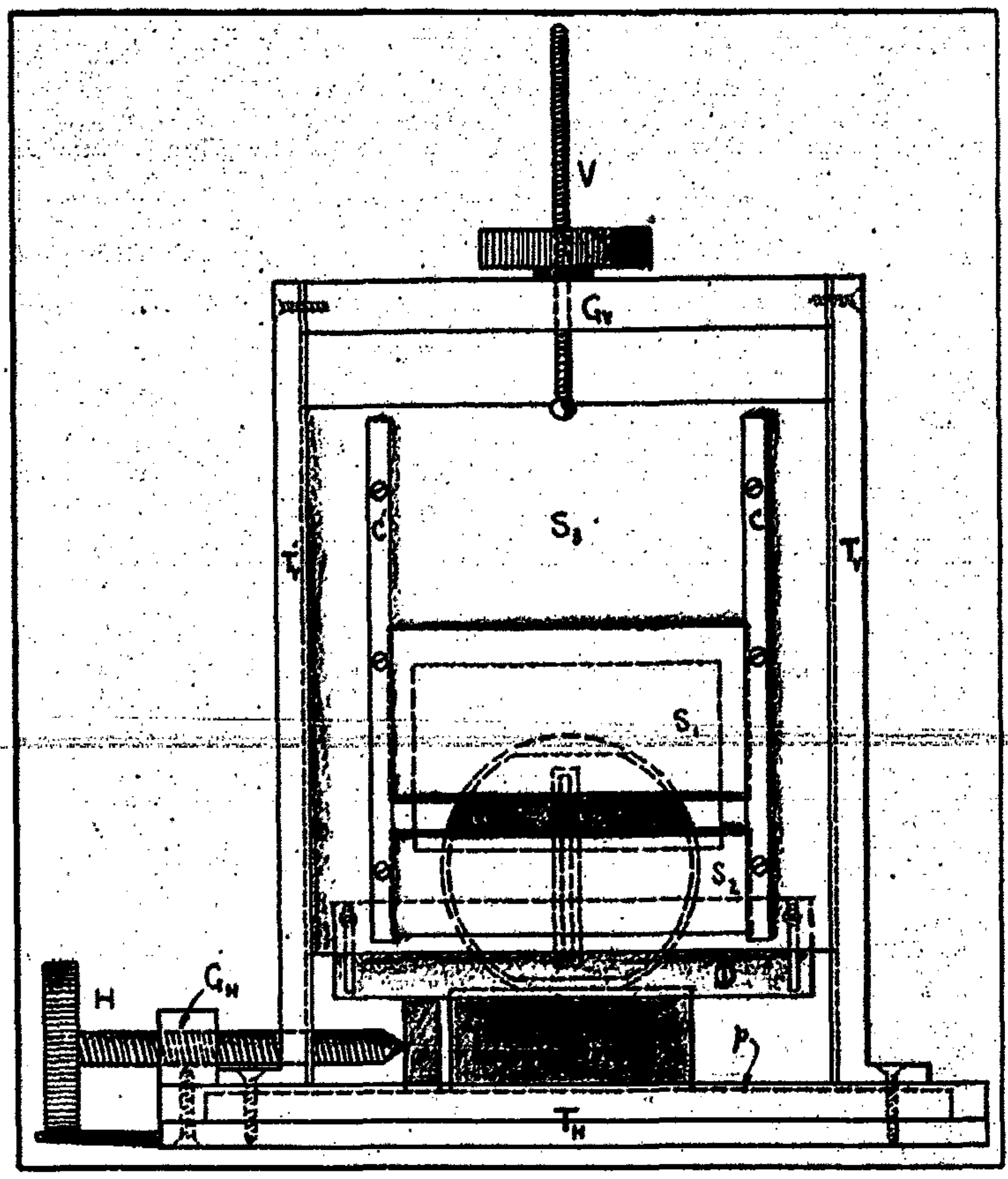

FIG. 4
Arrangement of Auxiliary Slit and Screw for Lateral Movement.

S_1,S_2 = Jaws of Auxiliary Slit.
T_V = Track for Vertical Movement of Auxiliary Slit.
V = Screw for Vertical Movement of Auxiliary Slit.
B = Base of Thermopile.
T_H = Track for Lateral Movement of Thermopile.
H = Screw for Lateral Movement of Thermopile.
P = Thermopile Face.

as the auxiliary slit is moved along the thermopile slit. The details of such an apparatus are shown in Fig. 4, while in Fig. 5, the observed variations for two typical line thermopiles, obtained when an auxiliary slit 2 mm. wide was moved along the surface, are shown as a function of the linear distance along the thermopile slit.

The magnitude of the error produced by these variations is obviously a function of the uniformity of the beam of light to be measured. The radiation from the standard lamps may be considered as filling the entire sensitive opening of the thermopile, with a uniform distribution of intensity. If the measured radiation has the same characteristics, no error will be produced.

If, however, it is of variable intensity distribution, or if it fills only a portion of the sensitive opening, a correction must be made.

In the case of monochromator beams, the intensity distribution is most uniform in the direction parallel to the monochromator slit. By placing the slit of the line thermopile parallel to the monochromator slit, and by adjusting relative lengths so that the light beam as it reaches the thermopile slit is exactly the length of the slit, it follows that the error due to surface variations will be reduced to a minimum.

The authors have made and confirmed the interesting observation that, although the pile sensitivity may vary by ±15% along the length of the sensitive opening, in most cases even an irregular beam falling on the whole opening is fairly accurately integrated and its absolute energy given directly by the pile. A rather extreme case of this is illustrated in Table VI. Here E_n represents the energy as calculated from the observed response as a 2 mm. wide auxiliary slit was moved at 2 mm. intervals along the thermopile opening while exposed to a uniform beam of light. E_{av} is the average value of E_n, and r_n, the relative sensitivity at each setting, is the ratio of E_n to E_{av}. Similarly, E'_n represents the observed response at different settings of the auxiliary slit when the pile was placed in a non-uniform beam. These values may be corrected for the surface variations in sensitivity by dividing by the corresponding value of r_n in each case, as is done in the last column of Table VI. The close agreement between the sums of the uncorrected and the corrected values indicates that the thermopile in this case "smooths out" the irregularities in the beam and acts as its own integrator. We have found this to be generally true. If the slit be only partially illuminated, the error naturally becomes larger, but even if the beam be only half the length of the slit, in few cases does the error become greater than 1 to 2%.

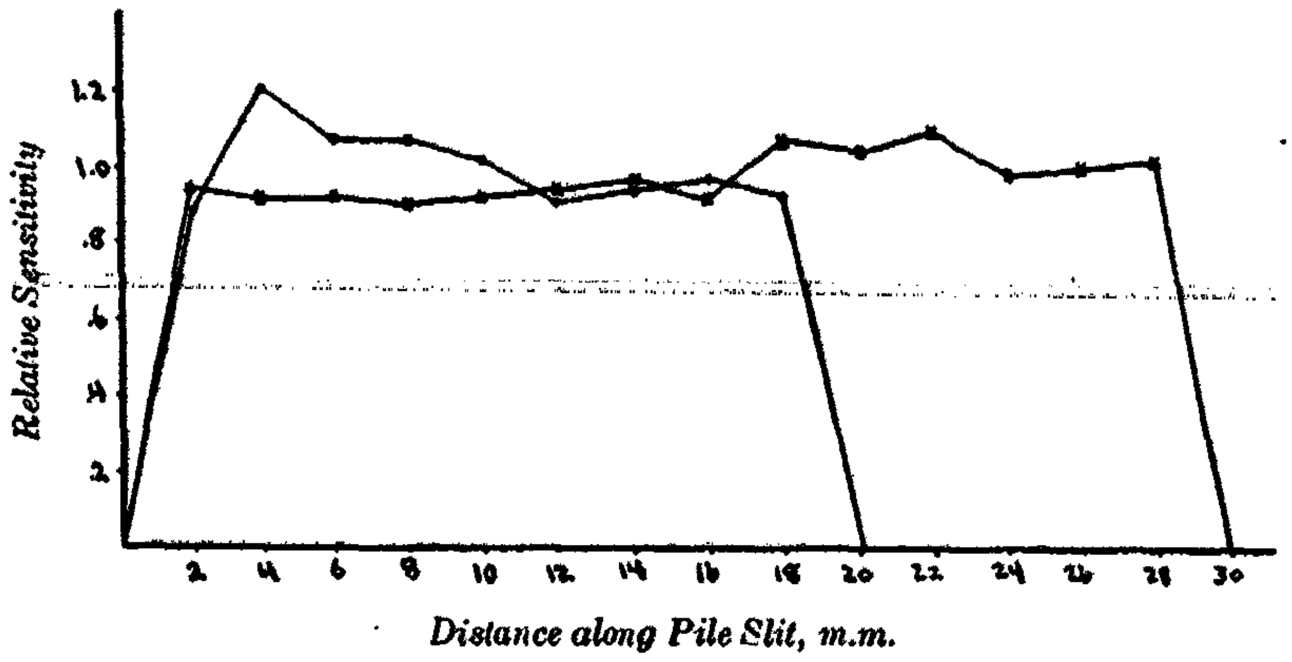

Fig. 5
Variations in Sensitivity along Surface for Two Thermopiles.

This encouraging result for line thermopiles cannot be said to hold for surface thermopiles. The three commercial surface thermopiles investigated by the authors showed such tremendous variations in surface sensitivity that

TABLE VI

Energy Correction by Vertical Integration

Setting	Uniform Beam		Relative	Non-uniform Beam	
n	E_n	E_{av}	Sensitivity r_n	E'_n	E'_n/r_n
1	78.6	89.2	0.88	141.9	161.0
2	107.9	"	1.21	142.3	118.0
3	95.3	"	1.07	95.3	89.3
4	95.3	"	1.07	55.9	52.5
5	91.1	"	1.02	40.1	39.3
6	81.7	"	0.91	45.8	50.5
7	83.9	"	0.94	62.1	66.1
8	87.0	"	0.97	56.9	58.4
9	82.8	"	0.93	48.2	52.0
				688.5	687.1

$$\text{Ratio}, \frac{E'_{obs.}}{E'_{corr.}} = \frac{688.5}{687.1} = 1.002$$

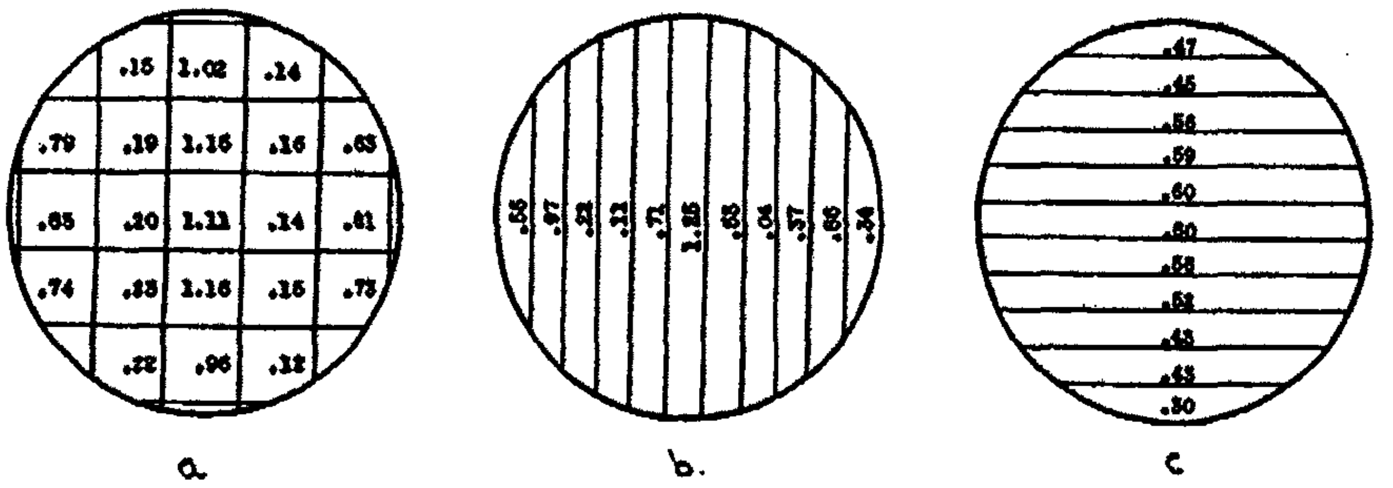

FIG. 6

Variations in Sensitivity over the Surface of a Surface Thermopile.

additional precautions become necessary. Fig. 6a is a typical example, and represents a surface thermopile with sensitive opening 22 mm in diameter, behind which 80 junctions were arranged in three rows. The pile was placed in a beam of uniform intensity, and a shield with an opening 4 mm. square moved across the face so that successive portions were exposed. The figures inserted in each portion represent the relative sensitivity, and were obtained by dividing the observed response by the area of that portion. Hence, the values given should be independent of the area exposed.

In Fig. 6b, a slit 2 mm. wide was moved at 2 mm. intervals across the face in a direction perpendicular to the rows of junctions, while in Fig. 6c the same slit was moved across the face in a direction parallel to the rows of junctions.*

As is clearly shown, the region about the center of each row of junctions is one of maximum sensitivity, while the region between each row is one of very low sensitivity.

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* We are indebted to Mr. R. A. Mortensen for these measurements.

Here, as with line thermopiles, if the thermopile be calibrated with standard lamp radiation which is of uniform intensity over the entire sensitive surface, and if it be used for measurement of a uniform beam which just covers the whole surface, no error will be introduced by the surface variations. But if the cross section of the beam is smaller than the sensitive opening of the pile, or if it is of non-uniform intensity, the error will become appreciable. For example, in one case the uncorrected use of the pile for an elliptical beam 20 mm × 10 mm in cross section resulted in an error of 22% in absolute energy values. Another example is given in Table VII, which shows the galvanometer deflection obtained when the thermopile was placed at different distances from the point of focus in a diverging beam, so that the area of the cross-section of the beam as it reached the pile was varied, while the total energy remained the same.

TABLE VII

Effect of Varying Cross-Section Area, Total Energy Constant

Diameter of Exposed Area	Galvanometer Deflection	Diameter of Exposed Area	Galvanometer Deflection
22.0 mm.	77.9	14.3 mm.	84.8
20.7	80.3	13.0	95.1
19.4	77.7	11.7	104.7
18.1	76.6	10.4	114.9
16.8	76.7	9.7	130.2
15.6	79.4	7.8	145.7

The error produced when the beam is 1/2 the diameter of the sensitive opening of the pile is about 45%.

Three methods of overcoming this error suggest themselves, viz.:

1. The radiation receivers may be covered with a disc of thin silver foil of the same size as the sensitive portion of the thermopile. The disc may be held in thermal contact with the junctions by means of a thin layer of shellac. The outer surface of the disc is blackened. Although this effectively reduces surface variations in sensitivity, it has the disadvantages of decreasing the total sensitivity of the pile and of prolonging the period, so that the swinging equilibrium method of reading cannot be used and it is necessary to thermostat the pile.

2. The thermopile may be converted to a line thermopile by shielding off all of the sensitive surface except a strip some 2 mm. wide along the center of the center row of junctions, and the energy of the beam integrated by the methods described in section 7. The thermopile so treated will not be as satisfactory as a simple line thermopile, because the unused junctions add unnecessarily to the resistance and materially increase the creep.

3. The cross section of a light beam from an ordinary prism monochromator usually shows a fairly uniform distribution of intensity in the direction parallel to the monochromator slit, and a shading off in intensity from center to edges in the lateral direction. Recalling that the thermopile is calibrated

in a beam of uniform intensity distribution which completely fills the sensitive opening, it is evident that errors due to surface variations will be minimized if:

a. The monochromator beam be adjusted to give maximum uniformity of intensity over its cross-section.

b. The thermopile be so turned that the direction of *maximum variation* in sensitivity of the pile shall coincide with the direction of *maximum uniformity* in intensity distribution of the light beam, in which case, of course, the direction of minimum variation in sensitivity will coincide with the direction of maximum variation in intensity distribution of the beam.

c. The thermopile be covered with a shield, set close to the junctions, of *exactly* the size and shape of the monochromator beam as it falls on the pile, and this shield be used both in calibration and measurement.

With these precautions, a surface thermopile will in many cases give reliable measurements of absolute energy. To illustrate, we have used a surface thermopile to measure the energy in a beam of λ 3130Å emerging from a prism monochromator by method (2) in which the pile was used as a line thermopile, and by method (3) in which the pile was turned on its side and the slit used in (2) replaced by a shield with opening of the exact size and shape of the beam.

A. Results by method (2). (see section 7 for method of integration.)

Micrometer Screw Reading (across beam)	Galvanometer Deflection	Micrometer Screw Reading (across beam)	Galvanometer Deflection
0 mm.	0.70	10 mm.	45.14
2	17.50	12	42.93
4	30.86	14	33.38
6	36.87	16	13.20
8	42.37	18	0.47

Sum = 263.4

Deflection with standard lamp = 16.77 cm.
Radiation from standard lamp = 8.47 ergs/mm²sec.
Dimensions of slit = 1.9 × 22.15 mm.
Micrometer screw interval = 2.00 mm.

$$\text{Radiation from monochromator} = \frac{22.15 \times 2.00 \times 8.47 \times 263.4}{16.77} = \mathit{5900}\ \text{ergs/sec.}$$

B. Results by method (3).

Deflection, trial 1. = 131.8 cm.
trial 2. = 131.9 cm.
Deflection, standard lamp = 71.7 cm.
Radiation from standard lamp = 8.47 ergs/mm²sec.
Area of thermopile opening = 380.7 mm².

$$\text{Radiation from monochromator} = \frac{380.7 \times 8.47 \times 131.8}{71.7} = \mathit{5930}\ \text{ergs/sec.}$$

Summary:

Result, used as line thermopile = 5900.
Result, used as surface thermopile = 5930.
Difference = 0.5%.

Even with the precautions observed in method (3) measurements with a surface thermopile must be checked with a line thermopile, as was done in the example just given, before any degree of reliance may be placed on the results. The surface variations in sensitivity of a surface thermopile are too complex to make a correction practicable, and in general, an ordinary line thermopile will be found more satisfactory for absolute energy measurements.

7. Methods of Integration

For the measurement, with a line thermopile, of the total energy, in absolute terms, of a beam of cross section larger than the sensitive opening of the thermopile, it is necessary to take readings at intervals over the cross section of the beam and then to properly integrate these individual values to give the total energy.

The process is much simplified if the length of the sensitive opening be equal to or slightly greater than the diameter of the beam in the direction of maximum uniformity of intensity distribution (section 6). The thermopile is mounted on a sliding base so that the long axis of the slit is parallel to this direction of maximum uniformity, and so that it may be moved across the beam in a lateral direction.[21,22]

If, now, the sliding base be equipped with a micrometer screw (Fig. 4) so that the readings may be taken at accurately known intervals, the procedure becomes still further simplified. If the intervals at which readings are taken are definitely known, it is only necessary to measure accurately the height or long dimension of the sensitive opening. Any desired width may be assumed for the sensitive opening, and the calculation is simplified by assuming the width is equal to the intervals through which the thermopile is moved. The following examples serve to illustrate this point.

Example A. Let us assume that a thermopile, with sensitive opening or slit exactly 1.5 × 20.0 mm. in size, is to be used to measure the total energy in a square beam 20 × 20 mm. in cross section, of uniform energy distribution. When exposed to any part of this beam so that the opening is fully covered, a deflection of 85 cms. is obtained. When exposed to standard lamp radiation of intensity = 7.0 ergs/mm^{2}sec., a deflection of 10.0 cm. is produced.

1. Take the thermopile slit width as 1.5 mm. The standard lamp radiation falling on the pile is 1.5 × 20 × 7 = 210 ergs/sec. As this produces a deflection of 10 cms., 1 cm. Δ = 21 ergs/sec. falling on the pile (neglecting changes in sensitivity with size of deflection), which is equivalent to 21 × 1/1.5 = *14 ergs/sec. per mm. of beam width.*

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[21] Villars: loc. cit., p. 330.

[22] W. G. Leighton and G. S. Forbes: loc cit., p. 3141.

a. Moving the thermopile across the beam with the micrometer screw, take 20 readings 1 mm. apart. Each reading gives a deflection of 85 cm. Then, the total energy in the beam = 85 × 14 × 20 = *23800* ergs/sec.

b. Take 10 readings, 2 mm. apart.

Total energy in beam = 85 × 14 × 2 × 10 = *23800* ergs/sec.

2. Assume the thermopile slit width is 1.0 mm. The standard lamp radiation falling on the pile then becomes by this assumption 1.0 × 20 × 7 = 140 ergs/sec., or 1 cm. △ = 14 ergs/sec. falling on pile = *14 ergs/sec. per mm. of beam width.*

a. Take 20 readings, 1 mm. apart.

Total energy in beam = 85 × 14 × 20 = *23800* ergs/sec.

b. Take 10 readings, 2 mm. apart.

Total energy in beam = 85 × 14 × 2 × 10 = *23800* ergs/sec.

3. Assume the thermopile slit width is 2.0 mm. The standard lamp radiation falling on the pile, by this assumption, becomes 2.0 × 20 × 7 = 280 ergs/sec., or 1 cm. △ = 28 ergs/sec. falling on the pile, which is equivalent to *14 ergs/sec. per mm. of beam width.*

a. Take 10 readings, 2 mm. apart.

Total energy in beam = 85 × 14 × 2 × 10 = *23800* ergs/sec. And so on.

In each case the same value is found for the No. of ergs/sec. *per mm. of beam width* required to produce 1 cm. deflection, regardless of what assumptions are made regarding the width of the thermopile slit, and the same value for the total energy is obtained, regardless of these assumptions.

Example B. In this example is presented the actual measurement of a beam of monochromatic radiation, of non-uniform intensity distribution laterally, as determined by two different thermopiles.

Pile No. 1, Slit 30.50 mm. long, assumed 3.0 mm. wide.

Readings taken at exactly 1 mm. intervals. $\frac{\text{Reading interval}}{\text{Slit width}} = \frac{1}{3}$.

Standard lamp calibration gave the following factors:

Deflection, cms.	Ergs/sec. falling on pile per cm. △	Deflection, cms.	Ergs/sec. falling on pile per cm. △
3	47.4	75	47.3
10	47.2	100	47.4
25	47.2	125	47.4
50	47.3	150	47.5

The readings across the monochromatic beam were:

Setting	Galvanometer Deflection	Ergs/sec. on pile	Setting	Galvanometer Deflection	Ergs/sec. on pile
1	3.5 cms.	166	8	99.5	4715
2	13.6	642	9	85.6	4049
3	33.1	1563	10	66.2	3132
4	60.6	2868	11	40.2	1900
5	84.7	4006	12	19.3	911
6	101.2	4795	13	6.0	284
7	106.3	5040	14	1.5	71
				Sum =	34142

Total energy in beam = 34142 × 1/3 = *11381* ergs/sec.

Pile No. 2, Slit 24.38 mm. long. Assumed 1.0 mm. wide, and readings taken at exactly 1 mm. intervals. $\frac{\text{Reading interval}}{\text{Slit width}} = 1.$

Standard lamp calibration factors:

Deflection, Cms.	Ergs/sec. falling on pile per Cm. Δ	Deflection, Cms.	Ergs/sec. falling on pile per Cm. Δ
3	20.9	75	21.2
10	20.5	100	21.4
25	20.6	125	21.5
50	20.9	150	21.6

Readings across monochromatic beam:

Setting	Galvanometer Deflection	Ergs/sec. on pile	Setting	Galvanometer Deflection	Ergs/sec. on pile
1	1.5 cm.	31	8	74.0	1568
2	13.0	267	9	57.2	1198
3	33.6	696	10	40.7	847
4	56.1	1174	11	18.7	384
5	73.7	1562	12	3.3	69
6	81.3	1728	13	0.7	15
7	81.7	1737			
				Sum =	11276

Total energy in beam = 11276 × 1 = *11276* ergs/sec.

$$\text{Ratio, } \frac{\text{Pile No. 1}}{\text{Pile No. 2}} = \frac{11381}{11276} = 1.009.$$

Thus the integrated values obtained by the two piles, for the total energy in the monochromatic beam, differ by only 0.9%.

In a beam of this sort, readings may be taken at intervals greater than 1 mm. without materially disturbing the accuracy. This may be demonstrated from the example just given. For either thermopile, if readings had been taken at 2 mm. intervals, the alternative values of those given above would have been obtained, and if readings had been taken at 3 mm. intervals, every third value would have been obtained.

Thus, for thermopile No. 1,

Readings at 2 mm. intervals (alternate values from above set)

	Total Energy in beam	Deviation from mean
Odd settings	$17008 \times \frac{2}{3} = 11339$	0.3%
Even settings	$17134 \times \frac{2}{3} = 11423$	0.3%

Readings at 3 mm. intervals (every 3rd value from above set)

	Total Energy in beam	Deviation from mean
Settings 1, 4, 7, 10, 13	*11490*	0.9%
Settings 2, 5, 8, 11, 14	*11334*	0.4%
Settings 3, 6, 9, 12	*11318*	0.5%

For thermopile No. 2, readings at 2 mm. intervals,

	Total Energy in beam	Deviation from mean
Odd settings	$5623 \times 2 = 11246$	0.3%
Even settings	$5653 \times 2 = 11306$	0.3%

The method just described may be termed the direct summation method of energy integration. For the greatest accuracy in the determination of total energy with a line thermopile, readings should be taken at short intervals, a curve of energy vs. setting drawn, and the area under this curve determined by graphical integration.

Fig. 7 represents a typical curve of this kind, for a beam of radiation issuing from a monochromator slit. The crosses represent thermopile readings. The direct summation method which we have illustrated in the preceding examples in effect takes the total energy of the beam as equal to the sum of the areas of the rectangles shown in Fig. 7, while the graphical method takes the energy as equal to the area under the curve. In the case illustrated, the area under the curve, or energy by graphical integration, was 9133 erg/sec., while the area of the rectangles, or energy by direct summation was 9130 erg/sec., a difference of 0.03%. If alternate readings (2 mm. intervals) are taken, the direct summation method gives 9175 erg/sec. for the energy, a difference of 0.46% from the graphical integration value.

The size of the interval between settings which may be used without material decrease in accuracy is a function of the width of the thermopile slit, the width of the beam, and the amount of variation in intensity across the beam. For narrow beams (less than 3 to 4 times the slit width) the interval should be equal to or less than the actual width of the thermopile slit. For relatively wide beams, of the order of ten times the slit width, if no sharp changes in intensity distribution occur, intervals of several times the slit width may be used.

These methods assume that the thermopile is capable of acting as its own integrator in the long direction of the slit; that is, that a beam of radiation of variable intensity distribution along the slit, or covering only part of the slit, gives the same deflection as it would if the same amount of radiation were evenly distributed over the entire sensitive opening. The limitations to this condition have been discussed in section 6. Precautions which must be observed in the direct integration of energy with a surface thermopile have also been discussed in section 6.

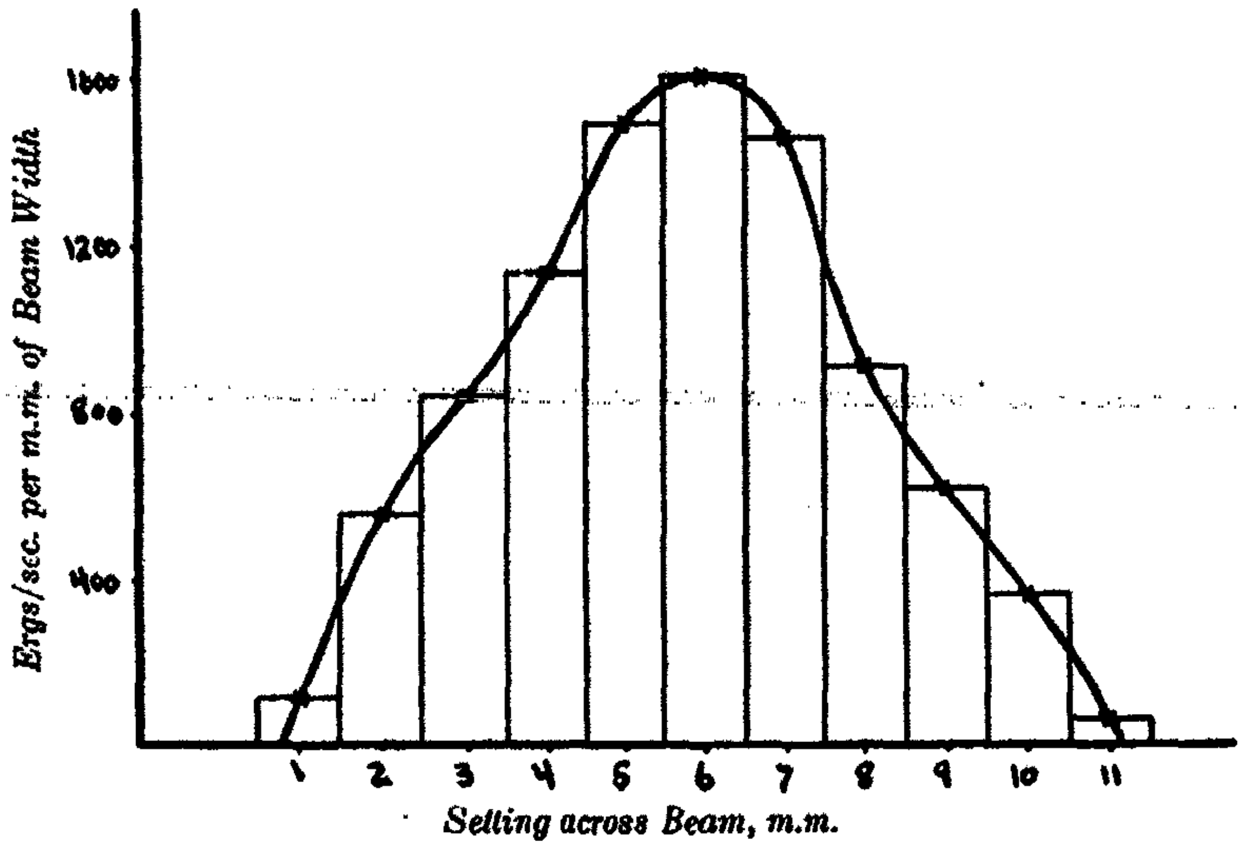

Fig. 7

Comparison of Graphical and Summation Methods of Energy Integration.

8. Variations in Sensitivity

Variations in sensitivity of the thermopile-galvanometer system with size of deflection, and with the position of the zero point on the scale, were discussed in section 3. The position of the zero point means, of course, the position of the mirror and moving coil with respect to the magnetic field. We have found the greatest sensitivity is produced when the mid-point of the swing finds the mirror parallel to the front face of the galvanometer, i.e., the coil parallel to the magnetic field. Changes from this point may produce as much as a 1% change in sensitivity for a 10 cm. shift in the zero point or mid-point of the swing on a scale 5 meters distant. On the other hand, quite considerable movements of the suspension adjustment, which may be necessary to obtain the same zero point for all readings, seem to be without marked effect on the sensitivity. To demonstrate, two carbon lamps were set up in front of a thermopile. Lamp A, fitted with a shutter, gave a deflection of approximately 29 cm., while lamp B, which radiated continually on the pile while burning, produced a deflection of 120 cm. Deflections caused by "A" were observed with and without "B" burning, the mirror being always set to give the same low point of swing.

Deflection, without B (before) = 29.35 cm.
Deflection, with B burning = 29.35
Deflection, without B (after) = 29.30

That is to say, with four times its own energy effect constantly flowing through the pile and galvanometer, the source A produced a swinging deflection identical with that produced when no energy came from B. Accordingly, it is not necessary to worry about outside radiation of constant intensity which falls on the pile during calibration or use.

Thermopile-galvanometer systems in general show a slightly different response from day to day to the energy from a standard lamp. Temperature and humidity seem to be chief among the factors causing these variations. Why humidity should play a part is not known. It should not be due to the absorption of infra-red radiation by the water vapor. The variations are no doubt due, to some extent, to changes in the standard lamp radiation, and in part to changes in the sensitivity of the recording system. Thus it is not possible wholly to correct for them, and the magnitude of these changes marks the limit of accuracy which may be expected from this method of absolute energy measurement. A partial correction may be made by calibrating a well seasoned carbon lamp, burning at definite amperage, by direct comparison with the standard lamps, and using this lamp as a secondary standard to check the thermopile sensitivity every day that measurements are made. Two secondary standards mounted side by side behind a shield, with another shield between and a shutter in front of each, gives a still more accurate check, as the danger of error due to individual variations in lamp intensity is lessened.

Coblentz[23] has suggested observation of the deflection produced by a known current generated by induction in the thermopile-galvanometer system as a means of checking the sensitivity. He also suggests the use of an induced current of known strength to attain the desired zero point and avoid drift. Usually the drift is too irregular to be avoided by any method of control except thermostating, but this suggestion is worthy of consideration in obtaining the desired zero point, if trouble should be experienced in obtaining it by moving the suspension.

In addition to day to day variations in sensitivity, slow changes extending over a considerable period are often experienced. Fig. 8 shows the variations in sensitivity of one thermopile-galvanometer system over a period of three years. Day to day variations were not included, the points given here representing average values. Experiments made over a period of several years also indicate that standard carbon lamps deteriorate somewhat both with use and age, and should be supplemented at intervals with new standards, at periods of not greater than three years.

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[23] Coblentz: Bur. Standards Bull., 9, 33 (1913).

In the "Instructions for using the Radiation Standards," issued with each radiation standard, the precaution is stated that "these lamps should be used as reference standards, and other lamps used as working standards. . ." This precaution cannot be over emphasized. It has been our experience, as illustrated in the following table, that a rate of deterioration of as much as 1/2% per hour of burning may be expected, at least during the first times the lamp is operated.

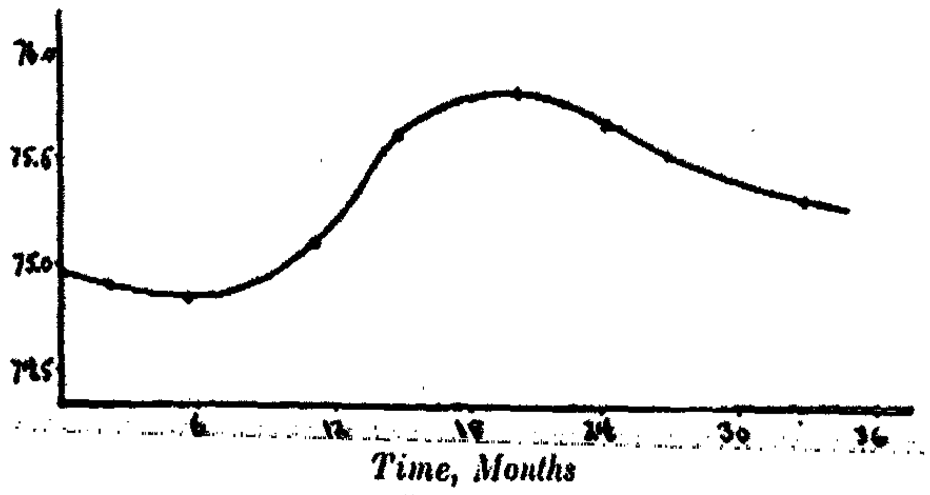

Fig. 8

Change in Sensitivity with Time.

TABLE VIII

Rates of Deterioration of Radiation Standards

Standard	*Time of Burning*	Deterioration	Rate per hour
C-39	9 hours	3.1%	0.35%
C-40	5 "	1.7%	0.35%
C-69	3/4 "	0.56%	0.75%
			Av. 0.5%

The above values were obtained as a result of a thorough inter-comparison of these three standard lamps, the calibration of C-69 being accepted as correct during the first few minutes of burning. The standards should best be used in pairs, so that any sudden deterioration of one lamp may be detected.

Summary

The measurement of the absolute intensity of visible and ultra violet light by means of a thermopile-galvanometer system has been discussed with particular reference to the conditions existing at the exit slit of a monochromator.

Various sources of error have been investigated, including those which are inherent in the galvanometer and in the thermopile, as well as certain sources of error created by employing a thermopile for the measurement of diverging light differing in wave length from that of the light from standard carbon filament lamps. Several important precautions have been emphasized, while, on the other hand, certain sources of error have been shown negligible. The advantages of linear thermopiles over certain surface piles of commercial make have been demonstrated.

The observation of galvanometer deflections under the conditions of "swinging equilibrium," successfully used by the authors and others at Harvard University and elsewhere, has been described. Details are included for integrating the total intensity of a light beam which presents a cross section greater than the active receiving area of the thermopile.

Three methods of extrapolating the thermopile-galvanometer sensitivity curve are outlined, none of these requiring the assumption of the inverse square law. A simple equation has been derived and verified experimentally which extends the calibration curve to include various resistance patterns useful at high intensities.

In concluding the authors wish to express their appreciation to Professor George Shannon Forbes of Harvard University under the direction of whom certain of the investigations in this paper were begun.

Thanks are also due Dr. Francis E. Blacet and Mr. Raymond A. Mortensen of Stanford University for some of the experimental data quoted, and to Dr. Curtis Haupt of Pomona College for his helpful criticism.

NOTE ON THE ABSORPTION OF OXYGEN BY SHEETS OF RUBBER

BY GEORGE A. LINHART

Very interesting and commercially very important experiments have recently been made in the Bell Telephone Laboratories by G. T. Kohman[1] on the absorption of oxygen by sheets of rubber. No attempt, however, was made to interpret the results mathematically. It is true, of course, that any empirical equation to express the course of the process would be merely a sort of garnish. It would be interesting, however, to show that these processes are not unique.

Some years ago the writer[2] published an equation which described the progress of many processes in the fields of chemistry, botany, biology, bacteriology, etc. The form of this equation is,

$$C = \frac{C_\infty \, b \, t^a}{1 + b \, t^a}$$

It is based upon the results of the tossing of a coin and represents in fact the law of uni-directional probability. The derivation of the equation is rather lengthy. In this note the equation will be applied to the process of the absorption of oxygen by sheets of rubber.

In the original article cited above the numerical data are not given, but they are so well shown on the graphs that the results may be read off to within one per cent. The amounts of oxygen, therefore, given in the table of this note are expressed in millimeters read off on the original graph, while the time is expressed in hours.

In Table I, C denotes the amount of oxygen absorbed at any time, *t*, and *a* and *b* are constants. Usually, *a* is the same for a given series of experiments even when the temperature varies, provided the other conditions are the same. However, in this note, the temperatures are the same, but the conditions under which each experiment is conducted are different, inasmuch as the sheets of rubber are subjected to different amounts of anti-agers. We should not, therefore, expect *a* to be the same for all experiments. Still, it does not differ to any great extent, as a glance at the table will show.

The equation in this note is of such nature that from the second differential with respect to (log *t*), we obtain the value for C_∞, since at this point (point of inflection with respect to log *t*), $C = C_\infty/2$. In many processes

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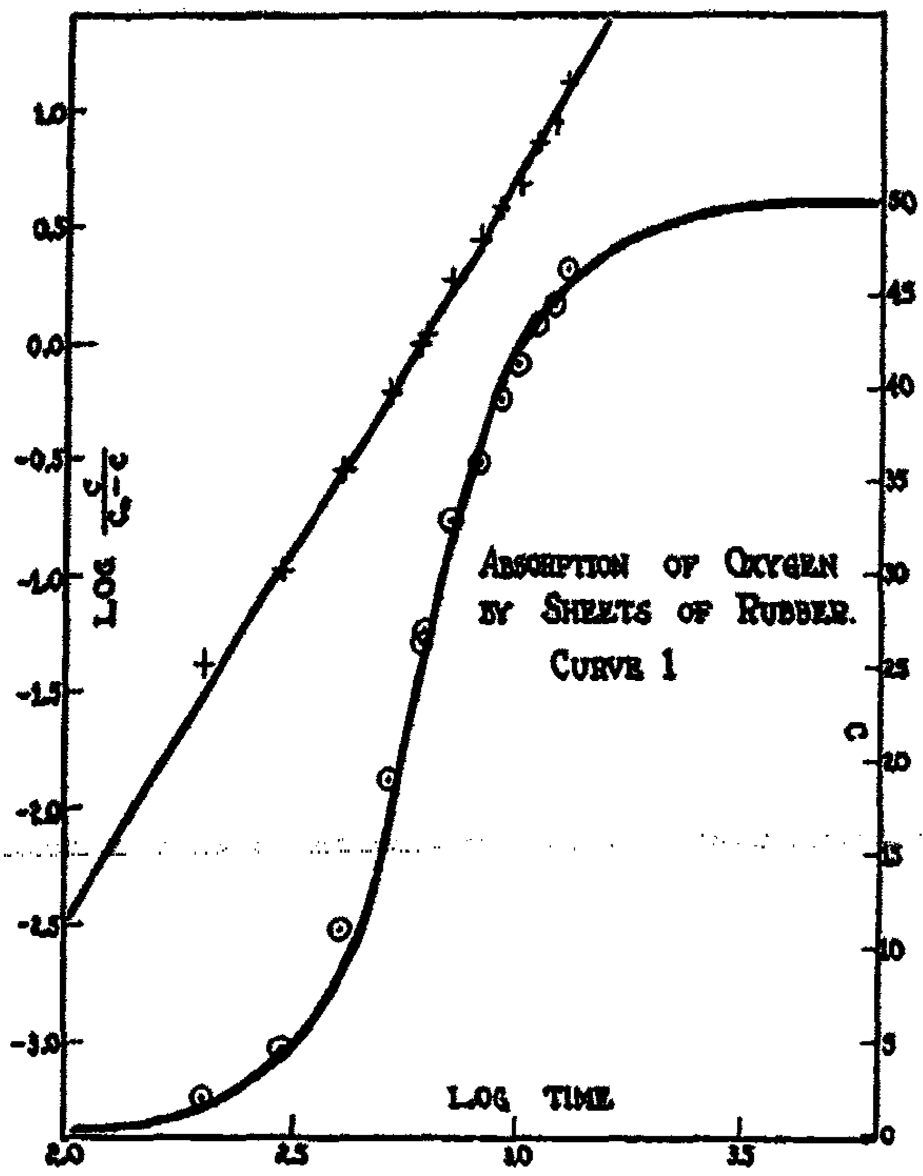
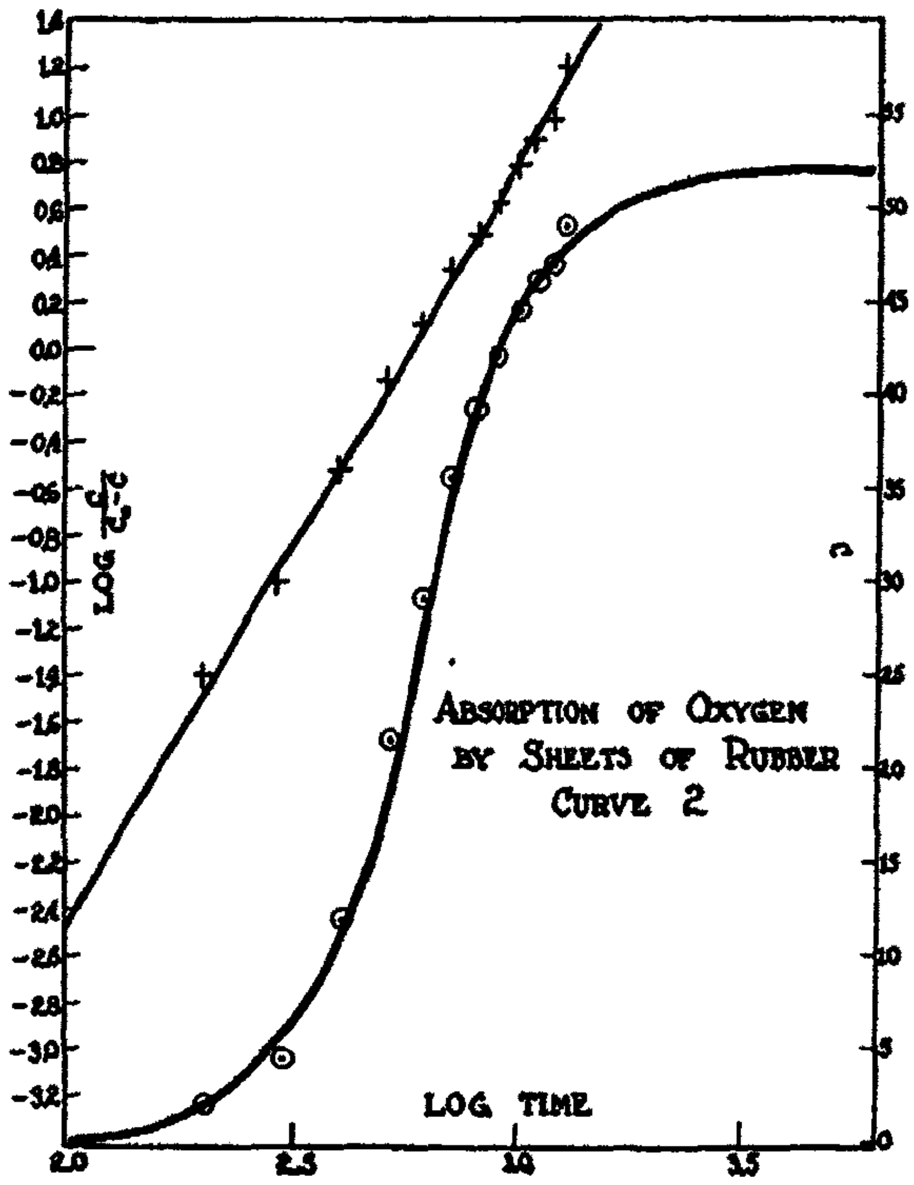
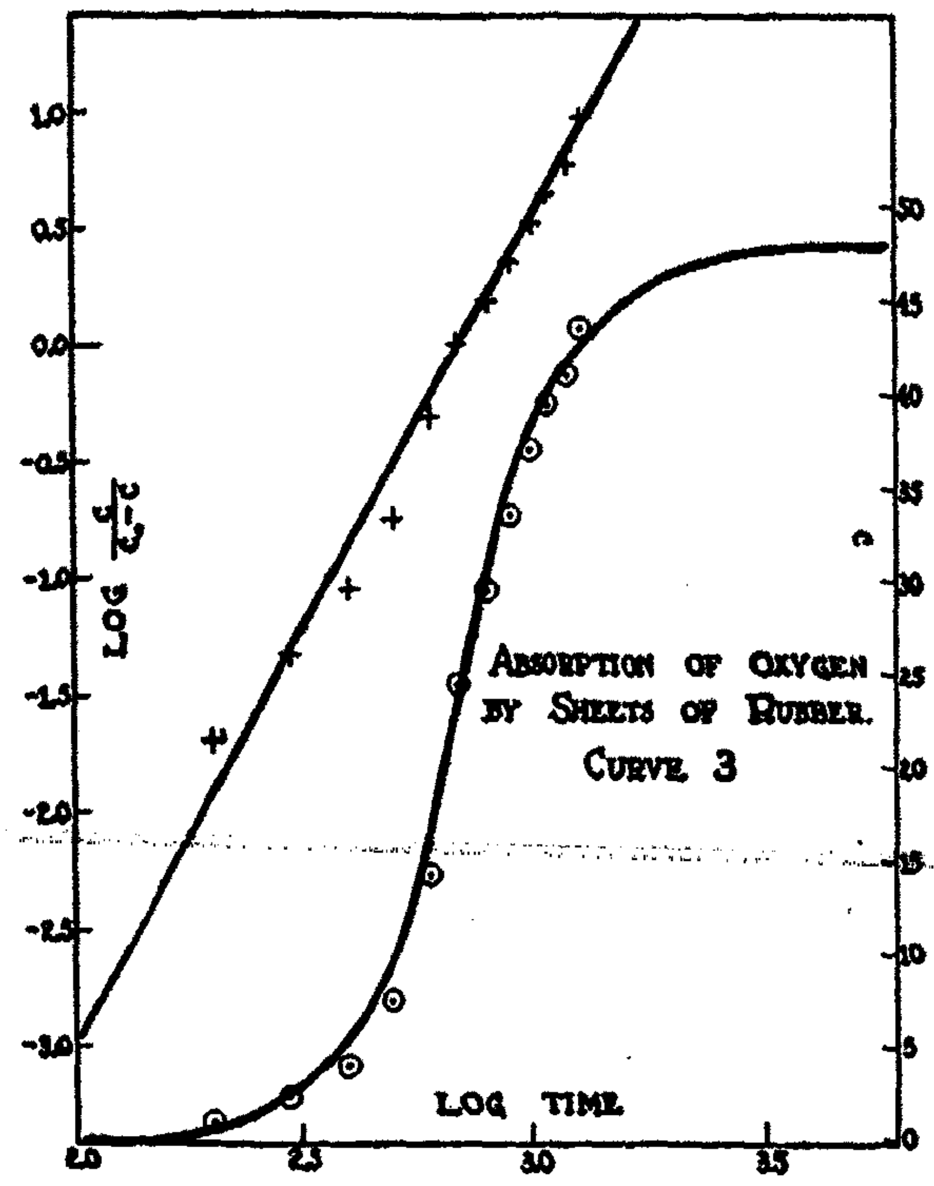
[1] J. Phys. Chem., 33, 226 (1929).

[2] Riverside Junior College Journal (Occasional Papers) May and June (1929); Eureka Junior College Journal (Occasional Papers) September (1921).


Absorption of Oxygen
by Sheets of Rubber.
Curve 1
LOG c/(c₀-c)
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
c
50
45
40
35
30
25
20
15
10
5
0
LOG TIME
2.0
2.5
3.0
3.5


Absorption of Oxygen
by Sheets of Rubber
Curve 2
LOG c/(c₀-c)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
-2.0
-2.2
-2.4
-2.6
-2.8
-3.0
-3.2
c
55
50
45
40
35
30
25
20
15
10
5
0
LOG TIME
2.0
2.5
3.0
3.5


Absorption of Oxygen by Sheets of Rubber.
Curve 3
LOG $\frac{c}{c_\infty - c}$
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
LOG TIME
2.0
2.5
3.0
3.5
c
50
45
40
35
30
25
20
15
10
5
0

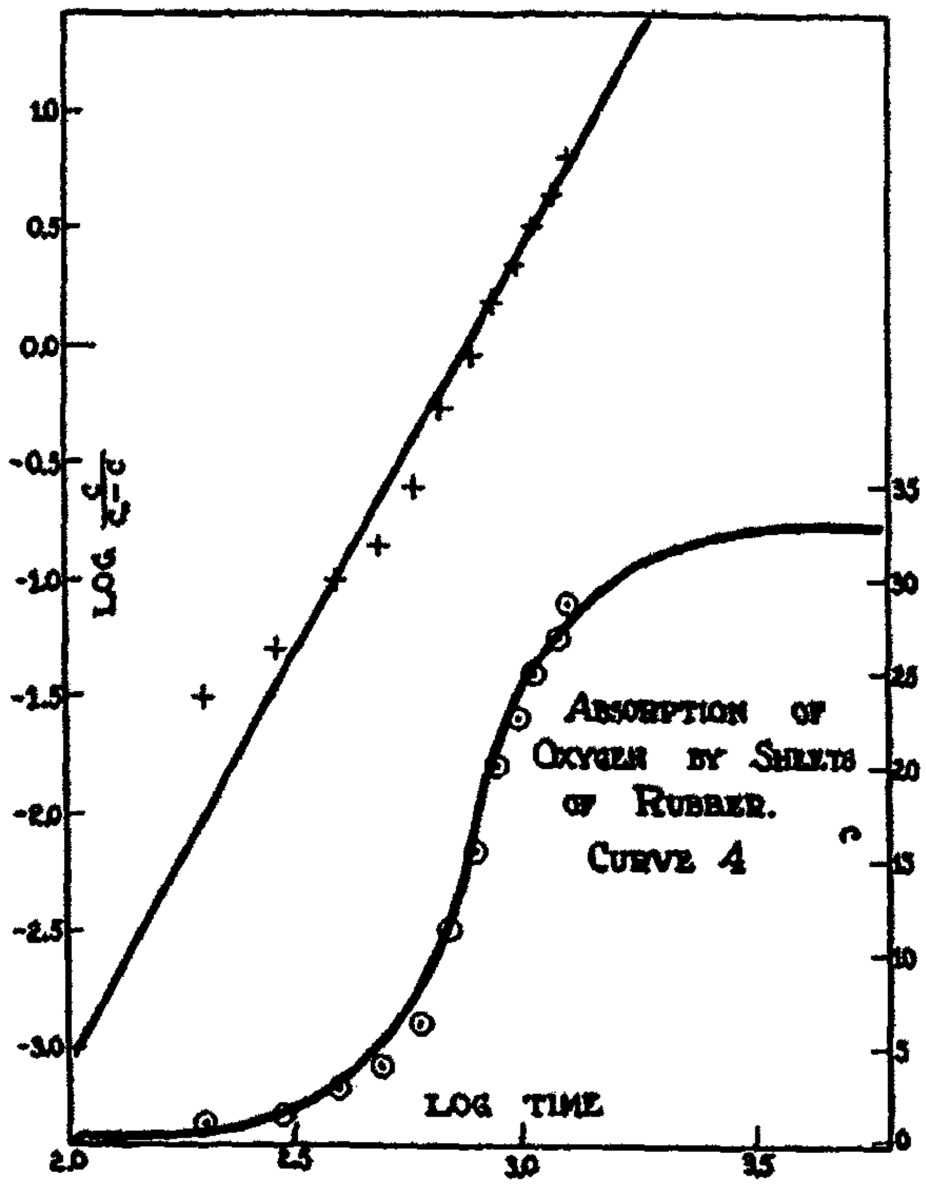

Absorption of Oxygen by Sheets of Rubber.
Curve 4
LOG $\frac{c}{c_\infty - c}$
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
LOG TIME
2.0
2.5
3.0
3.5
c
35
30
25
20
15
10
5
0

TABLE I

Figure 8 (original article)

	Curve 1		Curve 2		Curve 3		Curve 4	
	a = 3.296 log b = −9.15901		a = 3.257 log b = −8.99790		a = 3.490 log b = −9.94334		a = 3.465 log b = −10.01614	
t	C(obs.)	C(calc.)	C(obs.)	C(calc.)	C(obs.)	C(calc.)	C(obs.)	C(calc.)
200	2.0	1.30	2.0	1.6	1.0	0.6	1.0	0.3
300	4.6	4.55	4.6	5.5	2.3	2.3	1.6	1.2
400	11.0	10.36	12.0	12.0	4.0	5.8	3.0	3.0
500	19.0	17.65	21.5	19.9	7.5	11.1	4.0	6.1
600	26.5	24.50	29.0	27.5	16.0	16.8	6.5	9.6
700	33.0	31.15	35.5	33.8	24.5	22.6	11.5	13.5
800	36.5	35.90	39.0	38.6	29.5	29.1	15.5	18.9
900	39.5	39.55	42.0	42.0	33.5	33.6	20.0	20.6
1000	41.5	42.15	44.5	44.5	37.0	37.0	22.5	23.3
1100	44.0	44.00	46.0	46.3	39.0	39.6	25.0	25.4
1200	45.0	45.35	47.0	47.6	41.0	41.5	27.0	27.0
1300	46.5	46.35	49.0	48.5	43.5	42.9	28.5	28.3
..		50.00		52.0		48.0		33.0

C_∞ is known at the start. For example, in a chemical reaction, C_∞ is the initial concentration of the reacting substance. In other cases, C_∞ is only approximately known and is therefore given more accurately by the point of inflection. This is obvious from the symmetry of the curve where C is plotted against log *t*. The straight line plots are obtained by transforming the equation given above into the logarithmic form,

$$\mathrm{Log}\frac{C}{C_\infty - C} = a \,\mathrm{Log}\, t + \mathrm{Log}\, b$$

Considering the difficulty of controlling conditions in heterogeneous systems such as these, the agreement between the observed and calculated values is quite satisfactory.

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CATALYTIC OXIDATION OF n-PROPYL ALCOHOL

ALLAN R. DAY AND ABNER EISNER

It is a well-known fact that ceric oxide acts as a powerful oxidizing catalyst, expecially where the process is one of vapor phase oxidation. Ceric oxide is often recommended for this purpose in the combustion method for the determination of carbon and hydrogen. A better example is the great increase in light emissivity of thoria mantles when mixed with 0.9 per cent of ceric oxide. Swan[1] has shown that the greatest efficiency in the catalytic oxidation of electrolytic gas occurs at the same concentration of CeO_2 in ThO_2(i.e. 0.9 per cent). It is probable that the CeO_2 by acting as an oxygen carrying promoter brings about more rapid combustion and consequently higher temperatures.

In a previous paper[2] it was shown that this property was shared by the other rare oxides including the more basic La_2O_3. The great activity of these oxides makes it practically impossible to use them for the partial oxidation of organic compounds. Their use in small amounts with other less active oxidation catalysts should prove to be practical. A recent patent[3] has made use of such a combination. The patent recommends the use of a catalyst comprised of copper mixed with not more than 1 per cent of ceric oxide for the preparation of acetaldehyde from ethyl alcohol.

In a recent paper[4] the use of metallic silver alone and mixed with small amounts of samarium oxide as catalysts for the oxidation of ethyl alcohol was outlined. The results, while indicating that small amounts of the rare earth oxide did exert a promoter effect on the production of acetaldehyde, were scarcely definite enough to draw any general conclusions.

The results presented here on the oxidation of n-propyl alcohol confirm the conclusions of the above mentioned paper. It is shown that Sm_2O_3 when present in small amounts with silver does act as a promoter in the partial oxidation of n-propyl alcohol to propionaldehyde.

Experimental

The apparatus used was essentially the same as that used in the previous work. A wet-test meter was attached at the end of the absorbing train to measure the total volume of outlet gases. A gas-sampling tube was also placed in line and the mixed gases were analyzed in a modified Orsat. The temperature of the preheater was so regulated that the mixture of air and alcohol left the coil at a temperature of 125°C. Preliminary runs showed that the highest

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[1] J. Chem. Soc., 125, 780 (1924).

[2] Lowdermilk and Day: J. Am. Chem. Soc., 52, 3535 (1930).

[3] Brit. 344,554, Dec. 16, 1929.

[4] Day: J. Phys. Chem., 35, 3272 (1931).

aldehyde conversions were obtained at a thermostat temperature of 71°C., indicating this to be the optimum vaporization temperature for the formation of propionaldehyde.

The oxidation process was carried out by passing measured quantities of dry, carbon dioxide free air through the vaporizer containing the n-propyl alcohol which was maintained at constant temperature by means of a thermostat. The alcohol-air mixture was then passed through the preheater and into the catalytic chamber, the catalyst having been previously heated to 350°C. The heat of reaction was sufficient to maintain the reaction after it had once started. The catalyst temperatures were measured by means of a thermocouple. The latter was protected by means of a quartz jacket which was imbedded in the catalyst. The catalyst chamber (length 15 mm., diameter 17 mm.) was filled with the impregnated 12 mesh pumice. The length of each run was carefully timed by means of a stop watch. The products of the reaction were collected in absorption flasks which were part of the cooling system. The flasks were then emptied, rinsed and the resulting solution diluted to a definite volume. Aliquots of this solution were taken for analysis.

The following types of catalysts were employed:

A. 2.7928 g. of silver (equivalent to 3 g. of Ag_2O) deposited on 9 cc. of 12 mesh pumice.

B. 2.7894 g. of silver (equivalent to 2.99625 g. of Ag_2O) and 0.00375 g. of samarium oxide deposited on 9 cc. of 12 mesh pumice.

C. 2.7858 g. of silver (equivalent to 2.9925 g. of Ag_2O) and 0.0075 g. of samarium oxide deposited on 9 cc. of 12 mesh pumice.

D. 2.7788 g. of silver (equivalent to 2.985 of Ag_2O) and 0.015 g. of samarium oxide deposited on 9 cc. of 12 mesh pumice.

E. 2.7648 g. of silver (equivalent to 2.97 g. of Ag_2O) and 0.03 g. of samarium oxide deposited on 9 cc. of 12 mesh pumice.

It will be noted that catalysts B, C, D and E contain 0.125, 0.25, 0.5 and 1 per cent of samarium oxide respectively based upon $Ag_2O:Sm_2O_3$. The catalysts were prepared in the same manner as the catalysts used in the earlier work. Before use they were activated by heating in a stream of n-propyl alcohol vapor and air for an hour. Their efficiency as catalysts did not increase over longer periods of activation. Duplicate catalyst preparations were used for many of the runs and excellent check results were obtained, indicating the uniformity of the catalysts used.

Pure n-propyl alcohol (sp.g. $0.804^{20°}$) was used for all experiments. Approximately 15 g. of alcohol was passed over the catalyst during each run.

Determination of Propionaldehyde.—The aldehyde was determined by Ripper's bisulfite method.

Determination of Propionic Acid.—To a definite amount of standard sodium hydroxide solution was added a little barium chloride solution and a few drops of phenolphthalein. The resulting solution was then titrated with a portion of the condensate until the red color was discharged.

Gas Analysis.—The gas sample was transferred from the sampling tube to the Orsat and the usual methods employed for the determination of carbon dioxide, oxygen, alkenes and carbon monoxide.

The following table includes the results for the more important runs. Duplicate runs checked within 0.5 – 0.6 per cent (based on the aldehyde yields) and they are therefore not included in the table.

Table I

Thermostat Temp. 71°C

	Air Rate Liter/min.	Catalyst Temp. °C	Molar Conversions		
			Aldehyde %	Acid %	CO$_2$ %
A	0.94	505	71.5	3.5	4.2
	0.77	450	72.3	3.5	4.0
	0.65	395	72.1	3.3	3.4
	0.52	355	72.8	3.4	4.1
B	0.77	445	73.9	3.5	4.0
	0.65	390	75.4	3.4	2.7
	0.52	365	76.4	3.2	4.0
C	0.94	495	71.5	3.8	3.2
	0.77	455	72.6	3.6	4.1
	0.65	420	74.3	3.5	4.1
	0.52	380	75.5	3.4	4.2
D	0.94	498	70.0	4.1	2.0
	0.77	445	71.3	3.6	3.2
	0.65	385	74.0	3.6	2.7
	0.52	350	74.3	4.2	3.5
E	0.94	491	69.0	3.4	5.0
	0.77	460	71.4	3.3	3.8
	0.65	395	72.4	3.4	3.8
	0.52	345	73.1	3.6	4.5

Discussion of Results

There does not appear to be a careful study on the oxidation of n-propyl alcohol in the literature since the work of Orlov.[1] Orlov using metallic copper as the catalyst reported 50 per cent as his highest yield of propionaldehyde.

The results recorded in Table I show that the maximum conversions to aldehyde were obtained where the lower air rates were used. The results recorded for catalysts B and C show definite increases in the conversion to aldehyde. Even with catalyst D an increase in yield is shown where the lower

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[1] J. Russ. Phys.-Chem. Soc., 40, 203 (1908).

air rates were used (0.65 – 0.52 L/min.). It will be noted that while the yields of aldehyde were definitely higher, the amount of carbon dioxide formed did not appear to increase. This would indicate that small amounts of Sm_2O_3 do not promote complete oxidation under the conditions recorded in Table I, in spite of the fact that an excess of oxygen was present during the runs. At the thermostat temperature of 71°C. the ratio mols alcohol/mols O_2 was approximately 1/0.57-0.58 (theoretical 1/0.5).

At higher catalyst temperatures (higher air rate used) the samarium oxide did exert a promoter effect toward complete combustion. The amount of carbon dioxide increased with increase in temperature much more rapidly than in the cases where pure silver was used. However, one would not work at such temperatures if propionaldehyde were the desired product. The results in the table show that within certain catalyst temperatures (350-500°) the small amounts of Sm_2O_3 present did not enhance or produce any undesirable side reactions. The amounts of carbon monoxide and alkenes formed were not included in the table as they were in every case negligible quantities.

Summary

1. The optimum conditions for the oxidation of n-propyl alcohol to propionaldehyde, using metallic silver on 12-mesh pumice, have been determined.

2. It has been shown that the presence of small amounts of samarium oxide increases the yields of propionaldehyde.

3. Higher yields of propionaldehyde have been obtained by a one-step vapor phase oxidation of n-propyl alcohol than have been previously reported from similar methods.

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THE VARIATION OF THE SURFACE TENSION OF AQUEOUS SOLUTIONS OF CERTAIN COMPLEX ORGANIC SUBSTANCES WITH TIME

BY J. C. GHOSH AND MADHAB CHANDRA NATH

The growth of films on the surface of aqueous solutions of a number of organic dyes was first recorded by Rhode.[1] His method consisted in the suspension of a sheet of metal in the dye solution by a fine wire. Torsion was applied until the surface was broken. The angle of torsion was a measure of the thickness of the film, and the rate at which the torsion necessary for tearing up the film increases with time is a measure of the rate of growth of film. He concluded that the dyestuffs which in solution, show photo-electric effect, have the characteristic property of forming a film on the surface, the maximum photo-electric effect being obtained when the film-thickness becomes a maximum.

It is also possible that aqueous solutions of organic complex substances may show the gradual formation of surface-film and it appears that if a method could be devised for recording the variation of surface tension of aqueous solutions of these substances with time, some insight can be gained into the kinetics of the molecular processes which are responsible for producing a film on the surface. It is to be expected that with the growth of film on the surface, the surface tension of the solution should gradually diminish, arriving at a constant value when the growth of the film is at an end.

Indications are not wanting that the nature of the surface of a solution immediately after it is created is different from that of the surface after a certain time has elapsed and conditions of equilibrium have been established. This is specially true in the case of hydrophyllic sols like sodium oleate, gelatine, egg-albumin, saponin, etc. For these sols investigations of Rayleigh[2] and Berczeller[3] have shown that the surface tension measured by a dynamic method (where the surface tension of a freshly created surface is measured) is always considerably greater than that measured by a static method. The variation of surface tension of certain colloidal solutions with time has been measured by du Noüy,[4] and Johlin.[5]

According to Freundlich, "the method of adhesion rings is to be particularly recommended for determining the surface tension of any plane liquid surface, which it is desired to disturb as little as possible." In the experi-

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[1] Ann. Physik, (4) 19, 935 (1906).

[2] Proc. Roy. Soc., 47, 281 (1890).

[3] Intern. Z. physik. chem. Biol., 1, 124 (1914).

[4] Phil. Mag., [6] 48, 264 (1924).

[5] J. Phys. Chem., 29, 1129 (1925).

ments to be described in the following pages, the ring-method has been suitably modified to yield values of surface-tension of a surface at different intervals of time, not only without actually breaking the surface but also without disturbing the surface to any considerable extent.

Experimental Arrangement and Procedure

To obtain accurate and satisfactory results it is necessary to have a balance, in which the weights required to counterbalance the force of surface-tension would be continuously but very slowly increased. From one end of the balance-beam, (Fig. 1) was therefore hung a fine gold-chain; the other end of this chain was fastened to a vertical rod which could be moved up and down by means of a rack and pinion arrangement. A pointer attached to this vertical rod reads off its position against a vertical scale. The weight required to counterbalance the chain in different positions, was determined. The balance-pan at 'A' was replaced by an exactly circular flat basin 'B' made of thin nickel plate. Suspension was effected by means of a copper rod soldered to the centre of the plate. The basin was so made that the lower rim which was to touch the liquid surface, lay exactly in a horizontal plane when suspended from the hook 'A.' From time to time, the nickel basin was suspended just over a perfectly horizontal plane surface to observe if the lower rim remained horizontal, and distortion, if any, was set right.

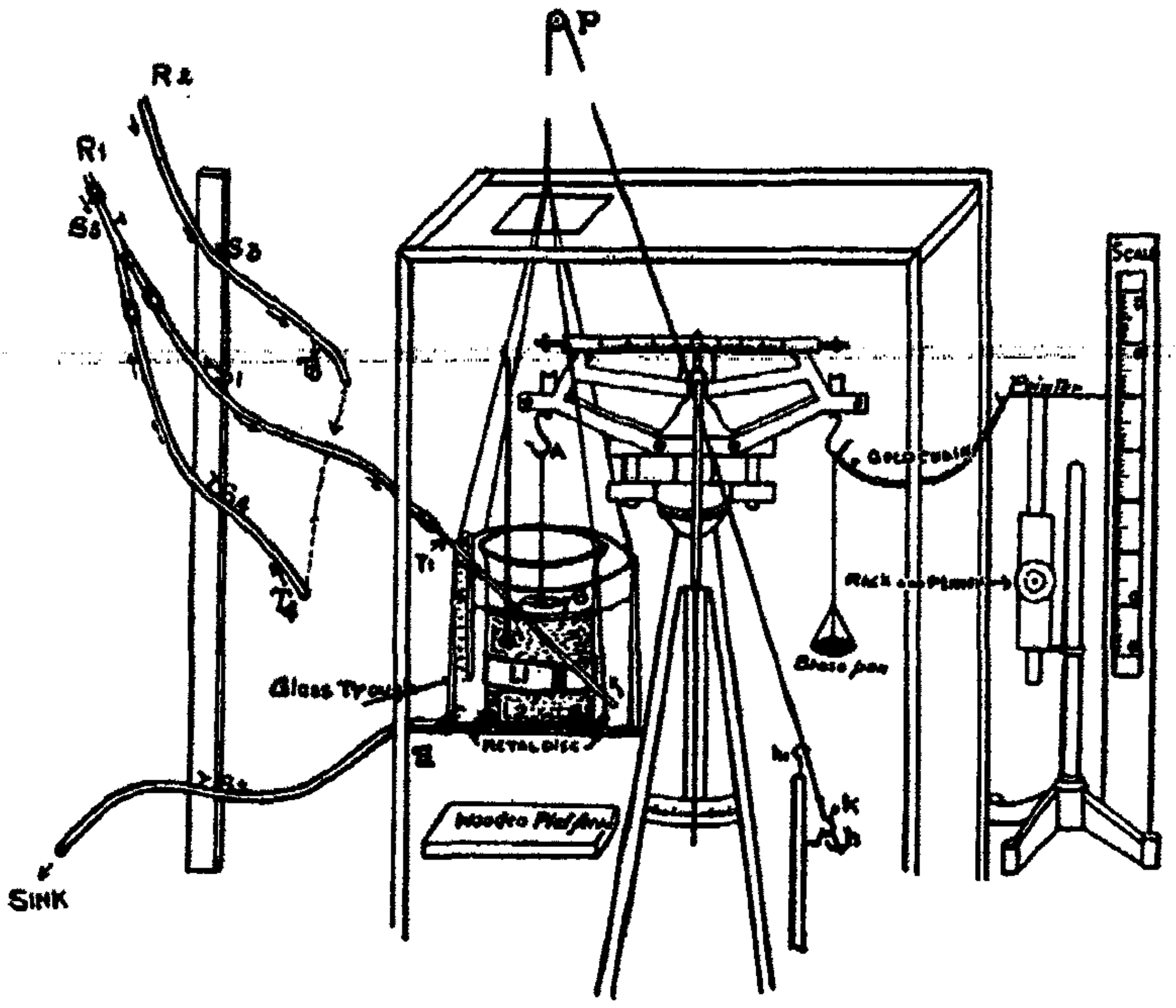

Fig. 1

Change of temperature has a great influence upon the actual value of surface-tension of a liquid or a solution; and sometimes it is likely to happen that the temperature of the room fluctuates more than 2°C during the course of the experiment extending over eight or nine hours. At room-temperature evaporation also takes place at a considerable rate from a liquid surface, whose level thus falls continuously. Hence it was absolutely necessary to devise some means by which the rate of evaporation could be very considerably reduced and the temperature of the solution of which the surface-tension was to be measured, could be kept fairly constant.

The solution for investigation was, therefore, kept at a temperature about 5°C below that of the room by circulating cold water through a glass trough in which the beaker containing the solution whose surface-tension is to be determined, was immersed. The temperature as well as the level of the water surface in the outer trough were kept constant by carefully regulating the flow of cold water by means of screw-clips S_1 and S_2. A lead plate L_1 was fixed round the beaker and another, L_2 interposed between the beaker and the glass-trough to avoid movement of the former in the trough. As it is neither possible nor safe to handle the whole trough, with a view to bring the solution in the beaker just beneath the inverted basin, a suspending arrangement was taken recourse to; and when pulled by the end K of the string, the trough as a whole (as in the cut) could be raised up to the desired level and kept fixed by means of the hook h.

After raising the beaker to its proper position, the balance-beam was freed from arrestment and when oscillation had ceased, the solution was poured in by means of a pipette and the beam brought to arrestment. This procedure was repeated until the lower rim of the basin completely touched the surface of the solution. Weight was then added to the small pan on one end of the beam till it was a little less than that required to counterbalance the weight of the basin and the force of surface-tension at the other side. The final addition of weight was made by lowering the chain. The pointer of the balance remains almost motionless until a critical weight has been added, when it begins to move to the left, indicating that the weight has counter-balanced the force of surface-tension and the weight of the basin. The motion is slow and the ring is not suddenly torn off the surface of the solution. The weight on the pan and the position of the chain,—as indicated against the pointer,—in the vertical scale, were recorded. When the pointer was just moving towards the left, the beam was brought to arrestment, to prevent the basin from being torn off the surface, and the weight was slightly diminished by raising the chain. The surface-tension was thus measured without actually breaking the surface and with the minimum disturbance of the molecular arrangement of the surface.

All the precautions necessary for obtaining accurate results, were taken. For example, conductivity-water was always used, the glass vessels and the nickel basin were washed alternately with dilute acid and alkali, finally with conductivity water, and the basin was dried inside a desiccator containing "Sulphuric Acid." Kahlbaum's pure substances were used in every case.

Theoretical

(a) The surface-tension was calculated as follows:—

Surface-tension of the solution $= \partial \times W_2/W_1$

where ∂ = Surface-tension of water at the temperature of the experiment.

W_2 = Additional weight required to raise the basin from the surface of the solution while just touching.

W_1 = Additional weight required to raise the basin from the surface of pure water.

In the case of aqueous solutions of some substances, the surface-tension diminished with time, attaining a constant value after some four or five hours.

(b) General classification of solutions:—

On the basis of the experimental results recorded here and from the previous work in this laboratory, it is possible to classify solutions in three types:—

Type A:—True solutions of simple molecules whose velocity of diffusion is fairly large, and the equilibrium-concentration at the surface is reached too quickly to be detected by this method of measuring surface tension.

Type B:—Solutions consisting mostly of multi-molecular aggregates having small velocities of diffusion. In such a solution we may consider that an equilibrium exists between the large multimolecular aggregates and the simple molecules thus

$$n.M \rightleftarrows M_n$$

where M represents simple primary molecules and M_n the molecular aggregates. When the solute exists mostly as multimolecular aggregates, the concentration of simple primary molecules is given by $C^{1/n}$ where C is the stoichiometric concentration. We assume that these simple molecules can only move up to the surface from the bulk of the solution. In the case of such a solution, on the air-liquid interface there is a competition for places on the surface between the solute and the solvent molecules. The kinetics of the formation of a solute film on this interface may be developed as follows:

The rate of diffusion of the solute molecules from the bulk of the solution into unit area of the surface may be considered to be proportional to the concentration of the simple solute molecules i.e. C. Now only a fraction of these solute molecules can condense on the surface. Those solute molecules which diffuse into the parts of the surface which are already covered with the solute are all reflected back. If at any time, x be the surface concentration of the solute molecule, and B be the area of the surface actually occupied by each solute molecule, then the uncovered surface per unit area is $1-Bx$. The rate of condensation of solute molecules on the surface is therefore

$$= K_1C^{1/n}. \alpha (1-Bx) \qquad (1)$$

where α is the accommodation coefficient. It is probable that the smaller number of places held on the surface by the solvent molecules, the more tenaciously will those places be held by them, and therefore the accommodation coefficient will diminish as the fraction of the surface covered by the solvent molecule diminishes.

or
$$\alpha = K_2 (1 - Bx)$$

Rate of condensation of solute molecules from the bulk of solution on the surface is given by

$$K. C^{1/n}. (1 - Bx)^2 \tag{2}$$

The rate of removal of solute molecules from the surface to the bulk of the solution is given by

$$X/T_1 \tag{3}$$

where T_1 is the average length of life of the solute molecules on the surface. If there are no forces of lateral cohesion between the solute molecules on the surface film, the value of T_1 remains constant for all surface concentrations of the solute at the same temperature. But, as a rule, it happens, that the forces of lateral cohesion have considerable magnitude and these forces will increase as the surface concentration of the solute molecules increases, or as the fraction of the unit area occupied by the solvent molecules diminishes. We may reasonably assume that

$$\frac{\Delta T + T_o}{T_o} = \frac{1}{1 - Bx}$$

where T_o is the average life when the surface concentration of solute is very small and ΔT is the increment in the average life when the surface concentration is x. Hence rate of removal of solute molecules into the bulk of the solution is given by

$$K'x (1 - Bx) \tag{4}$$

Therefore the rate of increase of surface concentration

$$dx/dt = K C^{1/n}(1 - Bx)^2 - K'x (1 - Bx) \tag{5}$$

or
$$\frac{1}{(1 - Bx)^2} \frac{dx}{dt} = K C^{1/n} - \frac{K'x}{1 - Bx}$$

or
$$\frac{d \dfrac{x}{1 - Bx}}{dt} = K C^{1/n} - K' \frac{x}{1 - Bx} \tag{6}$$

when equilibrium has been attained

$$K C^{1/n} = K' \frac{x_{t_\infty}}{1 - Bx_{t_\infty}} \tag{7}$$

Now, as is well known, the gas laws may be applied to the unimolecular surface layer, and a general equation

$$F (A - B) = iRT \tag{8}$$

true for all solutions, may be obtained by combining the equation of Volmer[1]

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[1] Z. physik. Chem., 115, 255 (1925).

$$F\,(A - B) = RT$$

and the Bancroft equation[1]

$$F - A = iRT,$$

F = the two dimensional gas pressure = $\sigma_{\text{solvent}} - \sigma_{\text{solution}}$
A = $1/x$; B is the area actually occupied by a molecule

or

$$F = \frac{iRT}{\frac{1}{x} - B} = iRT\frac{x}{1 - Bx} \tag{9}$$

Combining (9) with (6) we obtain

$$\begin{aligned} \frac{1}{iRT}\cdot\frac{dF}{dt} &= K\,C^{1/n} = K'\,F \\ &= K'\frac{x_{t_\propto}}{1 - Bx_{t_\propto}} = K'\,F \\ &= K'\,F_{t_\propto} - K'\,F \end{aligned} \tag{10}$$

or

$$dF/dt = iRT\,K'\,[F_{t_\propto} - F]$$

or

$$2.3\,\log_{10}\frac{F_{t_\propto} - F_{t_1}}{F_{t_\propto} - F_{t_2}} = K_1\,[t_2 - t_1] = 2.3\,\log_{10}\frac{\sigma_{t_1} - \sigma_{t_\propto}}{\sigma_{t_2} - \sigma_{t_\propto}} \tag{11}$$

where $K_2 = iRT\,K' = \dfrac{iRT.K.C^{1/n}}{F_{t_\propto}}$

and σ_{t_1}, σ_{t_2} and $\sigma_{t_\propto}$ are the surface tensions of the solution at times t_1, t_2 and $\propto$.

$\sigma_{t_\propto}$ is the value of surface tension obtained by extrapolation from graphs giving the variation of surface tension with time.

The values of K_1 as calculated between 1 and 2, 1 and 3, 1 and 4, 1 and 5 and so on are shown in tables in the experimental results. It will be noticed that for each substance the value of K_1 is practically constant for each experiment. K_1 also does not vary much with dilution indicating that $C^{1/n}/F_{t_\propto}$ is approximately constant.

Solutes belonging to type B are therefore, intermediate between truly crystalloidal and completely colloidal solutions.

Type C:—Colloidal solutions:—

Du Noüy has observed a continuous logarithmic diminution of surface tension of normal rabbit serum solutions with time. The measurements were made by means of his tensiometer and extended over a period of two hours. In the case of sodium oleate solutions he found a very rapid drop of surface tension in the course of ten minutes. During this period, the rate of diminution of surface tension with time had a constant value. According to him, the surface tension of sodium oleate solution remains practically stationary after fifteen minutes. In our experiments the surface tension was first measured about five minutes after the solution had been poured in the

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[1] J. Phys. Chem., **31**, 1504 (1917).

measuring vessel, and then a series of readings were taken at intervals of about an hour. We have found in the case of the colloidal solutions that we have studied, that the variation of surface tension with time is not regular—maximum and minimum being often observed.

It is also interesting to note that Teague and Buxton[1] have classified the dyestuffs into three similar divisions as a result of dialysing experiments.

(1) Schwach colloidal—of which methylene-blue is a representative.

(2) Mässig and höch colloidal—e.g. neutral red, which cannot be dialysed at room-temp. but is very quickly dialysed at 37°C.

(3) Vollständig colloidal—e.g. Congo-red.

Our classification is more or less similar to this, though the border lines between the different types are somewhat different.

Experimental Results

Type A:—Table I shows the results obtained for the surface tension of pure water and aqueous solutions of some substances of Type A, investigated at various time "t" (in minutes) reckoned from the time at which the first observation was made. The value of surface tension of solutions cannot be determined just at the moment a fresh surface is created. Hence the value of surface-tension given against the time "o" is the initial value obtained in every case.

TABLE I

Substance and temperature	Conc. in gr. mols. per litre	t_1	σ_{t_1}	t_2	σ_{t_2}
1. Water					
21°C.	—	0	72.36	185	72.36
2. Fuchsine red					
21°C.	.001	0	72.43	129	72.41
3. Salicylic acid	.01	0	60.64	281	60.50
21°C.	.02	0	59.25	252	59.02
4. Alizarin in caustic soda	.0005	0	72.31	231	72.47
21°C.	.001	0	71.40	285	71.30

Type B:—

Behaviour of solutions falling under the type B are recorded in Table II. The significance of this value of "K," has already been explained; the limiting values of surface tension σ_{t_∞} were obtained by extrapolation.

Type C:—

Peculiarities were observed while studying the aqueous solutions of Congo red. It is a lyophylic sol and does not dialyse through dialysing

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[1] Z. physik. Chem., 60, 479 (1907).

TABLE II

Substance and temp.	Conc. in gr. mols per litre	t_1	σt_1	t_2	σt_2	t_3	σt_3	t_4	σt_4	σt_∞	K_{1-2}	K_{1-3}	K_{1-4}	Mean K
Rhodamine B 20°C	.00063	0	60.34	39	59.05	135	57.06	225	55.63	54.50	.0064	.0061	.0072	.0064
	.001	0	52.23	36	51.29	109	49.75	188	48.84	47.80	.0066	.0075	.0071	.0070
	.0021	0	52.7	123	49.48	211	48.0	250	47.52	46.50	.0062	.0068	.0067	.0066
	.004	0	50.86	115	46.49	213	45.08	266	44.54	43.60	.0079	.0074	.0076	.0076
	.0065	0	49.21	103	44.91	218	42.99	378	42.02	41.50	.0079	.0075	.0072	.0075
Eosine yellowish 17°C	.002	0	71.89	69	70.38	136	69.34	241	68.21	65.15	.0036	.0034	.0038	.0036
	.01	0	65.13	74	63.90	147	62.83	240	62.05	59.81	.0035	.0038	.0036	.0036
	.03	0	62.66	60	61.33	190	60.38	300	59.68	57.85	.0042	.0033	.0032	.0036
	.05	0	60.78	180	57.85	253	57.34	344	56.82	55.80	.0040	.0037	.0035	.0037
α-Naphtholsulphonic acid 21°C	.0025	0	49.14	38	48.08	76	47.38	145	46.51	46.0	.0107	.0107	.0125	.013
	.01	0	46.90	63	44.17	148	42.74	244	41.74	40.85	.0094	.0096	.0099	.0096
	.05	0	41.48	66	38.05	138	36.40	207	35.66	34.80	.0109	.0102	.0099	.0103
B-Naphthylamine disulphonic acid 21°C	.001	0	64.86	72	63.10	183	61.40	282	60.40	58.50	.0044	.0042	.0040	.0042
	.005	0	51.97	37	51.40	103	50.53	180	49.61	47.40	.0040	.0036	.0040	.0039
	.016	0	49.61	114	47.38	188	46.87	267	46.40	43.0	.0031	.0030	.0033	.0031
Di-methyl p-phenylene diamine hydrochloride 24°C	.014	0	67.08	103	64.75	246	63.12	324	62.21	60.8	.0044	.0040	.0046	.0043
	.02	0	66.54	103	53.81	186	62.11	338	60.95	59.0	.0043	.0047	.0040	.0043
	.025	0	64.65	34	63.78	103	62.62	185	61.57	58.5	.0044	.0040	.0041	.0042

TABLE II (Continued)

Substance and temp.	Conc. in gr. mols per litre	t_1	σ_{t_1}	t_2	σ_{t_2}	t_3	σ_{t_3}	t_4	σ_{t_4}	σ_{t_∞}	K_{1-2}	K_{1-3}	K_{1-4}	Mean K
Dioxybenzoic acid 24°C	.0071	0	66.68	33	65.31	113	64.87	182	64.91	63.0	.0087	.0081	.0088	.0085
	.0224	0	58.03	66	57.0	134	56.16	207	55.66	55.5	.0083	.0080	.0081	.0081
	.049	0	56.37	70	54.90	135	54.23	233	53.44	52.9	.0089	.0075	.0079	.0081
α-naphthylamine hydrochloride 21°C	.005	0	55.54	108	52.84	219	51.37	291	50.85	49.65	.0056	.0056	.0050	.0054
	.007	0	51.70	73	50.00	175	48.78	210	48.27	47.0	.0059	.0057	.0059	.0058
	.0121	0	48.38	74	46.90	195	45.47	266	45.14	44.1	.0055	.0057	.0052	.0055
β-naphtholsulphonic acid 21°C	.0025	0	63.88	67	61.58	174	59.33	290	58.60	55.5	.0036	.0032	—	.0034
	.005	0	59.41	113	58.01	188	57.41	284	56.68	54.9	.0033	.0032	—	.0033
	.05	0	51.39	67	49.99	139	49.02	209	48.59	45	.0039	.0036	.0030	.0035
Aniline hydrochloride 24°C	.0018	0	70.37	112	69.16	255	67.98	449	66.71	66.30	.0029	.0031	—	.0030
	.0027	0	70.33	106	69.0	250	67.54	356	66.60	65.0	.0027	.0029	—	.0028
	.0939	0	64.75	131	60.85	198	59.56	266	58.76	52.60	.0026	.0029	—	.0028
Chinolin yellow 18°C	.0103	0	72.51	83	70.01	150	69.16	225	68.57	68.26	.0106	.0103	.0115	.0108
	2.56%	0	66.77	76	65.72	127	65.48	197	65.27	65.07	.0118	.0107	.0095	.0106
	5.8%	0	65.86	93	63.25	132	62.88	200	62.43	62.03	.0112	.0113	.0101	.0109
	about 6% (saturated)	0	64.92	73	63.16	229	62.16	273	62.03	61.86	.0116	.010	.0106	.0107

TABLE II (Continued)

Substance and temp.	Conc. in gr. mols per litre	t_1	σ_{t_1}	t_2	σ_{t_2}	t_3	σ_{t_3}	t_4	σ_{t_4}	σ_{t_∞}	K_{1-2}	K_{1-3}	K_{1-4}	Mean K
Biebrich scarlet 18°C	.0005	0	68.37	85	67.30	139	66.89	190	66.59	66.55	.0104	.0113	—	.0108
	.00093	0	65.31	190	64.19	206	64.12	228	64.06	63.95	.0091	.010	.0110	.0105
	.0031	0	59.24	117	57.42	171	57.16	207	57.06	56.84	.0101	.0117	.0115	.0111
Benzo-purpurin 17°C	.001	0	64.31	39	63.08	67	62.47	180	61.38	60.88	.0113	.0114	.0107	.0111
	.0021	0	62.29	70	59.96	136	59.09	212	58.57	58.12	.0116	.0107	.0105	.0109
	.008	0	57.95	39	57.36	140	56.69	178	56.52	56.27	.0110	.010	.0107	.0106
Victoria yellow 17°C	.001	0	63.62	39	62.24	58	61.99	80	61.80	61.34	.0237	.0216	.0200	.0217
	.002	0	58.38	89	57.12	122	57.03		—	56.95	.023	.023	—	.023
	.003	0	55.42	36	54.28	61	54.0	136	53.64	53.45	.023	.0209	—	.0219
Aniline orange (G.G.) 20°C	.003	0	70.87	76	67.78	145	66.79	218	66.12	65.80	.0123	.0113	.0111	.0115
	.006	0	65.69	34	64.60	101	63.36	175	62.75	62.29	.0113	.0114	.0109	.0112
	.010	0	64.85	62	60.88	168	58.61	230	57.72	57.15	.0116	.010	.0112	.0109
Chrysoidine crystal 17°C	.0005	0	61.48	62	56.65	129	54.78	235	53.56	52.75	.0127	.0111	.010	.0113
	.001	0	55.04	63	53.02	132	51.94	170	51.72	51.24	.0120	.0120	.0121	.0120
	.00199	0	54.69	38	52.95	94	51.68	175	50.68	50.0	.0121	.0108	.0110	.0113
Brilliant green (very dilute solution only)	.0005	0	63.46	71	59.46	147	57.82	216	57.15	56.0	.0115	.0109	.117	.0114

membranes.[1] After reaching a minimum value, the surface-tension increases rapidly, comes to a maximum and a fall for the second time ensues, thus causing the curve to show the variation of surface-tension with time to be an irregular one. The steepness of the curves increases with rise of concentration. Table III will make the points clear.

It is interesting to note that the aqueous solution of brilliant green falls under Type B, only when the dilution is very great. It behaves as a colloidal solution (as will be seen in Table IV) when the concentration increases.

TABLE III

Substance and Temp.		Conc. in gr. mols.	t_1	σ_{t_1}	t_2	σ_{t_2}	t_3	σ_{t_3}	t_4	σ_{t_4}
Congo red	(1)	.0022	0	71.78	69	68.60	189	67.78	240	67.41
20°C.	(2)	.0051	0	69.95	79	66.97	205	67.08	303	67.74
	(3)	.0102	0	68.11	108	63.95	137	63.90	235	64.12
	*(4)	.0051	0	65.89	68	63.88	121	63.13	240	62.75
Brilliant green	(1)	.00081	0	60.19	61	58.05	102	57.54	162	57.68
21°C.	(2)	.00201	0	53.76	77	52.12	109	52.42	187	54.43
	(3)	.004	0	53.26	45	53.07	111	59.98	218	60.42
	**(4)	.004	0	56.02	132	53.70	208	53.32	364	53.75

* Results obtained on studying the solution (2) after it was kept for about a month, are shown in (4). The values of surface-tension as well as the nature of its variation with time is found to be changed.

** When studied after keeping the solution (3) for about a month.

TABLE IV

Temp.	Substance and Conc.	t_1	σ_{t_1}	t_2	σ_{t_2}	t_3	σ_{t_3}	t_4	σ_{t_4}
21°C	Fuchsine red (.008)	0	71.78	32	71.76	85	71.74	125	71.76
21°C	Fuchsine red (.008) in .014 N. KCl solution	0	70.66	21	70.88	67	70.37	101	70.79
21°C	Fuchsine red in .032 N. KCl solution (.008)	0	66.55	20	65.55	76	66.77	120	67.53
21°C	Fuchsine red in .06 N. KCl solution (.008)	0	63.30	61	61.81	140	62.23	239	64.94
21°C	When KCl soln. added in excess (i.e. sufficient to precipitate the colloid)	0	72.23	16	72.23	90	72.25	125	72.25

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[1] Z. physik. Chem., 60, 479 (1907).

We have seen at the very beginning that the aqueous solution of fuchsine red shows no variation of surface-tension with time. (Table I.)

The addition of an electrolyte, such as potassium chloride or sodium chloride, to a true solution of fuchsine red renders it colloidal. It is therefore to be expected that a true solution of fuchsine red belonging to type A, will on addition of potassium chloride in quantities not large enough for coagulation begin to behave as a solution of type C. This has been actually observed, as will be seen in Table IV.

As will be seen in Table IV, the addition of increasing quantities of potassium chloride transforms a solution of fuchsine red from Type A to Type C through solutions of Type B.

The classification of solutions into three classes based on experiments on variation of surface tension with time has been corroborated, at least qualitatively, by dialysing experiments. The results are given in (Table V).

TABLE V

		Remarks
1. Substances dialysing very rapidly through collodion membranes at 27°C (e.g. of the type potassium chloride):—	I. Fuchsine red	Solutions of Type A—molecularly dispersed
	II. Methylene blue	
2. Dialysing rapidly at 27°C:—	I. Victoria yellow	Solutions of Type B—consisting mostly of small molecular aggregates in equilibrium with very low conc. of simple molecules
	II. Biebrich scarlet	
	III. Aniline orange (G.G.)	
	IV. Rhodamine B	
	V. Crystal violet	
	VI. Chrysoidine cryst.	
3. Dialysing slowly at 27°C:—	I. Brilliant green	Solutions of Type C colloidal solutions containing scarcely any simple molecule
4. Dialysing very slowly at 27°C, but somewhat rapidly at 60°C:—	I. Benzo purpurin*	
5. Dialysing not even at 60°C:—	I. Congo red	”

* Kraft classified benzopurpurin with congo red, as neither of the two was found to dialyse through parchment paper.

Our thanks are due to Mr. S. K. Sarkar for help in carrying out some of these experiments.

Chemical Laboratory,
University of Dacca.

9c-81

CHANGES IN PHYSICAL AND ELECTRICAL PROPERTIES OF A MINERAL INSULATING OIL, HEATED IN CONTACT WITH AIR*

BY HUBERT H. RACE

I. Object

To obtain a clearer insight into the changes in a mineral insulating oil resulting from heating in contact with air, the following properties were studied in portions of the same oil which had been oxidized under different conditions.

A. D-C. conductivity at 115°C.
B. Dielectric losses at 30°C. for frequencies between 10^3 and 10^6 cycles per second.
~~C. Oil spreading on water using Langmuir's method.~~
D. Ultramicroscope particle count.
E. Viscosity using modified Ostwald viscometer.
F. Refractive index using a Pulfrich refractometer.
G. Acid number.

These chemical, physical and electrical tests were all made on the same samples so as to correlate the results of the different types of measurement and determine whether sensitive electrical equipment could be advantageously used to supplement the usual chemical and physical tests.

II. Preparation of Samples

TABLE I

Physical Data for No. 5317 Oil

(1)	Flash Point	225°C.
(2)	Fire Point	265°C.
(3)	Acid value	4×10^{-5} grams KOH per grams of oil
(4)	Density at 30°C.	0.935 grams per cc.
(5)	Viscosity at 30°C.	10 poises

A portion of commercial cable oil having the general characteristics shown in Table I was divided into nine equal samples which were aged in contact with air in a G. E. Life Test oven according to the schedule shown in the first three columns of Table II. This procedure was used so that the results could be interpreted directly in terms of standard practice in the Cable Plant where resistivity measurements before and after heating 96 hours at 115°C. are used

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* This paper is based in part upon data presented at the fourth annual conference of the committee on electrical insulation, division of engineering and industrial research, National Research Council, held at Harvard University, Cambridge, Mass., Nov. 13-14, 1931. See Elec. Engineering, 51, 33 (1932).

in factory control. The time schedule for heating at the different temperatures was chosen so that corresponding samples at the different temperatures would show approximately the same change in conductivity. This was estimated from preliminary data on changes in conductivity with heating temperature.

III. Experimental Procedure and Data

A.—*D. C. Conductivity at 115°C.*

About two years ago the small oil conductivity testing set shown in Fig. 1 was developed for measuring the direct current conductivity of insulating oils. The wiring diagram for this set is shown in Fig. 2. Its main advantages are ease of operation and good control of the temperature of the sample under test. The extremely good electrical properties of these insulating oils require special care in the design of the testing cell. Fig. 3 shows such a cell, made of stainless steel

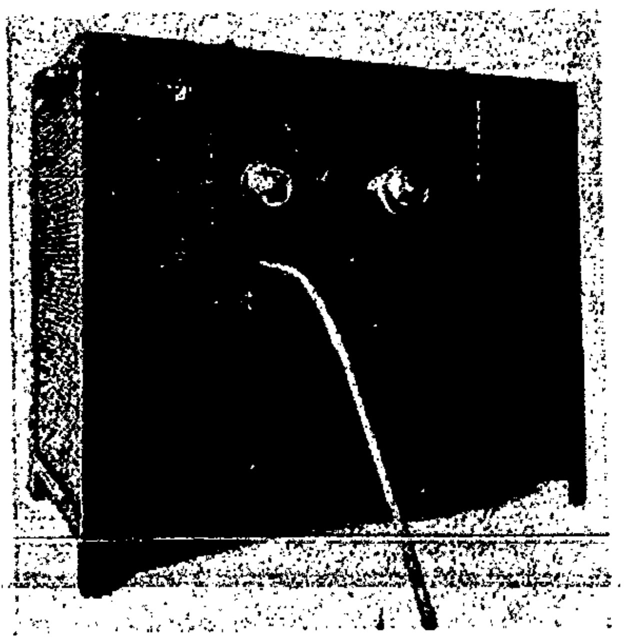

Fig. 1
Oil Resistivity Testing Set

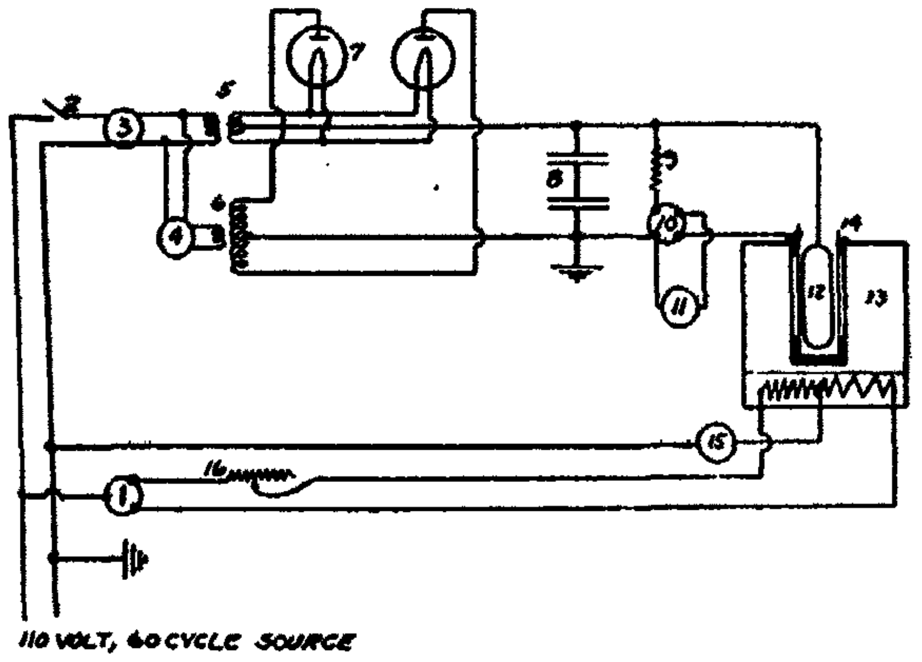

Fig. 2
Wiring Diagram

1. Two-circuit Heater Switch.
2. Safety Switches in Doors.
3. Transformer Switch.
4. Ten-second delay Relay.
5. Filament Transformer Y 2006.
6. Plate Transformer UP 1016.
7. Two Mercury Rectifier Tubes—PJ 28.
8. Two 800 volt, 1 microfarad Capacitors.
9. 10^6-ohm wire wound Resistor.
10. Special Galvanometer Switch.
11. Portable Insulation Testing Galvanometer.
12. Quartz insulated Oil Testing Cell.
13. Heater (not used when a cell is placed on an oil storage tank).
14. Textolite insulation between Cell and Heater.
15. Thermostat for controlling Heater (not necessary).
16. Variable Resistance for low Heat Control.

TABLE II

Summary of Experimental Results obtained by heating No. 5317 Oil in Contact with Air

			A	B	C	D		E	F
Sample No.	Oxidation		Conductivity at 115°C. γ	Max. loss Factor ϵ''_m	Spreading Area A_o	Particle count		Viscosity at 30°C. η	Index of Refraction at 30°C. (r)
	Time hours	Temp. °C.	mho. per cm. cube × 10^{-12}	(numeric)	Sq. cm. per gram of oil × 10^3	First No. per c.c. of oil × 10^6	Second No. per c.c. of oil × 10^6	poises	(numeric)
1	4	115	1.02	2.11	3.3	4	139	10.7	1.5098
2	28	"	2.62	2.20	12.0	5	56	10.4	1.5098
3	96	"	11.8	2.74	26.0	33	51	10.0	1.5102
4	2	130	0.84	2.15	3.4	67	253	9.7	1.5101
5	14	"	2.17	2.26	6.7	89	41	11.0	1.5095
6	48	"	8.35	2.6	22.0	166	45	10.7	1.5108
7	1	150	0.75	2.15	3.0	136	5	9.5	1.5108
8	7	"	1.45	2.27	7.0	32	75	11.9	1.5110
9	24	"	4.55	2.52	21.0	103	3	11.9	—

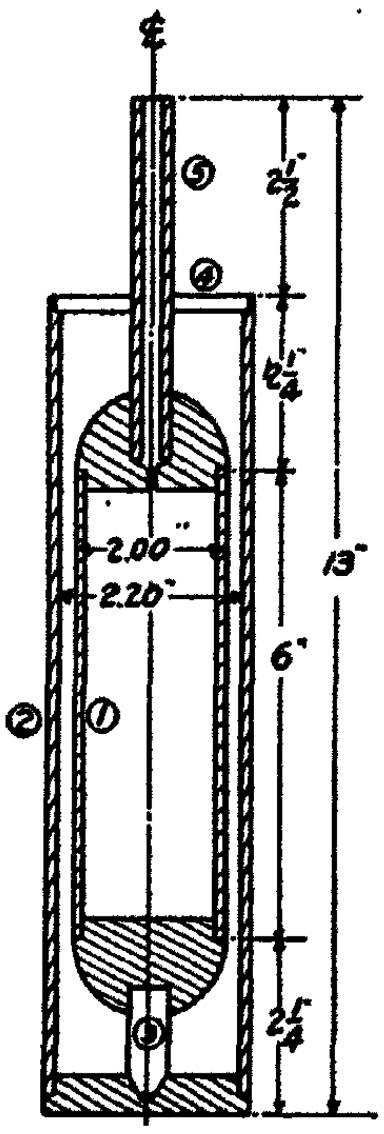

FIG. 3
Oil Resistivity Testing Cell

with fused quartz insulation. The inner electrode (1) is a hollow cylinder to which hemispherical ends have been welded using an atomic hydrogen flame. The bottom of the outer cylinder (2) has a central conical hole into which the fused quartz post (3) fits. This post is held by a friction fit in a central hole in (1) but it may be removed for cleaning. The top of the inner electrode is centered by a fused quartz collar (4) which is also made with a sliding fit so that the inner electrode may be easily removed for cleaning. The small cylinder (5) serves as a high lead to the cell, as the top centering post and as a container for a thermometer to indicate the temperature of the inner electrode. The major advantages of this cell are as follows:

(a) It is made of materials which are not attacked by the oil and do not act as catalysts on the oil.

(b) It is easily taken apart for cleaning, and

(c) Its calibration remains constant even though it is repeatedly taken apart for cleaning.

With the above equipment the conductivity of each sample was determined at 115°C., as is shown in Table II. The curves in Fig. 4, plotted from these data, indicate that, *the longer the aging time, the greater is the effect of high temperature on the conductivity.*

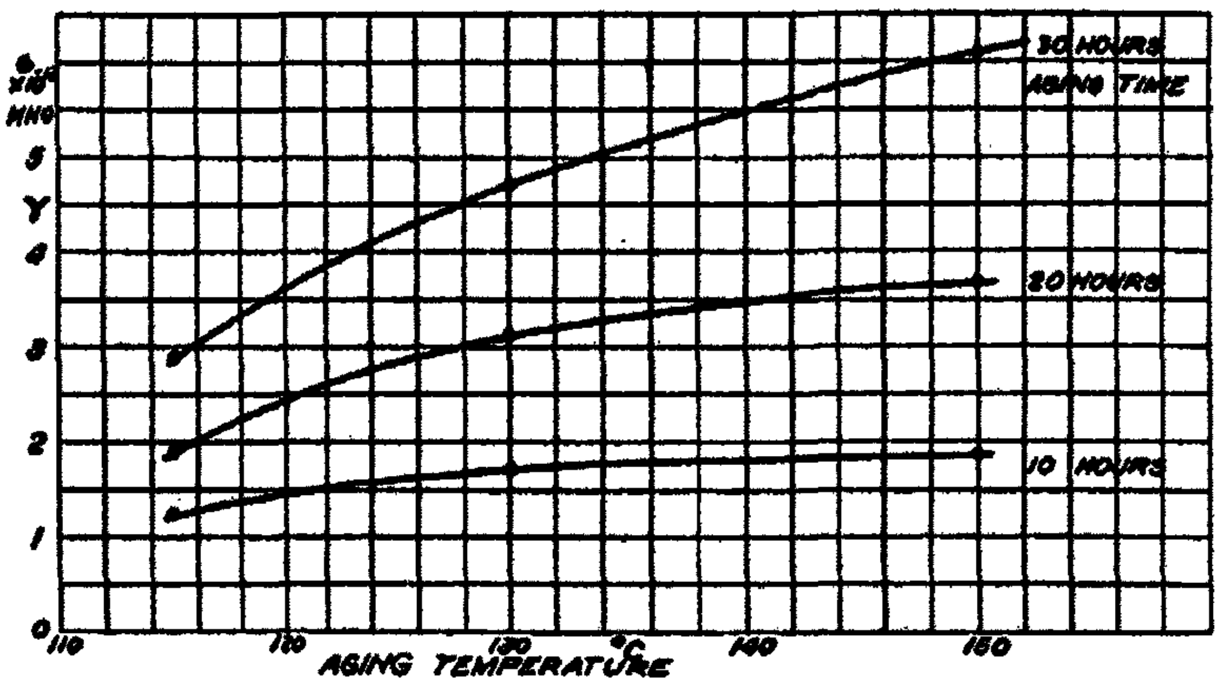

FIG. 4
Variation of Conductivity resulting from heating
5317 Oil in Air at different Temperatures

B.—*High Frequency Measurements of Electrical Properties.*

Previous work on the high frequency electrical properties of insulating oils has suggested the presence of polar molecules in oil and the possibility of estimating their size.[1,2]

It has been found convenient to interpret the high frequency measurements in terms of the equivalent parallel circuit shown in Fig. 5. The complex expression for the reciprocal impedance of the measuring circuit is given by the relation

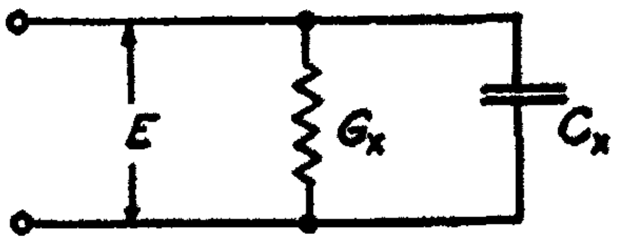

FIG. 5
Parallel circuit electrically equivalent to Sample

$$Z^{-1} = G_x + i\omega C_x = \omega C_v (\epsilon'' + i\epsilon') \qquad (1)$$

in which

G_x = the equivalent parallel conductance of the sample

C_x = the equivalent parallel capacitance of the sample

ω = $2\pi f$, where f = electrical frequency in cycles per second

i = $\sqrt{-1}$

C_v = capacitance of the same geometric arrangement of electrodes in vacuum.

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[1] D. W. Kitchin and Hans Muller: Phys. Rev., (2) 32, 979 (1928).

[2] H. H. Race: Phys. Rev., (2) 37, 430-446 (1931).

For comparative purposes it is convenient to study unit quantities which may be defined by comparing the two forms of equation (1) as follows:

$$\epsilon' = (C_x/C_v) = \text{capacitance factor* (Dielectric Constant)} \tag{2}$$

$$\epsilon'' = (G_x/\omega C_v) = \text{loss factor} \tag{3}$$

$$\sin \tan^{-1} (\epsilon''/\epsilon') = \text{power factor} \tag{4}$$

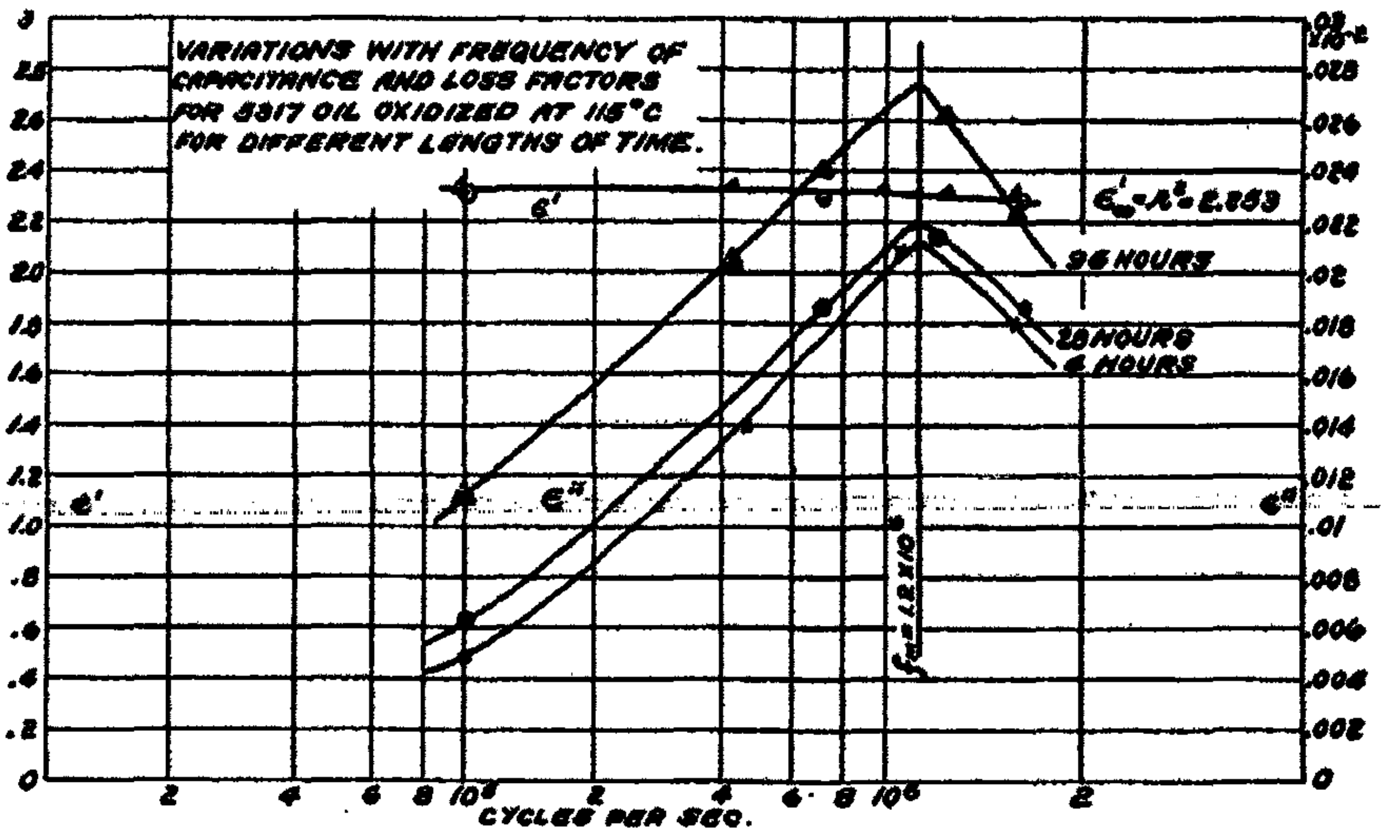

Fig. 6

Figs. 6, 7, and 8 show ϵ' and ϵ'' plotted against the logarithm of the frequency for the nine samples. The data have been presented in this way so that they may be studied in terms of Debye's theory of polar molecules.[3] From this theory expressions can be derived for ϵ' and ϵ'' as functions of frequency and the general form of these relations is shown by Fig. 9. For these oils the change of ϵ' with frequency is small, therefore, to more clearly show the changes predicted by the theory, Fig. 9 has been plotted for an assumed condition such that the decrease in capacitance with increased frequency is 50%.

The conditions required by the theory for the frequency (f_m) at which the dielectric loss is a maximum are particularly interesting. At this frequency the particular values of the capacitance factor (dielectric constant) and the loss factor[2] can be shown to be

$$\epsilon'_m = \tfrac{1}{2} (\epsilon'_o + \epsilon'_\infty) \tag{5}$$

$$\epsilon''_m = \tfrac{1}{2} (\epsilon'_o - \epsilon'_\infty) \tag{6}$$

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* This new name is suggested because ϵ' is not necessarily constant, but may vary with both frequency and temperature and because the word, *capacitance*, refers specifically to the reactive component whereas the word, *dielectric*, has a more general meaning. See Electrical Engineering, 51, 354 (1932).

[3] P. Debye: "Polar Molecules" (1929).

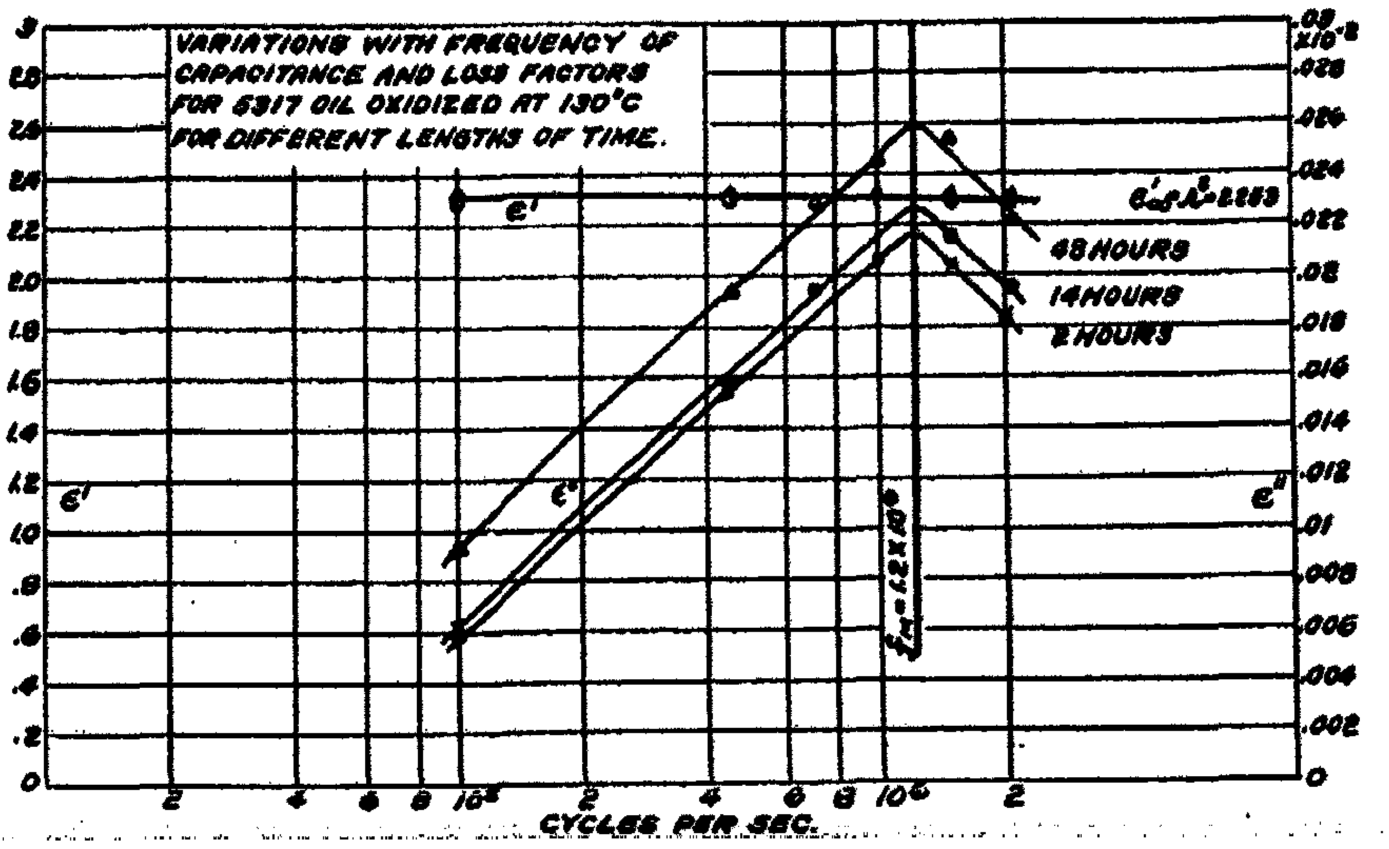


Fig. 7

where ϵ'_0 and ϵ'_∞ are respectively the capacitance factors (dielectric constants) at zero and infinite frequencies.

The curves in Figs. 6, 7, and 8 show small but definite decreases in ϵ' with increased frequency and are apparently approaching the limiting value $\epsilon_\infty = 2.253$, which is the square of the measured index of refraction as required by theory.

The loss curves all have their maxima at the same frequency, and show increasing loss with increasing oxidation. The maximum ordinate of the curve for ϵ'' should be calculable from the theory by eq. (6). For example the maximum ordinate of the 24 hour curve of Fig. 8 should be

$$\epsilon''_m = \tfrac{1}{2}(2.34 - 2.53) = .0435$$

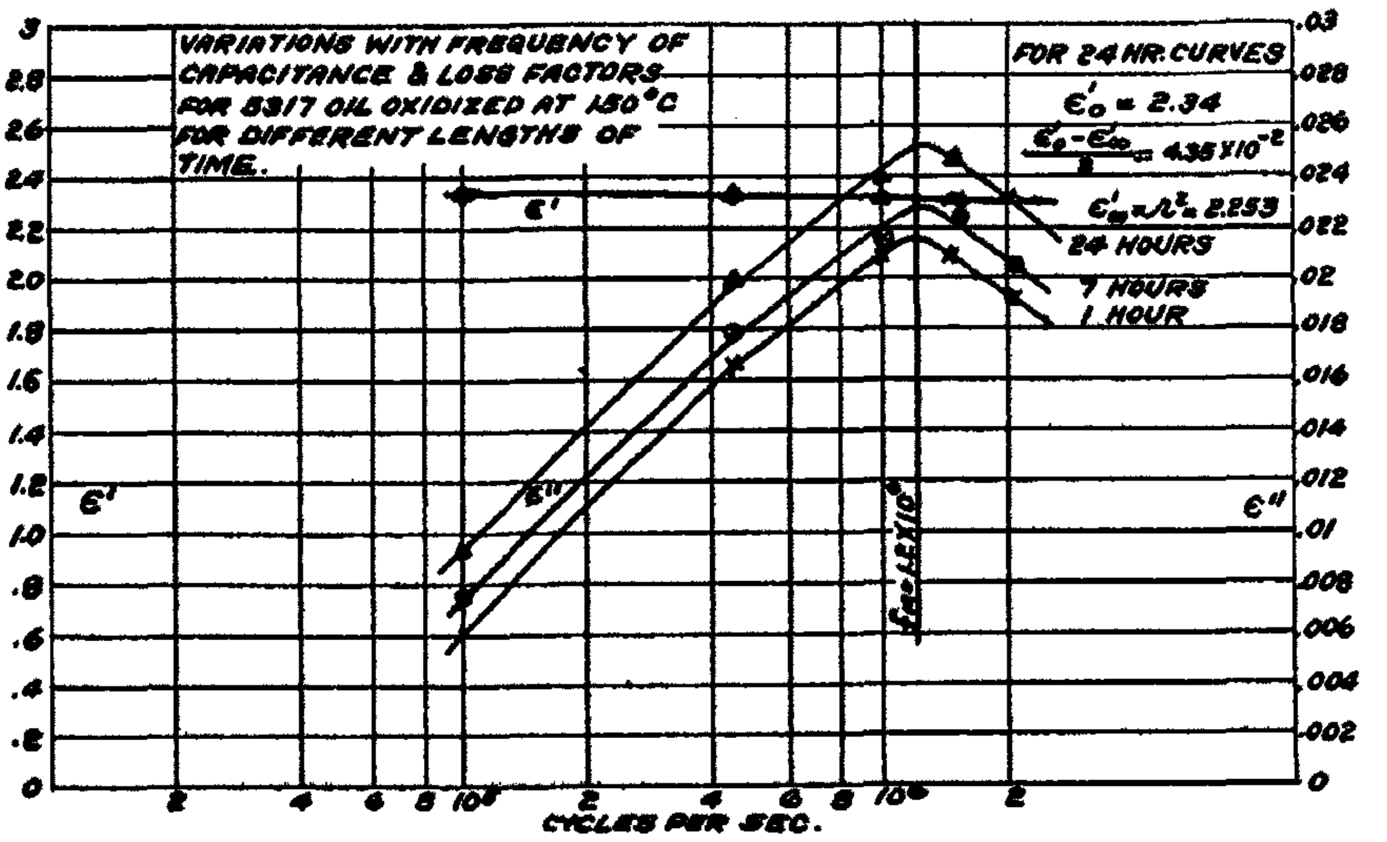


Fig. 8

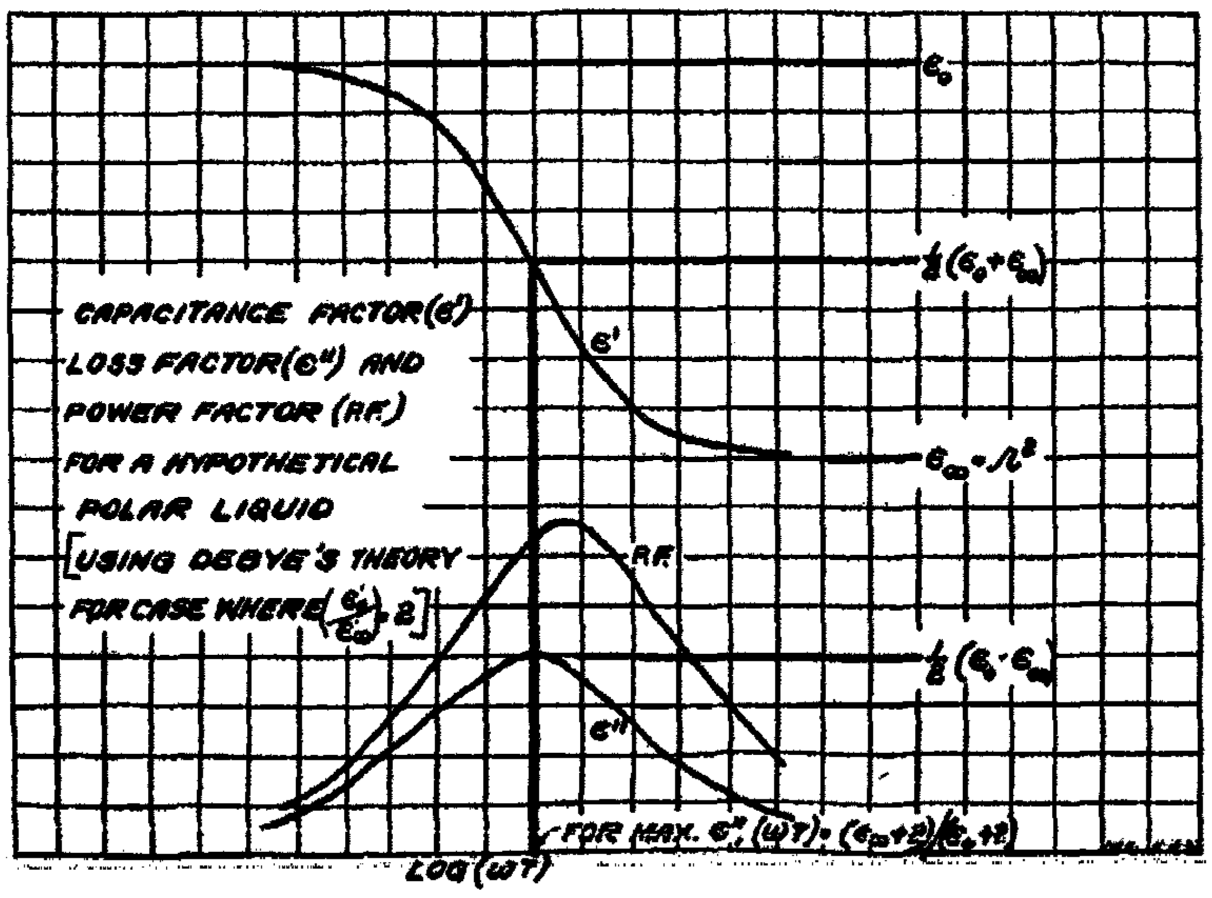
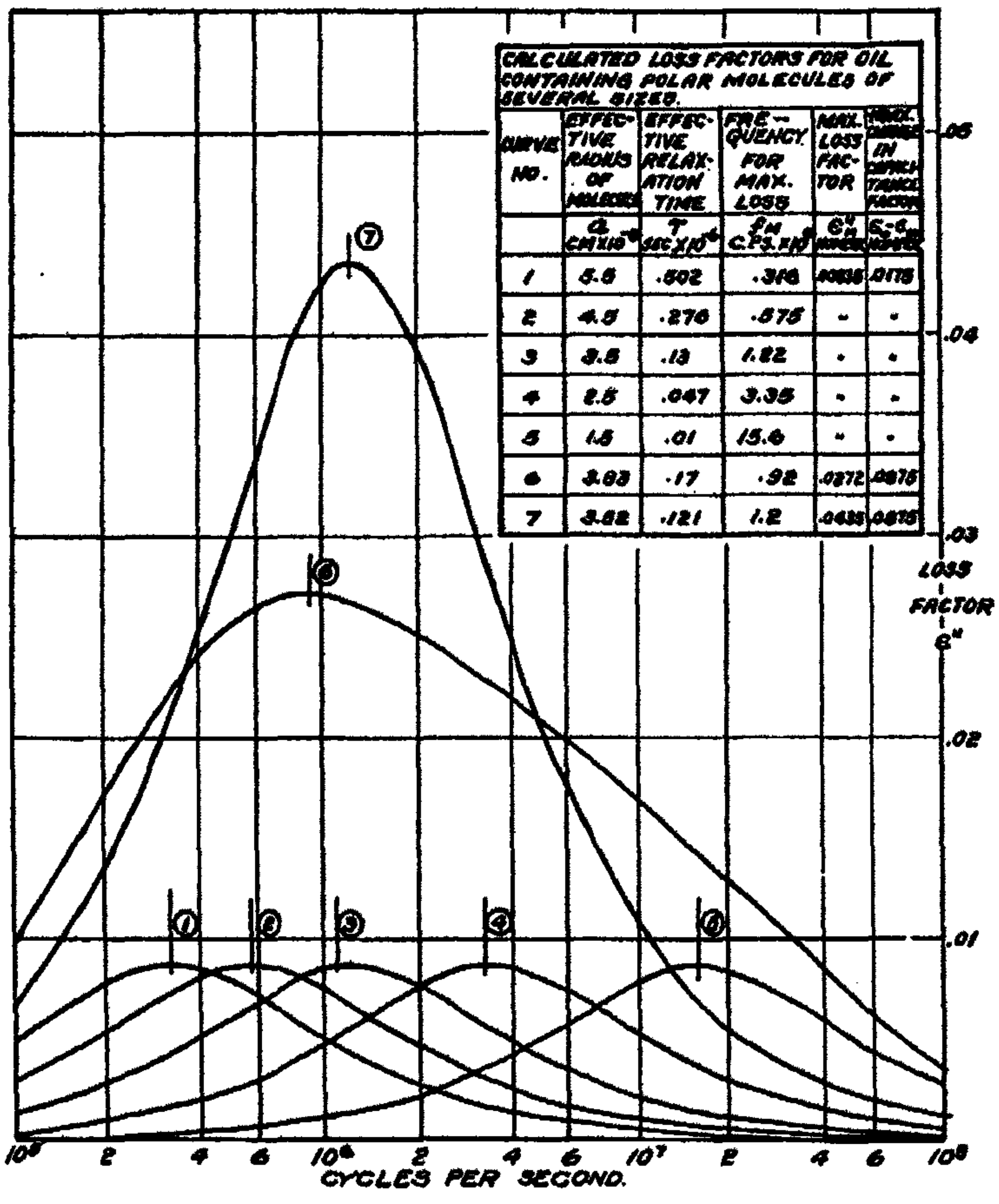


Fig. 9



CALCULATED LOSS FACTORS FOR OIL CONTAINING POLAR MOLECULES OF SEVERAL SIZES.

CURVE NO.	EFFECTIVE RADIUS OF MOLECULE	EFFECTIVE RELAXATION TIME	FREQUENCY FOR MAX. LOSS	MAX. LOSS FACTOR	MAX. CHANGE IN CAPACITANCE FACTOR
	a CM × 10^{-8}	τ SEC × 10^{-6}	f_M C.P.S. × 10^6	ϵ''_M	$\epsilon_0-\epsilon_\infty$
1	5.5	.502	.316	.0085	.0175
2	4.5	.276	.575	"	"
3	3.5	.13	1.22	"	"
4	2.5	.047	3.35	"	"
5	1.5	.01	15.6	"	"
6	3.83	.17	.92	.0272	.0875
7	3.82	.121	1.2	.0435	.0875

Fig. 10

The measured ϵ''_m is seen to be only .0253, however, a possible explanation for this difference is indicated in Fig. 10. Equation 7 is based upon the assumption that all observed effects result from the orientation of particles of one size only. If there are any polar molecules present, they are probably of several sizes. Then the change in ϵ' would represent the sum of the contributions of particles of all sizes, since at frequencies approaching zero they would all orient completely and at frequencies approaching infinity none of them would orient. The loss factors for the several sizes, however, would have their maxima at different frequences since the relaxation time depends upon the size of particle. Therefore the sum of the loss curves would have a maximum ordinate considerably less than would have been obtained if the particles had been all of one size. For example, in Fig. 10 the total change in ϵ' has been assumed to result from the orientation of equal numbers of molecules of five different sizes (arbitrarily chosen). For this assumed illustration curve (6) shows that the maximum ordinate of the sum of the five loss curves is only about 62% of the maximum ordinate of curve (7) for which all the particles are assumed to be of one size only. The resulting ratio is nearly the same as that found between the observed and calculated values of ϵ''_m corresponding to the 24 hour curve of Fig. 8 and indicates the plausibility of this explanation for the difference between the observed and calculated values.

From Debye's theory the relaxation time (τ) of the polar molecules is given by the expression

$$\tau = \frac{1}{2\pi f_m}\left(\frac{\epsilon_\infty + 2}{\epsilon_0 + 2}\right) = \frac{4\pi\eta a^3}{kT} \qquad (7)$$

where f_m = frequency at which maximum loss occurs

η = viscosity in poises

a = effective radius of the polar molecule in cm.

k = Boltzmann's constant = 1.37×10^{-16}

and T = absolute temperature

Using this relation, the effective size of the orienting particle can be obtained directly from the experimental measurements. For example from the 24-hour curve of Fig. 8,

$$a = \left[\left(\frac{1.37 \times 10^{-16} \times 303}{6.28 \times 1.2 \times 10^6 \times 12.56 \times 10}\right)\left(\frac{4.253}{4.34}\right)\right]^{1/3} = 3.4 \times 10^{-8}\text{cm.}$$

The exactness of equation 7 may be questioned because it assumes the validity of Stokes' law of viscosity which may not be an accurate measure of the frictional coefficient for an orienting particle in a viscuous medium. The calculated size of particle is considerably smaller than that expected for an oil molecule. For example Langmuir[4] shows that the stearic acid molecule has an effective cross sectional area of 22×10^{-16} sq. cm. and a length of 25×10^{-8} cm. *This leads to the conclusion that the whole molecule does not rotate but*

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[4] I. Langmuir: J. Am. Chem. Soc., 39, 1848 (1917).

rather the polar group moves with reference to the rest of the molecules so that the radius calculated from the electrical measurements is a measure of the effective size of the portion of the molecule which is contributing to the polar movement.

C.—*Oil spreading on Water.*

The oil spreading measurements were made in order to obtain an independent check on the formation of polar molecules during oxidation and to confirm the approximate correlation observed by Shanklin and Mackay[6] between conductivity and hydrophil measurements. The tests were made using apparatus similar to that employed by Langmuir[4] except for minor modifications and the results are shown in Figs. 11, 12, and 13. Each curve was obtained by increasing the compressive force applied to the film in definite steps and measuring the area covered by the film. These curves were then extrapolated to zero force in order to obtain the area of a monomolecular layer of the polar constituents of the oil on water. This area, A_0, is then the measure of the hydrophil content per gram of oil.

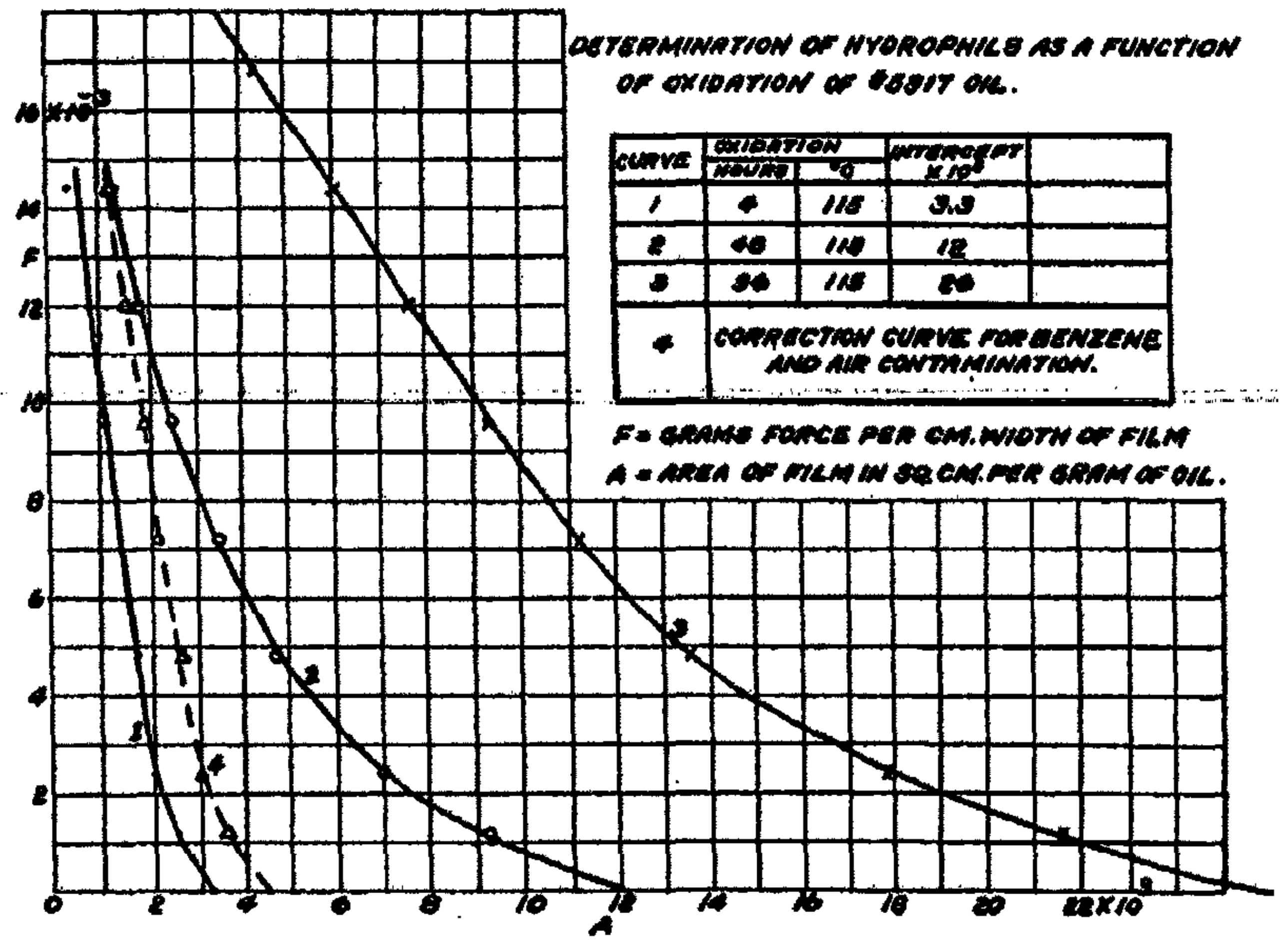

FIG. 11

Considerable care was necessary to minimize oil contamination. The benzene was purified by repeated redistillation and the apparatus was cleaned after every run. The magnitude of residual errors is indicated by curve (4) of Fig. 11 which illustrates the correction curve taken before each set of runs and subtracted from the observed readings. The residual errors account for more than 50% of the observed spreading for the least oxidized samples. For the most highly oxidized samples the errors are relatively small.

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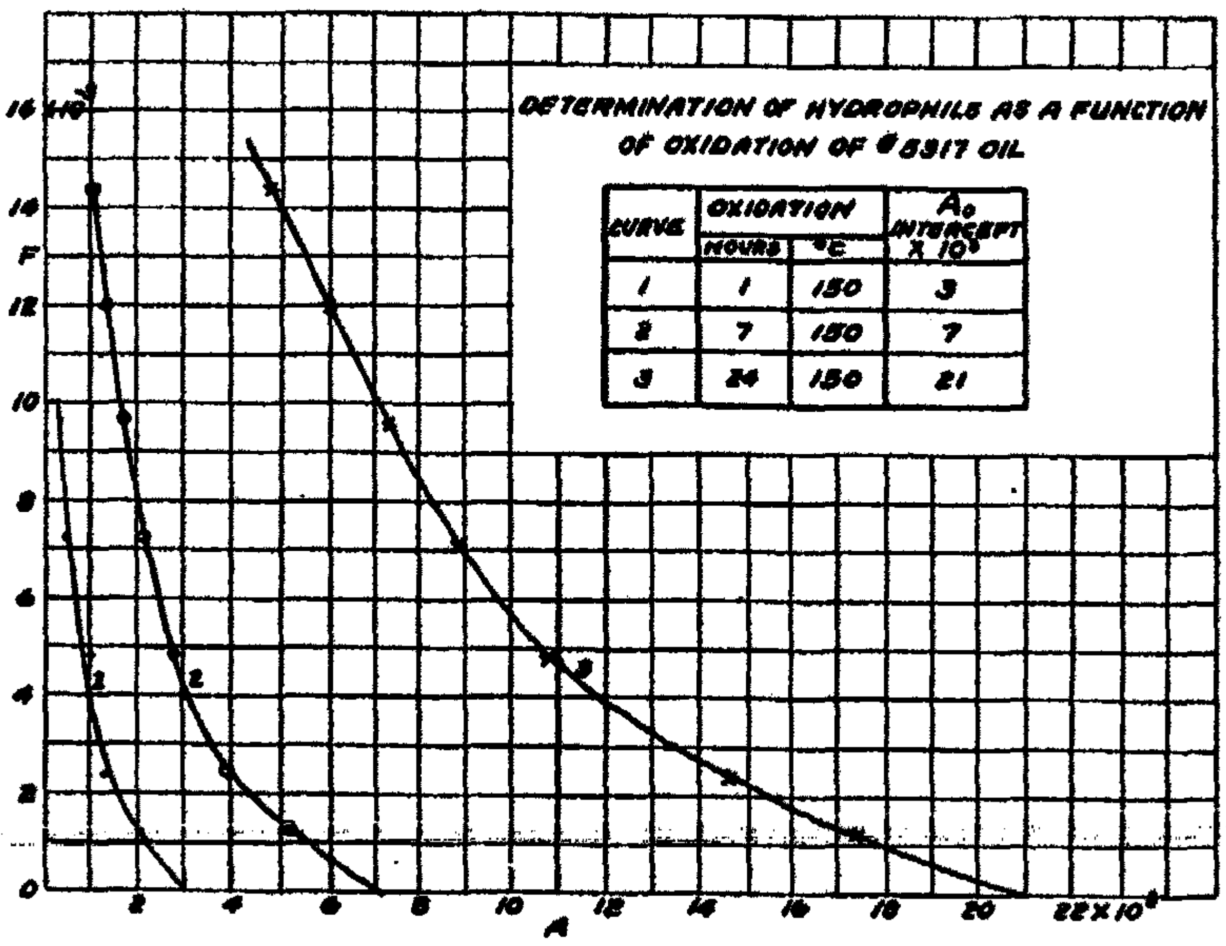
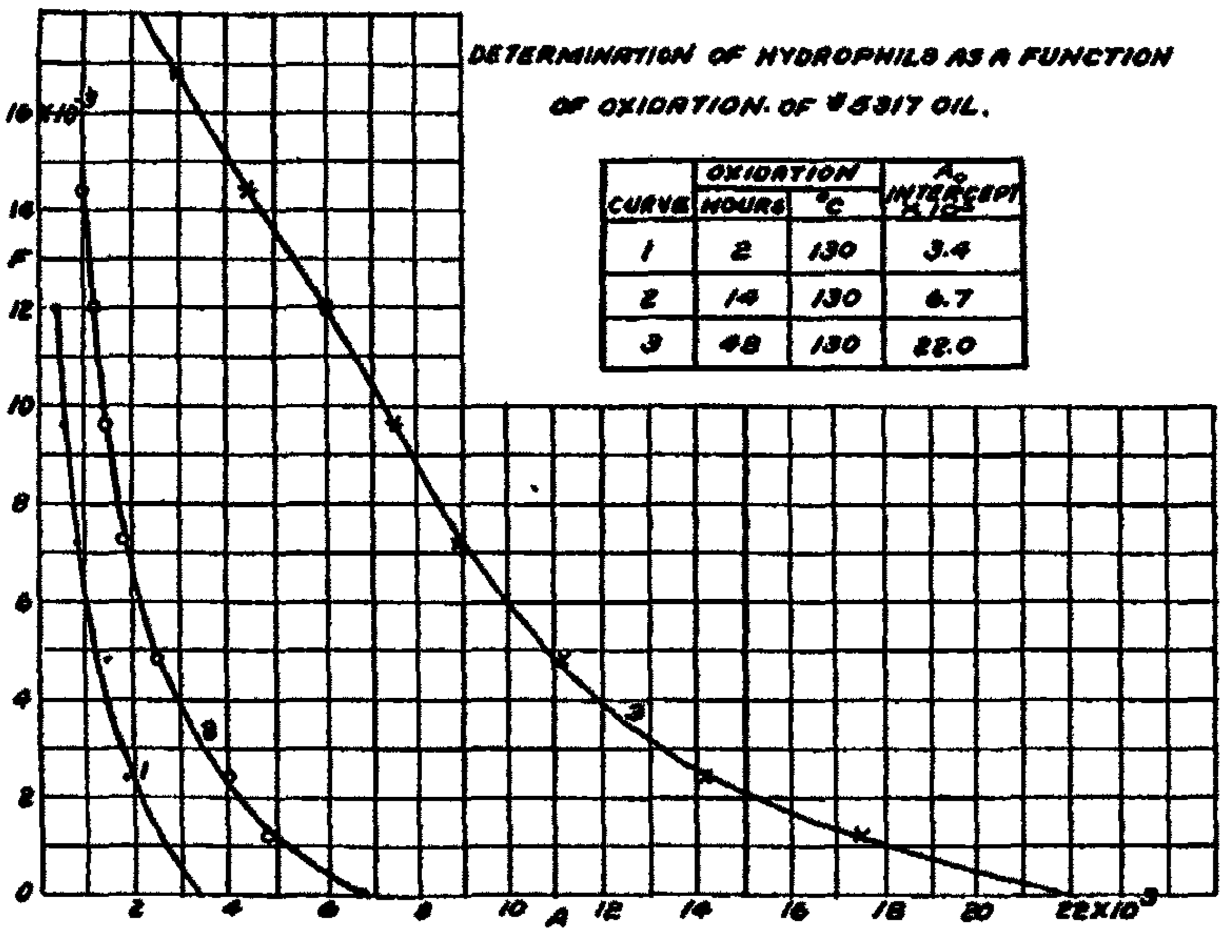
[6] G. B. Shanklin and G. M. J. Mackay: A.I.E.E. Trans., 48, 364 (1929).



CURVE	OXIDATION		A_0 INTERCEPT X 10^3
	HOURS	°C	
1	1	150	3
2	7	150	7
3	24	150	21

Fig. 12

The values of A_0 were plotted against aging time and points from these curves were replotted in Fig. 14 for direct comparison with corresponding curves showing changes in conductivity (Fig. 4). The trends of these two sets of curves are different and indicate that *oxidation at higher temperatures has a greater effect in producing polar particles than in producing particles capable of carrying a charge.*



CURVE	OXIDATION		A_0 INTERCEPT X 10^3
	HOURS	°C	
1	2	130	3.4
2	14	130	6.7
3	48	130	22.0

Fig. 13

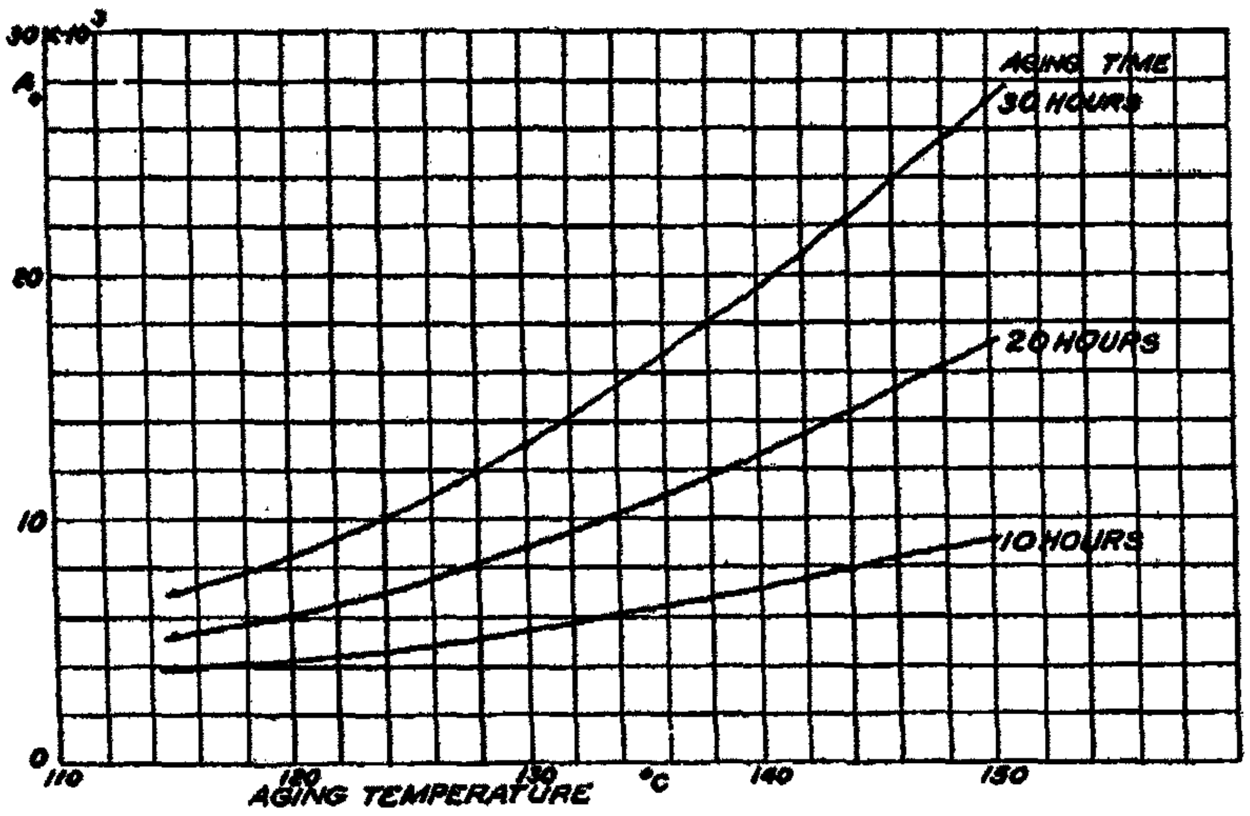
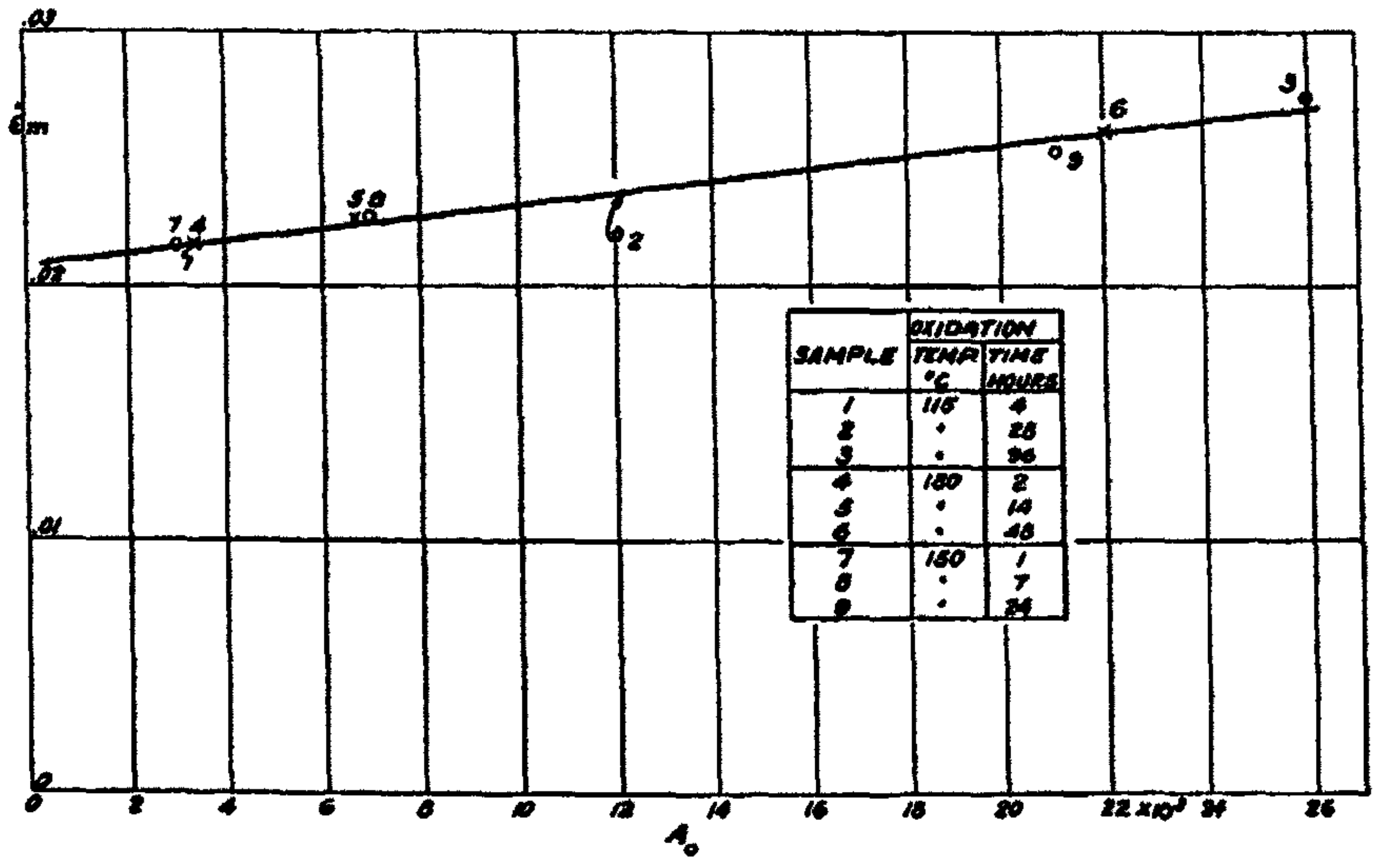


FIG. 14

Variation of Hydrophils produced by Heating 5317 Oil in Air at different Temperatures

A comparison between the maximum ordinate (ϵ''_m) of each curve of high frequency loss and the corresponding spreading area (A_o) on water is plotted in Fig. 15. This straight line relation is very interesting because it indicates that regardless of the temperature at which the oxidation occurred the increase in hydrophils was proportional to the increase in the number of polar particles responsible for the dielectric loss. The fact that this line does not pass through the origin can hardly be accounted for by experimental error. The apparent inference is that a large component of the loss is not caused by particles which spread on water. This means either that polar groups are formed which are not soluble in water or that there is some other



SAMPLE	OXIDATION	
	TEMP °C	TIME HOURS
1	115	4
2	"	28
3	"	96
4	130	2
5	"	14
6	"	48
7	150	1
8	"	7
9	"	24

FIG. 15

Proportionality between Loss Factor and Hydrophils for 5317 Oil oxidized at different Temperatures for different lengths of Time loss mechanism having a maximum response at approximately the same frequency. Such a mechanism might be the relative translational motion of ions of opposite sign in colloidal interfaces or in ionic atmospheres although no experimental data are available to substantiate this suggestion.

It is possible that further experimental work along this line may show that the effects can be explained in terms of an ionic atmosphere such as Debye and Falkenhagen[6] and Wien[7] employ to explain conduction measurements in strong electrolytes at high frequencies and high gradients.

D.—*Ultramicroscope Particle Counts.*

Careful ultramicroscope particle counts were made on portions of these nine samples in another laboratory where facilities were available. Results from one set of samples were quite erratic so second portions of the same samples were forwarded for duplicate determinations. The investigators reported that filters were used because of fluorescence in the oil and that the results were subject to considerable error because of apparent local concentration of particles at different points in the samples. The high viscosity of the oil prevented rapid random distribution of the suspensoids. The results of the two sets of measurements are shown in Table II and indicate *either that the methods of sampling, shipping and counting introduced large errors or that the suspensoids large enough to be seen in the ultramicroscope were entirely unrelated to those causing changes by the other experiments.* It seems that the latter is more probable.

E. *Viscosity Measurements.*

The viscosity of each sample was determined with a modified Ostwald viscometer which had previously been calibrated and used for measuring the viscosity of insulating oils. The results of these measurements are also shown in Table II and indicate that *if oxidation caused any consistent change in viscosity, this change was smaller than the experimental error which was about 2%.*

F. *Index of Refraction Measurements.*

As one step in interpreting the high frequency measurements it was necessary to determine the index of refraction (r) since by Debye's theory $\epsilon'_\infty = r^2$. Each of the samples was measured in a Pulfrich refractometer at 30°C., using the red mercury (c) line and the results are recorded in Table II. *The observed differences were of the order of 0.1% indicating either a slight trend toward higher refractive index with greater oxidation or erratic differences of this order between samples.*

G. *Acid Number.*

After all the other measurements had been completed, the remaining portions of the samples were too small to make the usual check for acid number. However, since titration for acid number is one of the routine

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[6] P. Debye and H. Falkenhagen: Physik. Z., 29, 401-426 (1928).

[7] M. Wien: Ann. Physik, 83, 327-361 (1927).

measurements made on all cable oils, a considerable amount of data is available. Only small differences in acid number have been observed between samples before and after the usual 96 hour – 115°C. aging tests. An average acid value for a large number of tests is about 5×10^{-5} grams of KOH per gram of oil. This can be converted to an approximate oil-spreading area by assuming that the polar molecules have the same cross section and molecular weight as a stearic acid molecule. 1 g. of KOH combines with $\frac{284}{56} = 5.07$ g. of stearic acid. Stearic acid contains $\frac{6.06 \times 10^{23}}{284} = 21.3 \times 10^{20}$ molecules per g. The cross section of stearic acid molecule $= 22 \times 10^{-16}$ sq. cm. Therefore $A_o = 5 \times 10^{-5} \times 5.07 \times 21.3 \times 10^{20} \times 22 \times 10^{-16}$ or $A_o = 1.19 \times 10^{3}$ sq. cm. per gram of oil.

This calculated area is considerably smaller than that observed for the three most highly oxidized samples. For example, the portion heated 96 hours at 115°C. showed a spreading area of $A_o = 26 \times 10^{3}$ sq. cm. per gram of oil. Thus the spreading for this sample was about 22 times greater than than calculated from the acid number. This difference indicates that *the acid number test is not suitable for detecting changes, produced by oxidation, of the polar constituents of an oil.*

IV. Conclusions

1. Oxidation considerably increases the ability of oil to spread on water, but corresponding changes in acid number are very small. For example, the measured spreading of sample 3 was twenty-two times greater than the value calculated from the acid number, indicating that the major proportion, if not all, of the non-volatile products containing polar groups could not be detected by the acid number test. This result may vary considerably with the type of oil used and emphasizes the value of the oil spreading measurements.

2. Oxidation increases the high-frequency dielectric losses but does not change the frequency at which the maximum loss in each sample occurs. If the applicability of Debye's theory is accepted, this means that oxidation increases the number of polar particles per unit volume, but does not change their size. The average radius calculated from the electrical measurements is 3.4×10^{-8} cm. which is considerably smaller than the expected size of an oxidized oil molecule, and supports the statement that the whole molecule does not orient but rather the polar group moves with reference to the rest of the molecule. Thus the measurements do not give the size of the whole molecule, but do give a measure of the effective size of the portion of the molecule which is contributing to the polar moment.

3. The observed changes in capacitance factor (dielectric constant) can be predicted from the observed changes in loss factor by using Debye's theory.

4. The increase in spreading on water and the increase in high frequency losses with oxidation are found to be proportional. Since the particles which cause the spreading on water are known to be polar, this may be taken as

an argument in favor of Debye's theory as the correct explanation of the observed high frequency losses. However, when plotted, this linear relation does not pass through the origin and if the relation between losses and spreading is extrapolated back to zero spreading area, a loss factor of .02 remains to be accounted for by some other mechanism.

5. The ultramicroscope particle counts were quite erratic and showed no correlation with the rest of the measurements. The counts showed from 3×10^6 to 300×10^6 with an average value of 70×10^6 particles per cu. cm. This indicates either that the methods of sampling or counting were subject to large errors or that the suspensoids large enough to be counted were entirely unrelated to those causing changes in the other types of measurement.

6. The viscosity measurements varied slightly but no correlation was found with results of the other experiments. The observed differences were erratic and within the experimental error which was about 2%.

7. Differences of the order of 0.1% were observed in the refractive index indicating either a slight trend toward higher refractive index with greater oxidation or erratic differences of this order between samples.

The author wishes to express his indebtedness to his co-workers Dr. E. H. Winslow, M. Poggenpohl, H. I. Reynolds, and H. E. Sennett in carrying out the experiments reported in this paper.

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THE ATOMIC MASS OF SODIUM

I. The End Point of the Sodium Chloride-Silver Titration*

BY CLYDE R. JOHNSON**

In recent papers[1] from this laboratory a new titration method for the accurate measurement of chemical atomic mass ratios is outlined. A unique feature of the method is the experimental elimination of all arbitrary factors in the determination of the end-point of the titration. The method is as easily applied as the usual arbitrary methods, and has the advantage of yielding far more trustworthy results.

Typical systems such as those to be obtained in the actual titration are prepared from the carefully purified products of the main analytical reaction. These systems are brought to equilibrium at a fixed temperature, and the supernatant liquids are analyzed. The equilibrium point is the correct end-point of the direct synthesis from the reactants, and may be used in deciding upon a suitable and accurate procedure for the analysis of the supernatant liquids. When, subsequently, weighed quantities of the reactants are mixed and brought to the same equilibrium point, exactly similar analyses give the data required for a correct evaluation of the ratio under consideration. The choice of the main analytical reaction, in view of the purpose of the investigation, ordinarily presupposes a complete "atom for atom" reaction in the formation and solution of the solid phase. As in all atomic mass determinations involving the formation of a precipitate in the analytical reaction, there remains a difficult question as to the purity of the precipitated compound, and adsorption effects. It is an additional advantage of the present approach to the problem that these factors may be taken into consideration.

Experimental

As an initial step in examining the general method, the conditions under which the nephelometer or potentiometer may be used in finding the correct end-point of the sodium chloride-silver titration were studied.

Reagents. The reagents used in this work were purified with extreme care, and tested to insure the absence of silver and chloride impurities. The *sodium nitrate* was a 225 gram central portion taken from 500 grams of C. P. material after six recrystallizations, with centrifugal drying. It was finally dried, fused, and weighed in platinum crucibles, without transfer. The *silver chloride* was flocculent precipitated material used in previous work, and subsequently thoroughly washed with pure water and aged over a period of ten months. This point is mentioned because of its bearing on the observed

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* Contribution from the Frick Chemical Laboratory, Princeton University.

** National Research Fellow in Chemistry.

[1] J. Phys. Chem., 35, 830, 2237, 2581 (1931).

solubility values, not because long extended soaking is considered essential to thorough washing, which may be effected quite rapidly. Other reagents were purified by the methods outlined by Scott and Johnson.[1]

Typical Analytical Systems. Each of the six test systems contained 13.5 grams of thoroughly washed solid silver chloride, 7.8796 grams of sodium nitrate, and 28.46 grams of hydrogen nitrate, per 1520.7 grams of solution.

Standard Solutions. Each 1520.7 grams of standard solution contained 7.8796 grams of sodium nitrate, 28.46 grams of hydrogen nitrate, and measured equivalent amounts of silver and chloride. Correction was made for the nitrate and sodium added with the silver and chloride. Sixteen of these standards, each about 1500 grams in weight, were made during this work. Most of these solutions contained from 0.000700 to 0.001270 grams of (dissolved) silver chloride per liter, and covered this range in steps of about 0.000050 gram.

Precipitating Reagents. Solutions of silver nitrate and sodium chloride containing 1.000 mg. of silver or its equivalent of chloride per milliliter were used as precipitating reagents. Two independently prepared sets of solutions were available.

In preparing the systems described above, all measurements were made with calibrated apparatus intended to give the measurements an accuracy of 1 part in 1000 or better. Two sets of weights and balances were required. One covered the ordinary analytical range, the other was capable of weighing the large systems, contained in glass-stoppered 3-liter Pyrex Erlenmeyer flasks.

Nephelometric Tests. The typical analytical systems were either (a) frozen and melted, or (b) cooled in ice, then held at 0.2°C. during the tests made upon the supernatant liquids. The flasks were shaken once or twice only after the removal of each set of samples.

For each test two 20.00 ml. portions were taken from a filtered 50 to 100 ml. quantity of the cold supernatant liquid and allowed to come to the same temperature as two similar portions of a suitable standard solution. It was found essential to filter the cold solutions before bringing them to room temperature. Platinum Munroe crucibles and Jena sintered glass mats were suitable for the filtration, although there was evidence that silver chloride is adsorbed by the unrinsed, freshly ignited platinum mats. The effect disappeared on continued use of the crucibles. Small amounts of the solutions used in rinsing the dry pipettes, filters, and receiver were considered well spent.

In analyzing the supernatant liquids for silver, one standard and one test solution sample were treated under identical conditions with equal 2.00 ml. portions of sodium chloride solution. In analyzing for chloride, the other pair of samples was treated similarly with 2.00 ml. portions of silver nitrate solution. For each set of four solutions, contained in matched Pyrex tubes, the rates of adding the precipitating reagents and stirring were the same. It was found that the most satisfactory results were obtained when the precipitating re-

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[1] Scott and Johnson: J. Phys. Chem., **33**, 1978 (1929).

agents were added rapidly, with the minimum amount of stirring required to give continuous, and, finally, complete mixing, before the opalescences were well formed. Four intercomparisons of the opalescences were made about an hour after their formation. Two of these comparisons constituted a "standard-solution analysis" giving the silver and chloride content of the typical analytical system. The other two comparisons were "equal-opalescence analyses" of the standard solution and the analytical system.

Concentrations were calculated from the nephelometer scale readings in the usual manner.[1] Somewhat greater accuracy may be attained by comparing the test solution with successively converging pairs of more and less concentrated standards, regarding the relative opalescences as one considers scale readings when using a sensitive galvanometer as a null-point instrument. However, the use of this refinement may well be reserved for actual measurement of atomic mass ratios. Its effective use requires a good preliminary measurement of the ratio, and is at present limited. Calibrated photoelectric cells or thermopiles may be substituted for the eye in making the nephelometric observations, but with no particular advantage.

Results of Analyses

Results obtained in the first series of tests made with the typical analytical systems are given in Part 1 of Table I. The result of each equal-opalescence "analysis" is expressed as the average ratio of the exposed length of the cup containing excess sodium chloride to that with excess silver nitrate, at the condition of equal opalescence, as shown by the nephelometer. That is, a ratio greater than unity indicates that the samples contained excess chloride; a ratio less than unity indicates that they contained excess silver. The "actual" and observed equal-opalescence ratios should agree, if the "analysis" actually shows the relative amounts of silver and chloride in the original test solution. All except the last two columns of the table refer to the typical analytical systems, or unknowns.

A careful examination of the reagents used in the synthesis of the typical analytical systems showed that the excess of silver in Systems 1 and 2 must have come from the thoroughly washed silver chloride. The sensitivity of the tests available for detecting chloride and silver in the other reagents left no doubt upon this point. For example, when 24 grams of the sodium nitrate were dissolved in 120 ml. of water and two 20 ml. portions were tested by the equal-opalescence method, both liquids appeared quite "black" when viewed in the nephelometer, the ratio being 1.0. This test showed that the sodium nitrate contained less than six parts in four million of silver or its chloride equivalent, —the smallest amounts of these impurities which produce an unmistakably detectable deviation from the unit ratio under the conditions of the test. In a similar manner the absence of silver and chloride in the other reagents was established.

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[1] J. Phys. Chem., 35, 832 (1931).

Summary of Analyses

TABLE I

Unknown Analytical Solution. Treatment	Time Cooled in Days	Standard Solution Analyses of Unknown. Milligrams Per Liter:		Equal Opalescence Tests: of Unknown. Equal Opalescence Ratio:		Equal Opalescence Tests: of Standard Equal Opalescence Ratio:	
		Silver	Chloride*	Obs.	Actual	Obs.	Actual
			Part 1				
1a	1	0.68	0.51	1.06	0.75	1.26	1.00
	2	0.70	0.52	1.04	0.74	1.22	1.00
1b	10	0.85	0.65	1.09	0.76	1.39	1.00
	14	0.73	0.53	1.12	0.73	1.66	1.00
	15	0.74	0.52	1.07	0.70	1.69	1.00
2a	1	0.87	0.53	0.96	0.61	1.26	1.00
	2	0.96	0.52	0.94	0.54	1.22	1.00
2b	4	0.98	0.68	1.00	0.69	1.40	1.00
	10	1.01	0.58	0.92	0.57	1.61	1.00
	14	1.03	0.56	0.89	0.54	1.35	1.00
			Part 2				
3a	1	0.60	0.59	1.25	0.98	1.25	1.00
	4	0.61	0.60	1.34	0.98	1.38	1.00
	7	0.61	0.61	1.31	1.00	1.30	1.00
	8	0.59	0.59	1.29	1.00	1.27	1.00
	9	0.58	0.61	1.24	1.05	1.33	1.00
	9	0.63	0.62	1.58	0.98	1.55	1.00
4b	1	2.45	2.07	0.80	0.84	0.99	1.00
	2	0.59	0.81	1.16	1.37	1.27	1.00
	3	0.72	0.58	1.11	0.81	1.53	1.00
	4	0.63	0.63	1.33	1.00	1.33	1.00
	6	0.67	0.64	1.35	0.96	1.31	1.00
	9	0.63	0.63	1.52	1.00	1.49	1.00
	9	0.63	0.65	1.68	1.03	1.66	1.00
	10	0.61	0.59	1.36	0.97	1.48	1.00
	11	0.62	0.62	1.20	1.00	1.21	1.00
	11**	1.12	1.19	1.13	1.06	1.00	1.00
	12	0.66	0.66	1.34	1.00	1.32	1.00

* The numbers in this column are chloride concentrations, in milligrams per liter, multiplied by the factor Ag/Cl.

** The container was shaken 100 times and then placed in ice for one minute before removing and filtering the samples.

These experiments led to the important conclusion that precipitated silver chloride repeatedly washed with pure water separates in such a way that an excess of silver remains with the precipitate, while the washing liquid carries away more chloride than silver.[1] They also show that at least part, and possibly all, of the excess silver is removed from the precipitate by 0.3 M nitric acid (and sodium nitrate). These conclusions were further confirmed by de-

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[1] See also: J. Phys. Chem., 35, 2241 (1931).

canting the supernatant liquids from the typical analytical systems and replacing them with fresh sodium nitrate-nitric acid solutions. The reagents and concentrations were the same as those used in the first syntheses. After saturating the solutions at room temperature, they were brought to 0.2°C., whereupon the results given in Part 2 of Table I were obtained.

Analyses made with the potentiometer and the two cells:

$$Ag/AgNO_3\,(0.1\ M)/KNO_3\,(0.1\ M)/\text{Analytical Solution}/Ag$$
$$Ag/AgNO_3\,(0.1\ M)/KNO_3\,(0.1\ M)/\text{Analytical Solution}/AgCl/Ag$$

agreed satisfactorily with the results of the nephelometric analyses. The measurements indicated that the potentiometer may be substituted for the nephelometer in these analyses without loss of accuracy. Since details of such potentiometric measurements, applied to another titration with an improved technique, are to be given elsewhere, they will be dispensed with here.

Summary

The conclusions to be drawn from the data given in Table I may be summarized: When silver chloride precipitated from nitric acid solution is repeatedly washed with pure water, the washing solution eventually contains excess chloride over silver. An excess of silver remains with the precipitate. If the non-acidified solution is decanted, and the precipitate treated with 0.3 M nitric acid (and sodium nitrate), a solution containing excess silver is obtained. If this solution is replaced by a fresh nitric acid-sodium nitrate mixture, a solution containing equivalent amounts of silver and chloride is finally obtained. The sodium nitrate has no apparent effect upon this equivalence. When the solution is frozen, melted, and cooled at 0.2°C. the solubility of the silver chloride assumes and maintains a constant value indefinitely. This equilibrium represents a suitable reference end-point for the sodium chloride-silver titration.

The solution cooled without freezing showed irregularities doubtless due to the slow coagulation of colloidal silver chloride, but reached practically the same equilibrium point as the other solution after the fourth day. Shaking the system may increase the solubility as a temperature effect; the increase is more probably due to the formation of colloidal silver chloride. The casual, arbitrary recommendations of "occasional and frequent shaking" and "a few hours cooling," as given by investigators who have used systems of this type in atomic mass determinations, are unsound and fatal to high accuracy.

The standard solution tests, made under the conditions specified in this report, yield correct analyses of the supernatant liquids, while the equal-opalescence tests give meaningless and erroneous results. This conclusion might have been reached independently from the fact that the basis of the standard solution method of analysis is absolutely sound,—the principle that two exactly similar solutions, treated with the same reagent, will behave in the same way. The equal-opalescence method of analysis has no sound experimental or theoretical basis.

The constant error in the equal-opalescence analyses in the present case is apparently due to the unbalanced action of the dissimilar precipitating re-

agents. The effect disappears as the concentration of silver chloride in the test solution (and standard) becomes larger, i.e., when the tests are made upon solutions saturated at room temperature. In any application of the equal-opalescence method to titrations of the type under consideration, serious errors will result when the analytical systems are cooled in ice. These errors will depend upon the volume of analytical solution used, the nature and amounts of the extra compounds present, and the conditions under which the tests are made. Averaging will not remove errors of this nature from the results of faulty analyses.

The solubility values for silver chloride given in this report do not agree with those given by Hönigschmid[1] for solutions at the end-point of the sodium chloride-silver titration. It seems very probable that the disagreement is due to the fact that this investigator adjusted his analytical systems to the equal-opalescence end-point. Strictly speaking, measurements made with systems so adjusted have only a limited applicability in estimating solubility values, or, for that matter, atomic mass ratios.

The Sensitivity of the Equal-Opalescence Method

Up to the present time all estimates of the sensitivity of the equal-opalescence method of analysis have been based mainly on opinion. A general method for finding the true sensitivity of any analytical method intended for use in titrations of the present type is given by the following illustrative experiment. Two of the typical analytical systems which had been shown to contain equivalent amounts of silver and chloride were saturated at room temperature. They were then titrated away from the end-point in opposite directions, with very dilute solutions of silver nitrate and sodium chloride. The values given in the table below are the average equal-opalescence ratios found one and twelve hours after the formation of the opalescences. The tests, which were made by the method of Richards and Wells,[2] covered a period of about three months.

No.	Deficiency of Silver Mg./Liter	Ratio after:		No.	Excess of Silver Mg./Liter	Ratio after:	
		1 Hour	12 Hours			1 Hour	12 Hours
5	0.00	0.86	0.87	6	0.00	1.00	1.01
	0.00	0.93	1.00		0.00	0.85	1.00
	0.00	0.93	0.97		0.00	1.00	1.04
	0.10	1.04	1.03		0.08	1.01	1.02
	0.10	0.98	1.00		0.08	1.01	1.04
	0.21	0.96	1.01		0.17	1.00	1.02
	0.21	1.03	0.99		0.17	0.98	1.01
	0.33	1.22	1.23		0.27	1.02	1.04
	0.33	1.21	1.24		0.27	1.00	1.02
	0.33	1.27	1.24		0.36	0.96	1.00
					0.36	1.00	1.03
					0.45	0.74	0.79
					0.45	0.79	0.80

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[1] Hönigschmid: J. Am. Chem. Soc., 53, 3012 (1931).

[2] Richards and Wells: J. Am. Chem. Soc., 27, 459 (1905).

These results removed the last apparent inconsistency between the data given in this paper and that recorded by Richards and Wells.[2] They explain why these investigators were consistently able to derive unit equal-opalescence ratios in "analyses" of solutions which, by their method of preparation, probably contained excess silver. In brief, the data in the above table show that the "classical" experiments of Richards and Wells do not provide an adequate experimental foundation for the use of the equal-opalescence method of analysis in the accurate determination of atomic mass ratios. There is an uncertainty of more than 0.57 milligrams of silver or its chloride equivalent *per liter* of analytical solution, in titrations made with the equal-opalescence method at room temperature. In these titrations it has been customary to use from one to five liters of solution and 0.5 to 10 gram samples of silver, in each analysis.

The failure of the equal-opalescence tests to respond to the additions of the analytical reagents may be due to the mere insensitivity of the method, or to adsorption of the added silver and chloride salts by the silver chloride precipitate. The sharp change in the nephelometric ratios eventually found on either side of the end-region argues in favor of the latter possibility. If such effects are characteristic, only the application of corrections based on analyses of the precipitated silver chloride can justify the use of the data obtained in titrations of this type, in "revising" atomic mass values.

The standard solution method of analysis is not exempt from errors due to adsorption. However, it offers the unique advantage that the absolute quantities of material entering and leaving the analytical system, and the quantities present in the liquid phase, are known at all stages of the titration. This information is essential in any attempt to analyze the precipitated compound or study adsorption effects.

General Discussion

In the case of the sodium chloride-silver titration, the standard solution method permits the excess or deficiency of silver in the analytical solutions to be determined to about 0.02 milligram for every ten grams of silver used. That is, in so far as the determination of the end-point limits the experimental accuracy, it is possible to obtain analyses correct to one part in 500,000, by the use of the procedure outlined in this paper, or by some form of *unequal-opalescence* method. Such a degree of accuracy is comparable with that which may be attained in careful weighings with a good balance, and in the other simple steps of manipulation in the analytical procedure. In general, in many other similar titrations, by the same approach, a method may be devised for bringing the analytical systems to a correct reference end-point, where the absolute amounts of excess reactant in the liquid phase may be determined by non-arbitrary tests. By working with correctly weighed amounts of the pure reactants, and applying a correction for impurities in the insoluble product, atomic mass ratios free from all sources of constant error may be obtained.

On the other hand, the application of the equal-opalescence method to the sodium chloride-silver titration would, in general, yield incorrect values for the ratio, as the data recorded in this paper show. For example, the method of Richards and Willard,[1] if applied to this titration, might be expected to yield a low value for the sodium chloride-silver ratio. With the method of Richards and Wells,[2] one could obtain practically any desired or expected value, within rather wide limits, simply by making the "analyses" of the supernatant liquids under the requisite arbitrary conditions. There is evidence[3] that these two equal-opalescence methods, which have been used without essential modification in many attempts to evaluate a wide variety of atomic mass ratios, fail even more seriously in other titrations.

In this connection, the fallacy of a prevalent notion concerning the high accuracy of nephelometrically determined atomic mass ratios may be pointed out. It is a peculiarity of conventional equal-opalescence atomic mass determinations that the quantities of material representing the antecedent and consequent of the ratio to be measured are weighed and combined in amounts calculated from an assumed value for the ratio. While the final adjustment to the end-point, based on tests of the supernatant analytical liquids, presumably determines the final measured value of the ratio, the initial adjustment is usually made with the expectation that the supernatant liquids will be at the end-point. With an arbitrary method of testing for the end-point, or a method insensitive to the addition of the analytical reagents to the system at the end-point, both the final value found for the ratio and its "probable error" are largely predetermined by mere opinion. The equal-opalescence method of analysis, as applied in the past, fulfills both of these requirements. The "determination of the atomic mass" by such a method is exactly analogous to the procedure of "proving" that a mass of 1.001 gram has a mass of 1.00000 gram, by showing that it gives the same point of rest, when compared by substitution weighing with a correct 1.00000 gram mass, on a balance insensitive to the difference between the masses.

It is thus quite unfair to compare the atomic mass values derived from equal-opalescence analyses with those derived by other and independent methods, using the "probable error" of the measured ratios as a criterion of their relative accuracy. The nephelometrically determined values would be given a false appearance of high accuracy and undue weight. Much excellent analytical work in this field has been overshadowed by inferior nephelometric analyses as a result of this very practice.

It may be suggested that the present tendency to reject atomic mass values from other sources in favor of nephelometrically determined values might best be justified by carrying out nephelometric analyses in a manner which would indeed make them superior to other analyses. It is with this idea in mind that the approach to the problem of accurate atomic mass measurements illustrated in the present paper has been proposed, as a general means of actually attaining the high accuracy of which the nephelometric method of analysis is capable.

Princeton, New Jersey.

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[1] Richards and Willard: J. Am. Chem. Soc., **32**, 32 (1910).

[2] Richards and Wells: J. Am. Chem. Soc., **27**, 459 (1905).

[3] Johnson: J. Phys. Chem., **35**, 2581 (1931).

VON WEIMARN'S PRECIPITATION THEORY AND THE FORMATION OF COLLOIDAL GOLD

BY HARRY B. WEISER AND W. O. MILLIGAN

Referring to his law of corresponding states for the precipitation process von Weimarn[1] says: "Without any doubt my law of corresponding states for the crystallization process is truly a quantitative natural law." While this may be the case, one of us[2] has pointed out that von Weimarn's formulation has been simplified to the point where its usefulness in certain cases may be open to question. Others[3] have likewise questioned the general usefulness of von Weimarn's theory. This leads von Weimarn[4] to state: "Recently H. B. Weiser [See his book "The Colloidal Salts."] has repeated and still further extended the false view of the precipitation theory which has been credited to me. [Rept. Imp. Res. Inst. Osaka, 9, 107 (1928)]. The theory which is criticized by the authors named, did not originate with me and I yield with pleasure the honor of its discovery to one of the critics. Moreover, I have no time to clear up these misunderstandings specifically."

Von Weimarn's theory has been of such outstanding importance in pure and applied colloid science[5] that no one can question its value. At the same time, it can do no harm to call attention to its limitations as a research tool. The recognition of such limitations in usefulness does not result from misunderstanding owing to incomplete knowledge, as von Weimarn seems to think. On the contrary, a broad comprehension of the applicability of the theory is essential to an understanding of its limitations.

In the following paragraphs the applicability and limitations of the von Weimarn theory will be considered briefly, after which its inadequacy to predict results in certain instances will be illustrated by the case of the formation of colloidal gold by reduction.

Theoretical

Von Weimarn points out that precipitation from solution takes place in two stages: the first in which the molecules in solution condense to crystalline nuclei; and the second which is concerned with the growth on the nuclei as a result of diffusion. The initial rate of precipitation W is expressed in von Weimarn's equation

$$W = K\frac{Q - L}{L} = K\frac{P}{L}$$

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[1] Kolloid-Beihefte, 18, 55 (1923).

[2] Weiser: "The Colloidal Salts," (1928).

[3] Buchner and Kalff: Rec. trav. chim., 39, 135 (1920); Bancroft: J. Phys. Chem., 24, 100 (1920); Freundlich: "Kapillarchemie," 631 (1922).

[4] Kolloid-Z., 53, 366 (1930).

[5] Cf. Weiser and Moreland: J. Phys. Chem., 36, 1 (1932).

where K is a constant; Q the total concentration of the substance that is to precipitate; and L its solubility. $Q - L = P$ is the absolute supersaturation and P/L is the percentage supersaturation.

The velocity of growth, V, on nuclei is given by the Nernst-Noyes equation

$$V = D/S \cdot O \cdot (Q - L)$$

where D is the diffusion coefficient; S, the thickness of the adherent film; O, the extent of surface; and Q and L have the same significance as above.

In actual practice W cannot be measured and V either cannot be measured at all or only with greatest difficulty. Accordingly von Weimarn introduced what he termed the "precipitate form coefficient" N, which is related to the mean magnitude of the single crystals in gram molecules Gm, by the expression

$$Gm \times N = \text{constant.}$$

N may be represented qualitatively and in some cases approximately quantitatively by the expression

$$N = P/L$$

which means that in the simplest case, the form of a precipitate is determined exclusively by the prevailing percentage supersaturation at the moment the precipitation starts. If this is approximately true then for the substances x, y, and z:

$$N_x = \frac{P_x}{L_x};\ N_y = \frac{P_y}{L_y};\ \text{and } N_z = \frac{P_z}{L_z}.$$

Now if the mean size in gram molecules of the particles in the several precipitates is to be the same; that is,

if, $$N_x = N_y = N_z$$

then, $$\frac{P_x}{L_x} = \frac{P_y}{L_y} = \frac{P_z}{L_z}$$

This is the simplest form of von Weimarn's law of corresponding states for the precipitation process.

As would be expected the simple formulation is seldom applicable quantitatively, since in most cases there are a number of factors other than percentage supersaturation which influences the value of N and hence the mean particle size; and the magnitude of these factors is, in general, different with different substances. To take care of these several factors von Weimarn introduces a multiplier, J, into the equation for N which now becomes

$$N = J\,P/L.$$

But the value of J is in general not the same for different substances; hence the expression for von Weimarn's law of corresponding states becomes

$$J_x \frac{P_x}{L_x} = J_y \frac{P_y}{L_y} = J_z \frac{P_z}{L_z}$$

in which J_x, J_y and J_z are specific variable multipliers "the product of all other factors in addition to P/L which influence the crystallization process."

These factors must be expressed in abstract numbers equivalent to that for P/L.[1] This means simply that von Weimarn's law becomes quantitative and generally applicable by using variable multipliers which may include an indefinite number of unevaluated variables. Among the several factors which are lumped together in the variable multipliers are: the effect of the viscosity of the reaction medium, solvation as connected with molecular association, polymerization of the reactant molecules, molecular complexity of the reactants, adsorption, the presence of dust particles, the extent of agitation on mixing, the specific tendency to form nuclei, the specific tendency to grow on nuclei, the change in solubility with particle size, etc.

The significance of the expression: $N = J\ P/L$ is that the mean size of the particles in a precipitate is determined by the product of the initial percentage supersaturation and of all other factors in addition to percentage supersaturation which enter into the process. In other words, the size of the precipitated particles is determined by all of the factors which enter into the precipitation process. One cannot question the truth of this statement; but it is obvious that it may not be particularly helpful in certain cases.

Fortunately, in a number of cases the von Weimarn formulation may be used to advantage in its simplest form. This is true under the following conditions: (1) if the factors influencing the precipitation process which are lumped together in von Weimarn's J are relatively unimportant as compared with the prevailing P/L value at the moment of precipitation; (2) if the factors included in J are significant but are approximately equal for the precipitation of the two or more substances under consideration. On the other hand, the von Weimarn formulation may cease to be very helpful in case the J values in the precipitation processes being compared are far from equal. This is especially true if the factors collected together in J should happen to be of greater importance than the prevailing percentage supersaturation in determining the form of the precipitate. This appears to be the case in the formation of colloidal gold by certain reduction processes to be considered in the next section.

The Formation of Colloidal Gold

In 1906 von Weimarn[2] formulated the rule that the mean magnitude of the individual crystals of precipitates will decrease progressively with progressively increasing concentration of reacting solutions, providing the process of direct crystallization is complete. If the form of the precipitate is determined in large measure by the prevailing percentage supersaturation, it follows from the expression

$$\mathrm{N} = \mathrm{J}\,\frac{\mathrm{Q} - \mathrm{L}}{\mathrm{L}} = \mathrm{J}\,\frac{\mathrm{P}}{\mathrm{L}}$$

that N will be larger and hence the mean size of the particles will be smaller the larger the value of Q, that is, the higher the concentration of reactants. The formation of colloidal gold by certain reduction processes is an apparent

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[1] Von Weimarn: Kolloidchem-Beihefte, **18**, 48 (1923).

[2] J. Russ. Phys.-Chem. Soc., **38**, 267, 624 (1906).

contradiction to this rule. Thus Zsigmondy[1] showed in the case of the reduction by formaldehyde of $HAuCl_4$ made slightly alkaline with K_2CO_3, that the greater the dilution of $HAuCl_4$ the higher the degree of dispersion of the particles and *vice versa.* A similar behavior was noted by Svedberg[2] who employed $N_2H_4 \cdot 2HCl$ in alkaline solution as the reducing agent. This result would never be predicted by the von Weimarn relationship but after the fact, von Weimarn explains the apparently anomalous behavior by assuming that hydrolysis of gold salt, $HAuCl_4$ or $KAuO_2$ with the formation of $Au(OH)_3$ sol which is subsequently reduced to blue $Au(OH)$ sol, is the initial and therefore the significant state in determining the degree of dispersity as it is influenced by concentration of reactants. In such instances, "the principal reacting molecules are obviously the molecules of water, and it is by the ratio of their number to the number of hydrolyzing salt molecules that the velocity, as well as the degree of completeness, of the hydrolytic process, is determined."[3] In other words, the greater active mass of the water and not the lower concentration of $HAuCl_4$ in the more dilute solutions is assumed to account for the higher dispersity in such solutions, since the higher the dilution the greater the number of nuclei formed by hydrolysis and hence the smaller the individual particles. From this point of view, it follows that if the primary particles of the $Au(OH)$[4] sol which is assumed to form as an intermediate product, are very small and the reducing agent insufficient, the reduction will be very slow and yet the particles will be small. On the other hand, if the originally formed particles of $Au(OH)$ are relatively large the complete transformation to gold takes place slowly and the particles will be large. That is, the mean size of the primary particles in a gold sol prepared by the formaldehyde method stands in direct relation to the size of the particles of $Au(OH)$ sol, the reduction of which results in the formation of colloidal gold.

The mechanism of the formation of colloidal gold which von Weimarn proposes in order to show that the process is strictly in accord with his theory is ingenious but there are certain lines of evidence which indicate that it is not correct:

In the first place Thiessen[5] has shown that all the conditions which increase the degree of hydrolysis of $HAuCl_4$ solution decreases the number of particles that are formed in a given time on adding a suitable reducing agent. This is well illustrated by observation of the effect of temperature and age of $HAuCl_4$ solutions on the number of particles formed in a given time with hydrogen peroxide as reducing agent. In these experiments 1 cc of 0.6% $HAuCl_4 \cdot 4H_2O$ solution was added to 100 cc of water and treated with 500 cc of 5% H_2O_2. After a definite time interval 50 cc of 0.08% $N_2H_4 \cdot 2HCl$ was added. The latter reducing agent is known to cause rapid growth on the nuclei already present and to inhibit the formation of new nuclei. A count of

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[1] Zsigmondy-Alexander: "Colloids and the Ultramicroscope," 132 (1909).

[2] Kolloid-Z., 4, 168 (1909).

[3] Von Weimarn: Chem. Review, 2, 227 (1926).

[4] Probably hydrous Au_2O.

[5] Kolloidchem-Beihefte, 29, 122 (1929).

the number of particles gives the number of nuclei that are present after a given time interval. The results of some observations are given in Fig. 1. The upper curve was made with freshly prepared solutions at 15°; the middle curve with freshly prepared solutions at 21° and the lower curve with solutions previously heated to boiling and cooled suddenly to 15°. The conductivity of the fresh solution at 15° was 1.25×10^{-4} mhos and of the boiled solution at 15° was 1.37×10^{-4} mhos. The increased conductivity is indicative of an increase in hydrolysis; yet the number of particles formed with the more highly hydrolyzed solution was much less and the size correspondingly greater than with the less hydrolyzed solutions. Similarly, the number of particles in a sol formed with a 10-minute old solution having a conductivity of 1.27×10^{-4} mhos was twice as great as with a 40-minute old solution with a conductivity of 1.34×10^{-4} mhos. Similar results were obtained with CO as reducing agent. These observations show that the greater the hydrolysis of the solution prior to the addition of the reducing agent, the fewer the number and hence the larger the particles. This result is diametrically opposed to what one would predict from the von Weimarn mechanism. The presence of larger particles in the more highly hydrolyzed solutions is attributed by Thiessen to a retardation of the spontaneous formation of nuclei by the hydrolysis products.

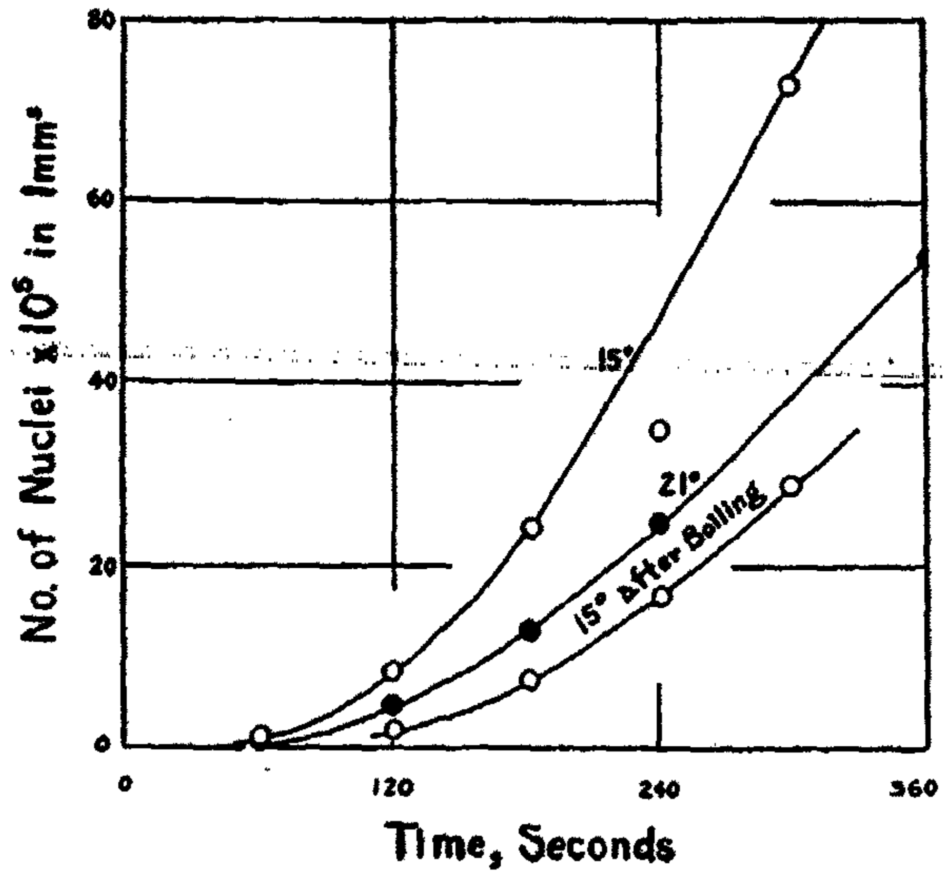

Fig. 1

Effect of treatment of $HAuCl_4$ Solution on the Number of Particles in a Gold Sol obtained therefrom. (Thiessen).

In the second place the number of particles in a gold sol is greater the higher the dilution of gold salt even when the latter undergoes little or no hydrolysis. This conclusion is reached as a result of the following experiments.

Experimental

Although a number of procedures have been described for the preparation of colloidal gold, in all but a few cases the gold was reduced from a solution of chlorauric acid. This is prepared by dissolving metallic gold in aqua regia and evaporating to dryness. The product when dried over $CaCl_2$ is considered to be $HAuCl_4 \cdot 3H_2O$.[1] However, some $AuCl_3$ will be present unless the chlorauric acid is purified in some manner. Since von Weimarn believes that the hydrolysis of the gold salt plays a significant if not a predominate part in the mechanism of the reduction of gold compounds to colloidal gold, it was thought desirable to use a gold solution in which there is little likelihood of hydrolysis. Potassium chloraurate was chosen as the most suitable gold compound for the present experiments since it is the salt of such a strong base and strong acid that it will hydrolyze but little if at all.

Preparation of $KAuCl_4$. Pure sheet gold was dissolved in aqua regia, the excess acids removed by boiling, and the resulting chlorauric acid extracted from the aqueous solution with ethyl acetate.[2] The chlorauric acid was crystallized from the ethyl acetate, dissolved in distilled water, and allowed to react with the calculated quantity of recrystallized potassium chloride. The resulting $KAuCl_4$ was crystallized from aqueous solution by slow evaporation in a vacuum desiccator over H_2SO_4. Finally the best crystals were separated mechanically, washed with anhydrous ether,[3] and the excess ether removed in a vacuum desiccator. The gold content of the crystals was obtained without attempting to dry them to any definite composition. A 0.01 molar stock solution of $KAuCl_4$ was made up from which other solutions were prepared by dilution.

The Distilled Water. The purity of the distilled water used is an important factor in the preparation of colloidal gold. Much has been written by Zsigmondy and others[4] concerning the necessary purity of the distilled water. In view of the fact that a solution of electrolytes is reduced and electrolytes are formed as products, it is apparent that slight traces of electrolyte impurities in the water employed will have little or no effect. Organic material, dust particles, etc., which can serve as nuclei are the undesirable variable impurities that may be in the distilled water. Accordingly water of minimum conductivity is not necessarily the best to use. In the present investigation water prepared by a single distillation of ordinary laboratory grade distilled water in a copper still with a block tin condenser gave the same results as the same water distilled twice more from $KMnO_4$ and H_2SO_4 respectively, in a pyrex still with a block tin condenser. However, care was used to let the distilled water stand for several days in an aged bottle, and to syphon off the water, taking the precaution not to disturb the lower layer, into which the undesirable dust particles had settled.[5] This distilled water was used in the experiments about to be described.

Size of Au Particles in Sols formed by Reduction of $KAuCl_4$ with H_2O_2. Amounts of solution as indicated in Table I were mixed together in the follow-

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[1] Lengfeld: Am. Chem. J., 26, 328 (1901).

[2] Lenher and Kao: J. Phys. Chem., 30, 126 (1926).

[3] Mylius and Hüttner: Ber., 44, 1315 (1911).

[4] Zsigmondy-Thiessen: "Das kolloide Gold" (1926).

[5] Zsigmondy-Alexander: "Colloids and the Ultramicroscope."

ing manner: To the water in a 250 cc pyrex flask was added first the $KAuCl_4$ solution and then 0.2 cc of 30% H_2O_2. The latter was allowed to flow in from a pipette while the contents of the flask were shaken with a rotary motion. The reduction was carried out at room temperature. A tint of color appeared in about 30 seconds, and the reaction was complete as evidenced by no further change in color in two or three minutes. Tests disclosed the absence of unreduced gold in the supernatant solution after coagulation of the sol. A clear, red, colloidal gold solution was obtained in each case. The number of particles

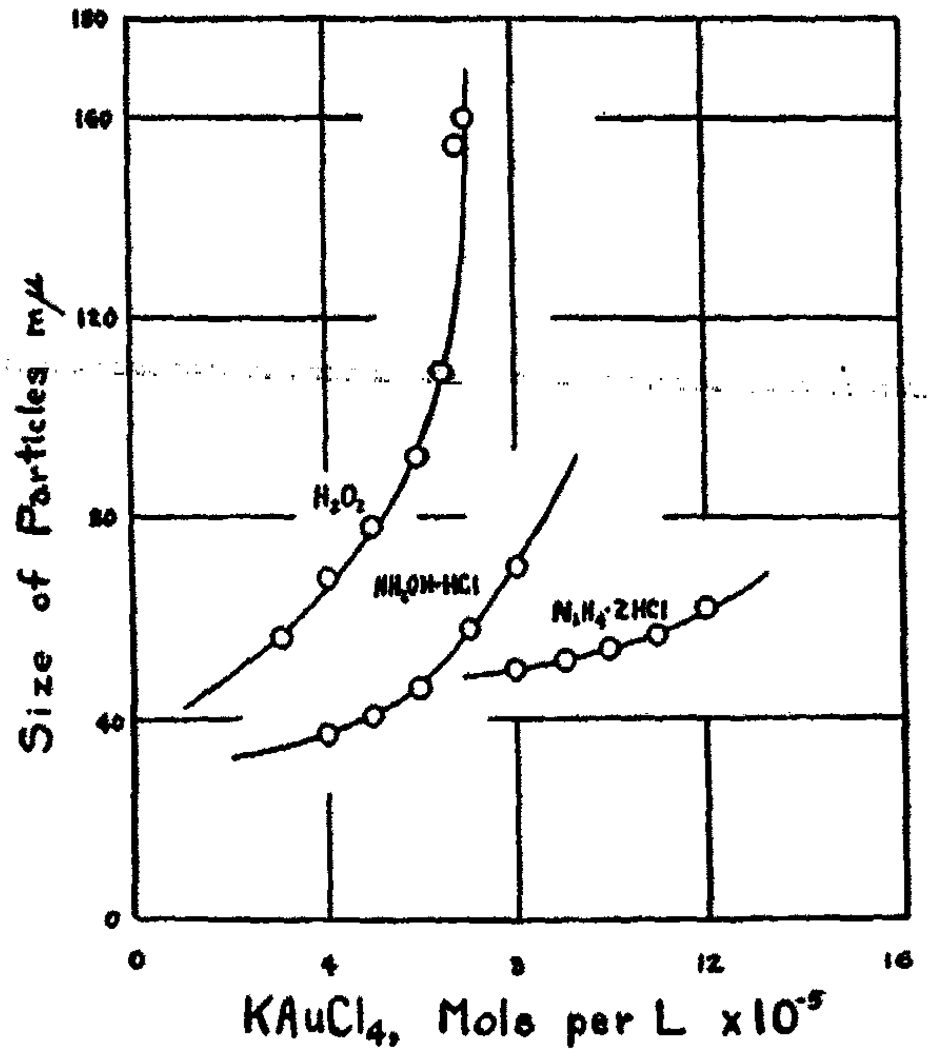

FIG. 2
Effect of Concentration of Gold Salt Solution on the Size of Particles of Colloidal Gold obtained by reduction with H_2O_2, $NH_2OH \cdot HCl$ and $N_2H_4 \cdot 2HCl$.

TABLE I

Size of Au Particles formed by Reduction of $KAuCl_4$ with H_2O_2

Solutions mixed			Resulting concentration of $KAuCl_4$ Molarity $\times 10^{-5}$	Mean linear dimension of Au particles mμ
$KAuCl_4$ 0.001 M cc	H_2O cc	H_2O_2 30% cc		
7	92.8	0.2	7	160
6.75	93.05	0.2	6.75	155
6.5	93.3	0.2	6.5	109
6	93.8	0.2	6	92
5	94.8	0.2	5	78
4	95.8	0.2	4	68
3	96.8	0.2	3	56

in a definite volume of sol was counted in the usual way by means of the Zeiss Slit Ultramicroscope. From the data so obtained the particle size was calculated assuming the particles to be cubic. The results are given in Table I and shown graphically in Fig. 2.

Size of Au Particles in Sols formed by Reduction of $KAuCl_4$ with $NH_2OH \cdot HCl$. In the reduction with H_2O_2, a constant amount of reducing agent was used. This was permissible since the excess H_2O_2 has little or no effect on the size of the particle.[1] Since this is not the case with many reducing agents, in the subsequent experiments a constant mole ratio of the $KAuCl_4$ and the reducing agent was maintained. Solutions *A* and *B* prepared as indicated in Table II were mixed together. In every case a clear, red colloidal gold solution resulted. The particle size in each was determined with the results recorded in the table and shown graphically in Fig. 2.

TABLE II

Size of Au Particles formed by Reduction of $KAuCl_4$ with $NH_2OH \cdot HCl$

Solutions mixed				Resulting concentration of $KAuCl_4$ Molarity $\times 10^{-5}$	Mean linear dimension of Au particles mμ
A		B			
$KAuCl_4$ 0.001 M cc	H_2O cc	$NH_2OH \cdot HCl$ 0.00375 M cc	H_2O cc		
8	42	8	42	8	70
7	43	7	43	7	58
6	44	6	44	6	46
5	45	5	45	5	41
4	46	4	46	4	37

Size of Au Particles in Sols formed by Reduction of $KAuCl_4$ with $N_2H_4 \cdot 2HCl$. The reducing agent was added to the several concentrations of $KAuCl_4$ solutions as given in Table III. The size of the gold particles in each of the clear red sols was determined. The results are given in the table and shown graphically in Fig. 2.

TABLE III

Size of Au Particles formed by Reduction of $KAuCl_4$ with $N_2H_4 \cdot 2HCl$

Solutions mixed			Resulting concentrations of $KAuCl_4$ Molarity $\times 10^{-5}$	Mean linear dimensions of Au particles mμ
$KAuCl_4$ 0.001 M cc	H_2O cc	$N_2H_4 \cdot 2HCl$ 0.001 M cc		
12	76	12	12	62
11	78	11	11	57
10	80	10	10	54
9	82	9	9	52
8	84	8	8	50

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[1] Westgren: Z. anorg. Chem., 93, 154 (1915).

Conclusions

The particles of colloidal gold formed by reduction processes are larger the higher the concentration of the gold salt reduced. This is not in accord with von Weimarn's theory which states that, provided the process of crystallization is complete, the mean size of the individual crystals is smaller the higher the concentration of the reactants. Von Weimarn explains this anomalous behavior by postulating that hydrolysis of the gold salt with the formation of $Au(OH)_3$ which is subsequently reduced to $Au(OH)$ and finally to Au is the initial and therefore the important step in determining the degree of dispersity as it is influenced by the concentration of reactants. From this point of view the greater hydrolysis at lower concentrations accounts for the greater number of nuclei and hence the smaller size of the particles in low dilution. Against this point of view are: (1) Thiessen's observations that the greater the hydrolysis of the gold solution prior to the addition of the reducing agent, the fewer the number and hence the larger the particles; and (2) the observations herein recorded which show that in the absence of appreciable hydrolysis of gold salt the gold particles are smaller the more dilute the solution.

It is apparent from these considerations that the percentage supersaturation at the beginning of precipitation is not the only factor and may not be the most important one in determining the primary particle size in the formation of colloidal gold. In the absence of added nuclei, the size of the primary gold particles in a sol will be determined, for a given concentration of reactants by the velocity with which nuclei form spontaneously and the velocity with which the particles grow on the spontaneously formed nuclei. Now it is to be expected from the Nernst-Noyes formulation that the velocity of growth on added nuclei will be greater the greater the absolute supersaturation of the solution with respect to gold; in other words, the greater the initial concentration of gold salt. The same thing will apply to the rate of growth on nuclei formed spontaneously. In general to obtain very highly dispersed particles, the velocity of formation of nuclei must be relatively rapid and the growth on the effective nuclei must be relatively slow. Since gold is extremely insoluble, the percentage supersaturation of the metal is relatively high at all concentrations of the gold salt under consideration. Under these conditions the rate of formation of nuclei is not directly proportional to the percentage supersaturation but is relatively more rapid at the higher dilutions. Moreover, at the higher dilutions the rate of growth on nuclei is relatively slower so that relatively more nuclei can form before the supply of gold is exhausted. For both of these reasons the size of the primary particles is smaller in the sols formed from the more dilute solutions of gold salt.

Von Weimarn may contend that larger particles formed in the more concentrated solutions are aggregates rather than primary particles. There is no evidence to support this view under the experimental conditions herein described. All the sols were perfectly clear and the ultramicroscopic examination showed no indication of aggregate formation. Moreover, it is well known that particles grow by direct precipitation of gold on gold nuclei added to the reduction mixture and there is no reason to believe that the process is any different in the presence of spontaneously formed nuclei. In this connection, if one insists that $Au(OH)_3$ and Au(OH) are precipitated as intermediate products in the reduction process, then the growth on gold nuclei must result from initial precipitation of $Au(OH)_3$ on such particles followed by reduction to Au(OH) and subsequently to gold. While this could be true to a certain extent, it seems to be altogether unnecessary to assume such a mechanism since it is probably not in general accord with the facts.

Summary

The following is a brief summary of the results of this article.

1. Von Weimarn's formulation of the precipitate form coefficient and the law of corresponding states for the precipitation process have been considered from the standpoint of their applicability and limitation as a research tool.

2. The particles of colloidal gold formed by reduction processes are in general larger the higher the concentration of the gold salt reduced. This would not be predicted from the von Weimarn theory which states that, provided the process of direct crystallization is complete, the mean size of the individual crystals is smaller the higher the concentration of reactants (the higher the percentage supersaturation at the moment precipitation begins).

3. Von Weimarn explains the apparently anomalous behavior noted in (2) by postulating that hydrolysis of gold salt with the formation of $Au(OH)_3$, which is subsequently reduced to Au(OH) and finally to Au, is the initial and therefore, the important step in determining the degree of dispersity as it is influenced by the concentration of reactants.

4. Against von Weimarn's general point of view are the observations: (a) the greater the hydrolysis of gold solution of a given concentration, prior to the addition of reducing agent, the fewer the number and hence the larger particles of gold (Thiessen); (b) the observations recorded in this paper which show that in the absence of hydrolysis of gold salt, the gold particles are smaller the lower the concentration of the salt reduced. This was found to be true for the reduction of solutions of $KAuCl_4$ with H_2O_2, $NH_2OH{\cdot}HCl$ and $N_2H_4{\cdot}2HCl$.

5. Because of the very low solubility of gold in water, the percentage supersaturation of the metal is relatively high at all concentrations of gold salt reduced. Under these conditions the rate of formation of nuclei is not directly proportional to the percentage supersaturation but is relatively more rapid at the higher dilutions. Moreover at the higher dilutions the rate of growth on nuclei is relatively slower so that relatively more nuclei can form before the supply of gold is exhausted. For both of these reasons the size of the primary particles is smaller in the sols formed from the more dilute solutions of gold salt.

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THE THERMAL DECOMPOSITION OF DIMETHYLAMINE

BY H. AUSTIN TAYLOR

Previous kinetic studies of the decompositions of ethylamine,[1] of propylamine[2] and of isopropylamine[3] have shown that although the reactions are complex it is reasonably certain that the initial process is homogeneous and unimolecular in each case. The observed decrease in the rates of decomposition for propylamine and isopropylamine, with decreasing pressure led to the conclusion that activation of a single vibrational bond alone was involved. Such an apparent simplicity is to be contrasted with the very complex mechanisms involved in the activation process of other unimolecular reactions. In an effort to see what effects a secondary amine would have on such results the present investigation was carried out and although appearing on the surface to be very similar, its extreme complexities suggest that the simplicity of mechanism of activation is probably fortuitous due to a mutual compensation of several reactions. Further work on the amines is still in progress but it seems advisable that a report of the type of complications involved should be given since a similar condition may possibly account for certain peculiarities in other cases.

The apparatus and procedure were identical with those already published. The results at pressures below 15 mms. were obtained by the use of a sloping manometer whereby the pressure change was multiplied by a factor of 8.26. The dimethylamine was redistilled from an Eastman sample and showed a small trace of a primary and tertiary amine. The decomposition was studied over the temperature range 480-510°C. at pressures from 3.75 to 600 mms. The pressure increase during reaction averaged 120 percent although a slight drift with pressure was noticeable, the increase being greater at lower pressures. No effect of temperature on this value could be observed.

The increases in pressure plotted against time give typical unimolecular rate curves showing, however, a very slow but continued pressure increase towards the end of the reaction. It was necessary therefore to follow a reaction which for example had a quarter life of 3 minutes, about 15 hours to obtain a reliable end-point.

In Table I are given the quarter lives for the various temperatures and pressures studied, calculated as the time taken for the pressure to increase by one-quarter of the total change.

The natural conclusion from such a constancy of the quarter lives at the higher pressures is that the reaction is unimolecular. At lower pressures the order of reaction would appear to be between one and two.

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[1] J. Phys. Chem., 34, 2761 (1930).

[2] J. Phys. Chem., 35, 2658 (1931).

[3] J. Phys. Chem., 36, 670 (1932).

TABLE I

Initial Pressure in mms.	t_{25} mins.	Initial Pressure in mms.	t_{25} mins.
	Temperature 480°C.		
88	9.9	279	5.8
133	8.8	333	5.3
181	7.8	597	4.6
	Temperature 490°C.		
81	6.5	229	4.6
120	5.6	303	3.8
176	5.2	555	3.0
	Temperature 500°C.		
5.8	10.0	161	2.8
15	8.0	198	3.0
53	5.4	251	2.4
105	3.5	315	2.2
116	3.1	547	2.1
	Temperature 510°C.		
3.75	7.8	297	1.5
14.8	4.9	404	1.4
44	3.6	409	1.5
90	2.6	421	1.5
160	2.2	486	1.4
173	2.2	522	1.5
225	2.0	524	1.3
252	1.8	622	1.45

Since a change in end-point had been observed with change in initial pressure it seemed possible that the reaction might be in part at least heterogeneous. On increasing the surface of the pyrex reaction vessel by the addition of measured lengths of pyrex tubing whereby the surface to volume ratio was increased 3.4 times, the quarter lines given in Table II were obtained.

TABLE II

Increased Surface (S/V = 3.4) Temperature 510°C.

Initial Pressure	t_{25}
4	8.0
41	4.0
161	2.2

These values, it will be seen, are in substantial agreement with those previously quoted showing the absence of any marked heterogeneity.

Assuming then the reaction to be homogeneous and unimolecular it will be seen that at 510°C. the velocity constant appears to fall off below about 300 mms. It is of interest to see the effects of various added gases. The effect of the reaction products was first investigated. The decomposition of 120 mms. of dimethylamine was allowed to go to completion. A further charge of amine was then added and the rate followed in the usual manner. Two such runs were made in the pressure region where the reaction rate had fallen off namely at 94 and 44 mms. each with the products from 120 mms. of the amine present. The quarter life was 2.0 minutes in each case as compared with 2.6 and 3.6 minutes, respectively, obtained in the absence of products. It appears, therefore that the products are capable of maintaining the rate somewhat in the lower pressure range. A similar effect was observed with hydrogen, ethane and ammonia. With 200 mms. of hydrogen the quarter lives of 39 and 161 mms. of amine were 2.4 and 1.6 minutes, respectively, compared with 3.9 and 2.2 minutes without hydrogen. A similar amount of ethane gave times of 2.8 and 1.6 minutes for 47 and 162 mms. of amine whilst 200 mms. of ammonia gave for 46 and 164 mms. of amine quarter lives of 2.8 and 1.6 minutes. In all the reactions involving either the products, hydrogen or ethane the end-point of the decomposition was the same as in the absence of added gases. With ammonia, however, the total pressure increase rose from 125 to 135 percent of the initial amine pressure which might suggest some actual chemical interaction although even this extent of change is not as great as the 150 percent observed with 4 mms. initial pressure of amine alone. With ethylene as added gas more definite evidence of reaction was obtained. Even making due allowance for the pressure decrease due to polymerisation of the ethylene, data for which were obtained from a blank run with ethylene alone, the observed pressure increase due to the amine was only 80 percent of the initial pressure. The general course of the reaction too was quite changed notably with respect to the end-point which was reached very sharply after only 40 minutes in comparison with the several hours necessary with amine alone. A comparison of the rate of reaction in presence of ethylene with that in its absence is thus impossible.

One definitely inert gas was tried namely nitrogen and found to be without effect at any stage of the reaction. When 200 mms. of nitrogen were added to 161 and 485 mms. of amine quarter lives of 2.2 and 1.5 minutes were obtained in complete agreement with the values obtained for the amine alone.

Such a behavior by a reaction would appear to be best explained on the assumption that the reaction is unimolecular. The constancy of rate at higher pressures, its falling value at lower pressures, the absence of effect of truly inert gases at any pressure, the maintenance of the high pressure rate in the low pressure region by certain complex molecules with absence of effect by the same molecules in the high pressure range are all usually accepted as unequivocal evidence of unimolecularity in a reaction.

The reaction rates obtained may thus be compared with others similarly obtained. The energy of activation obtained by plotting the logarithms of the limiting quarter lives at higher pressures against the reciprocals of the corresponding absolute temperatures and taking the slope of the straight line so given is found to be 44,300 calories. The value is identical within the limits of error with that obtained for ethylamine and for propylamine. With this value one can calculate that a reaction would occur with a velocity constant of 0.00158 sec.$^{-1}$ corresponding to a quarter life of 3.0 minutes at 489°C. At this temperature the value of E/RT would be 29.3 as compared with 28.2 obtained for ethylamine and 28.9 for propylamine. Taking the falling off as occurring around 400 mms. at this temperature, the number of molecules entering into collision under these conditions is 2.7×10^{28} per cubic centimeter per second using a molecular diameter of 7×10^{-8} cms. The number of molecules reacting similarly is 4×10^{15} giving a ratio of 1.5×10^{-13}. The value of $e^{-E/RT}$ is 1.8×10^{-13} an agreement which would only be possible with a molecular model involving one or two effective degrees of freedom, a condition similarly found for the other amines studied.

Despite the apparent consistency between all the amines so far studied there is certain evidence that the results may be misleading, certainly in this case with dimethylamine and possibly in the previous ones also. It seems hardly conceivable that an extremely complex reaction could yield reaction rates which on the surface appear to agree so well with accepted theories of unimolecular reactions. The percentage pressure increase during the reaction could well be accounted for on the basis of a single molecule yielding two molecules on initial decomposition followed by a small further decomposition of the products. Such a split in the case of dimethylamine might be presumed to yield ammonia and ethylene. An analysis of the products of decomposition after one of the above runs showed no ammonia present and no unsaturated hydrocarbon. The quantity of material available for analysis in any single experiment as actually carried out in a static manner being small, a definite weight of the dimethylamine was sealed in an evacuated glass bulb and placed in the furnace for a sufficient time for reaction to be complete. The bulb was then cooled and the contents analysed. The appearance of the bulb before opening was surprising, for despite the fact that the vessel used in the static experiments was perfectly clean after several hundred runs and that only a small amount of a dark brown liquid had collected in the capillaries just outside the furnace, the bulb was black and quite opaque to light. It should be noticed, however, that the actual concentration in the latter case was very considerably greater than in any one of the static experiments. The bulb was opened over water in such a way that the insoluble gases could be collected and measured. For about an hour after the bulb had been opened a contraction in the volume of the system was observed pointing to a slow solution of some constituent. Analysis of the fixed gas showed it to contain 65 percent methane, 30 percent ethane and 5 percent hydrogen, no free nitrogen being present. An acid titration of the aqueous solution yielded only 0.4 of the nitrogen initially present in the amine taken. The bulb still carrying its black coating was next examined. The odor was entirely different from that of an amine, being almost putrid. The addition of hydrochloric acid, however, caused most of the black coating to dissolve as a dark brown solution carrying a small amount of a black solid in suspension, presumably carbon. The amount of this latter acid addition made up almost completely for the nitrogen content of the amine taken. By subtracting the amount of hydrogen and carbon found from the initial amine taken an empirical formula for the residue of CH_5N_3 was found. Though probably not guanidin, as this might suggest, the final product must be some complex nitrogenous material of that type.

In an effort to isolate any intermediate substances that might be formed during the reaction several dynamic runs were made. The dimethylamine was allowed to evaporate under its own vapor pressure at room temperature through a small capillary into a furnace kept at 500°C. The products obtained consisted of a colorless liquid with strong ammoniacal odor but penetrating after-effect suggestive of a hydrazine. It boiled over a range from about 70 to 110°C., reduced silver oxide in the cold and decomposed at 500°C. in a static run with a pressure increase at a rate almost ten times as great as that of the dimethylamine. The liquid contained a small amount of a white solid, soluble in water but insoluble in ether, which sublimed without melting at about 250°C. and gave a dull orange precipitate with iodine in potassium iodide. Analysis of the fixed gases showed 60 percent of hydrogen and 40 percent of ethane. The aqueous solution over which the gases were collected showed unchanged secondary amine and a trace of ammonia shown by the insoluble sodium ammonium cobaltinitrite. It seems probable, therefore, that the products contain chiefly methyl hydrazines, the solid being probably hexamethylene tetramine.

On raising the temperature of the furnace to 600°C., using the same rate of flow of amine as previously, the liquid which collected was no longer colorless but decidedly brown, its complexity being shown by its boiling point range from about 40 to 130°C., there being some constituent present decidedly more volatile than in the liquid previously obtained at the lower temperature. This more volatile constituent decomposed at 500°C. in a static experiment with a pressure decrease at a rate which was about five times as rapid as the rate of pressure increase of the original amine. Furthermore, the brown liquid maintained at 100°C. gradually developed larger quantities of the more volatile constituent decomposing with a pressure decrease. This pressure decrease was undoubtedly due to a polymerisation to a high boiling product which subsequently condensed in the capillaries outside the furnace, as considerable difficulty was experienced in evacuating the system after these experiments.

The decomposition of dimethylamine under the conditions of the static experiments therefore must be extremely complex and the observed rate of pressure increase, a composite of at least two rates in opposing directions. It would appear that methyl hydrazines are the chief constituent in the lower temperature dynamic runs and presumably therefore are easily formed from dimethylamine. Their formation should occur as a bimolecular reaction. If the subsequent decomposition of the hydrazine was unimolecular one would expect an induction period in the net rate unless the primary bimolecular reaction was much more rapid than the unimolecular. In this latter event a lowering of temperature might possibly permit a separation of the two. No such change could actually be found. This of course may simply mean that the energies of activation of the bimolecular and unimolecular rates are approximately the same.[1] In any event the very rapid rate of decomposition of the hydrazines is being offset by the reaction with the pressure decrease.

It seems almost phenomenal that such a complex reaction should yield what are apparently simple data and one naturally wonders whether it is possible to reproduce for example pressure-rate curves such as are being accepted as typical of true unimolecular reactions by a counterbalancing of effects in two or more reactions proceeding simultaneously. It may be shown in certain cases that a bimolecular polymerization proceeding simultaneously with a unimolecular decomposition may give a logarithmic relation between initial pressure and half-life as calculated from the observed pressure change. Should the form of this logarithmic relation be such as to bring the asymptotic portion of the curve within easily measurable pressure ranges an apparently constant half-life with changing initial pressure would be observed and might be mistaken for a true unimolecular reaction whose rate decreased at lower initial concentrations. Whether such is the explanation of the case here studied remains for further work to prove.

One rather significant feature of the results obtained, lies in the rapidly falling values calculated for the velocity constants in any run, despite the fact as shown that the products of the reaction tend to maintain the high pressure

TABLE III

Temperature 510°C. Initial pressure 486 mms.

Time	ΔP	k_1	$k_2 \times 10^3$
1	125	.217	.379
2	205	.193	.368
3	269	.182	.378
4	314	.169	.376
5	351	.159	.380
7	407	.144	.390
9	441	.130	.390
11	469	.120	.390
13	489	.111	.389
15	503	.103	.382
20	527	.087	.364
25	543	.076	.350
30	553	.067	.331
40	567	.054	.303
50	578	.047	.291
60	587	.042	.288

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[1] A case in point is actually found in the decomposition of ethyl mercaptan to be published shortly.

rate. Table III gives a typical example of the calculated velocity constants, k_1 being the unimolecular constants, k_2 the bimolecular constants. It will be noted that the values of k_2 are much better than k_1 although from the quarter lives the reaction cannot possibly be bimolecular.

In conclusion one further point may be raised. The accompanying diagram shows the curves obtained by plotting the quarter lives against initial pressures at the four temperatures studied. The forms of the curves might well be those of a unimolecular reaction were it not for the fact that the reaction rate appears to decrease at a higher pressure the lower the temperature. Such a variation is contrary to the usual expectation for a unimolecular reaction. A plot of the quarter life against the reciprocal of the initial pressure gives at each temperature curves showing such a marked curvature that an extrapolation to determine the limiting quarter life at high pressures is doubtful but would indicate that the limiting value has not been reached at 600 mms. at the lowest temperature studied.

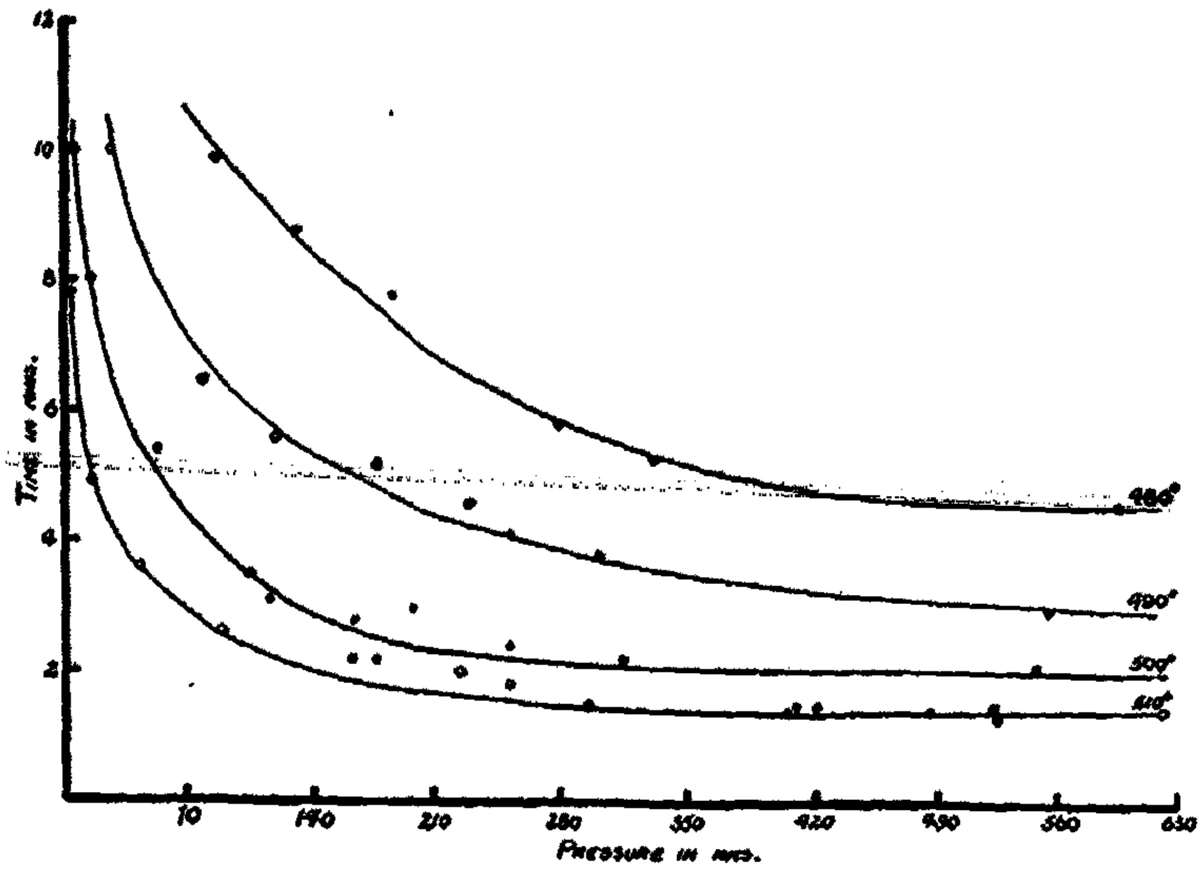

Fig. 1

Summary

The rate of pressure increase in the decomposition of dimethylamine over a temperature range from 480 to 510°C. appears to indicate a homogeneous unimolecular reaction with an energy of activation of 44,300 calories. Dynamic investigations show the reaction to be so extremely complex as to cast doubt on the above interpretation. Further work is in progress.

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THE MELTING POINT OF BENZENE

BY ALAN W. C. MENZIES AND D. A. LACOSS

A few months ago, Irvine Masson reported[1] that he had found the melting point of benzene, measured by duly standardized thermometers, at 5.58°. As to the benzene used, he considered that "the impurity, if any, was . . . extremely small." He therefore stated that it appeared that "the melting point of benzene suggested by T. W. Richards[2] as 5.493° is about 0.1° too low and should not be taken as a fixed point in precise thermometry."

It may be pointed out that, while Richards' benzene was saturated with "air," Masson's was presumably saturated with hydrogen, and that one would, therefore, have anticipated, on account of the lower solubility of hydrogen in benzene,[3] that Masson's freezing point would be higher. But the difference anticipated from this cause would, we compute, reach only 0.017°, and is thus insufficient to account for the discrepancy.

We have recently reported[4] that a number of the physical properties of liquid benzene, as recorded in the literature, exhibit an alteration of rate of change with temperature at a temperature near 40°. Having established this unexpected abnormality for benzene, which seems to have escaped notice these many years, we were prepared for any other abnormality of benzene that might present itself.

Masson froze his specimen of benzene rather slowly, so that it took eleven hours to freeze out 210 gm. In the work of Richards, the rate of freezing was doubtless much faster.

In these circumstances it seemed worth while to examine the freezing point of the same sample of benzene under conditions which would permit of varying widely the rate of formation of the solid phase.

In our other work with benzene, we have used the highest qualities of coal tar benzene obtainable commercially, and, after taking precautions to remove such impurities as thiophene, carbon bisulphide and water, have obtained freezing points in air at atmospheric pressure in agreement with Richards. The same thing is true of samples which we have prepared from benzoic acid of the highest purity. For the present purpose, we employed a sample of this kind, purified by fractional distillation and fractional freezing and dried by refluxing over three separate quantities of metallic sodium, the last of which remained bright. The refractive index for the D lines of sodium was 1.5014 at 20°.

Using a technique which we employ in experiments on intensive desiccation, we sealed up about 20 grams of liquid benzene along with nitrogen at

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[1] Nature, **128**, 726 (1931).

[2] Richards, Carver and Schumb: J. Am. Chem. Soc., **41**, 2019 (1919).

[3] J. Horiuti: Sci. Papers Inst. Phys. Chem. Research (Tokyo), **17**, 125 (1931).

[4] Menzies and Lacoss: Proc. Nat. Acad. Sci., **18**, 144 (1932).

atmospheric pressure in the space, of annular cross-section, between two Pyrex glass tubes of about 10 and 20 mm. bore, respectively, one of which lay coaxially within the other. Both of these tubes, of lengths about 8 and 12 cm., respectively, were closed at one end; at the other end, the outer was closed by a ring seal to the inner tube, which was prolonged into a graduated capillary, bent at a convenient angle. The inner tube and its capillary extension were charged, by the boiling-out process used in filling thermometers, with ethyl ether in such a way as to form a differential thermometer sensitive to 0.005°. The bulb of this thermometer was thus situated in the central portion of an all-glass chamber which was two-thirds filled with the benzene. The benzene chamber was furnished with an air-jacket, and the whole could be immersed and rocked mechanically in a thermostat. Crystallization could be induced in the benzene when even only slightly under-cooled by touching a portion of the glass enclosing the liquid momentarily with carbon dioxide snow. The rate of growth of the benzene crystals could be controlled with great ease by regulating the temperature of the thermostat. Slower cooling gave much larger crystals, in spite of the rocking motion of the apparatus.

In one experiment about 14 grams of crystals were grown uniformly over a period of six hours, which is slower than Masson's rate of growth. In another experiment the rate of growth was twenty times as fast, which is presumably faster than that of Richards' experiments. In all cases the equilibrium temperature for solid and liquid benzene was remarkably steady, whether the environment were hotter or colder, and we found no difference in temperature dependent on rate of freezing exceeding 0.01°.

Although we were interested primarily in relative rather than absolute values, we redetermined the zero points of and made comparison with two thermometers furnished with Reichsanstalt certificates of corrections to ± 0.02° at 0° and 10°; and, further, made comparison, through the courtesy of a colleague, at two points distant not over 1° from the benzene freezing point with a platinum resistance thermometer of which we believe the readings are good to hundredths of a degree. These agreed in yielding a freezing point for our nitrogen-saturated benzene under atmospheric pressure of 5.49 ± 0.02°, a value in concordance with that reported by Richards. The small temperature difference which would be attributable to the molecular solubility difference of nitrogen as opposed to air is well within our error of experiment.

Summary

1). Although liquid benzene has been shown to exhibit an anomalous behavior near 40°, this liquid, at constant pressure, solidifies at a constant temperature, independent of the rate of freezing.

2). Contrary to the recent criticisms of Masson, we find no reason to doubt the value for the benzene freezing point reported by Richards, Carver and Schumb.

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NINTH REPORT OF THE COMMITTEE ON CONTACT CATALYSIS*

BY J. N. PEARCE

The yearly contribution of research in the field of heterogeneous catalysis is increasing with leaps and bounds. It overlaps and permeates other fields and, in turn, is overlapped and permeated by these to such an extent that it is difficult sometimes to differentiate between that which should be included in such a report and that which should be excluded. To read critically each of the numerous papers appearing yearly in this field is a considerable task. Many of these deal with new applications of old processes or new syntheses with familiar catalysts,—all of which are valuable indeed. There are those which contribute new ideas, new viewpoints and new theories. These theories may in time prove to be unsound and may be relegated finally to the museum of forlorn attempts to arrive at an understanding of the processes in heterogeneous catalysis. Whether right or wrong, they are of value in that they stimulate research, the results of which may help us, or those who follow, someday, sometime to know the truth.

While many accounts of catalytic reaction are recorded, an attempt has been made to include, when possible, those researches which deal with the theory and mechanism of adsorption. It is possible that some important work may have been passed over too lightly, or omitted altogether. Since the same opinions are not shared by all, apologies are extended for both sins of omission and commission.

Surface Considerations

Ogawa[1] was the first to observe that only those charcoals will adsorb alkali from solution which have been activated at moderate temperatures. This adsorptive property is for the most part destroyed by activation at high temperatures. Dubinin[2] has found that charcoals which are activated at 550° are capable of adsorbing alkalies; they lose this property when heated to 1100° in a vacuum; exposing the glowed charcoal to air for a short time at moderate temperature is sufficient to restore its activity and its adsorptive capacity for alkalies.

Schilov and Tschmutov[3] have shown that in the adsorption of electrolyte by charcoal, which has been in contact with air, carbon dioxide is formed as a result of hydrolytic cleavage in the solution. Exposure of gas-free charcoal to

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* Report of the Committee on Contact Catalysis of the Division of Chemistry and Chemical Technology of the National Research Council. Written by J. N. Pearce with the assistance of the other members of the Committee: Messrs. Homer Adkins, E. Frankland Armstrong, Oliver W. Brown, Robert E. Burk, J. C. W. Fraser, E. Emmet Reid, Guy B. Taylor, H. S. Taylor, and W. D. Bancroft, Chairman.

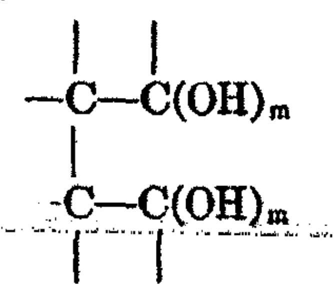
[1] Ogawa: Biochem. Z., **161**, 275 (1925); **172**, 249 (1926).

[2] Dubinin: Z. physik. Chem., **140**, 81 (1929).

[3] Schilov and Tschmutov: Z. physik. Chem., **133**, 188 (1928).

air for a short time is sufficient for the formation of detectable amounts of carbon dioxide in the charcoal.

It was these relations that led Schilov to the view that the adsorption of alkalies is accomplished through the carbon dioxide formed by the oxidation of the charcoal. Recent experiments[1] show that with increase in pressure from 10^{-6} to 2 mm. there is formed on the surface a complete film of active oxide which cannot be removed by evacuation or heating. Since the magnitude of the adsorption depends only on the amount of surface oxide, the quantity of hydrochloric acid adsorbed by the charcoal is constant and independent of the oxygen pressure. The adsorption then increases rapidly to about a fourfold value and again remains practically constant with further increase in oxygen pressure. This primary oxide reacts with the water forming a "carbon hydroxide":

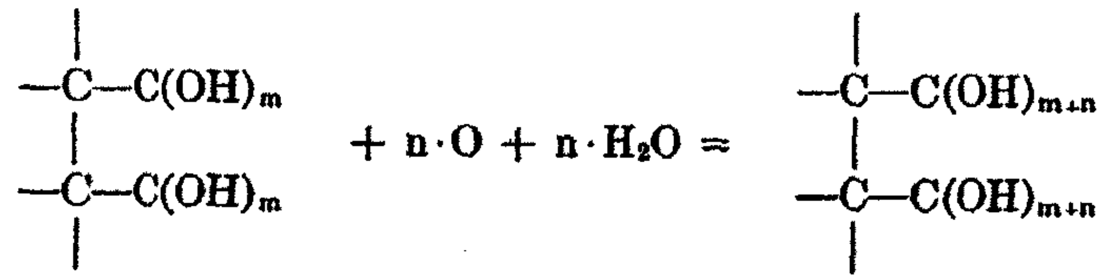


$$\begin{array}{l} -C-C(OH)_m \\ \;\;| \\ -C-C(OH)_m \end{array}$$

They assume that the adsorption of the hydrochloric acid at low oxygen pressure is a reaction between this hydroxide and the hydrochloric acid.

The steep rise in the curve corresponds to a further oxidation and the subsequent approximate constant portion points to a saturation of the carbon surface. The surface becomes electrically charged through the formation of oxide and hydroxide and can take up definite amounts of molecular oxygen. This carbon hydroxide can form hydroxyl ions: hence the active surface can adsorb acids, but it cannot adsorb alkalies.

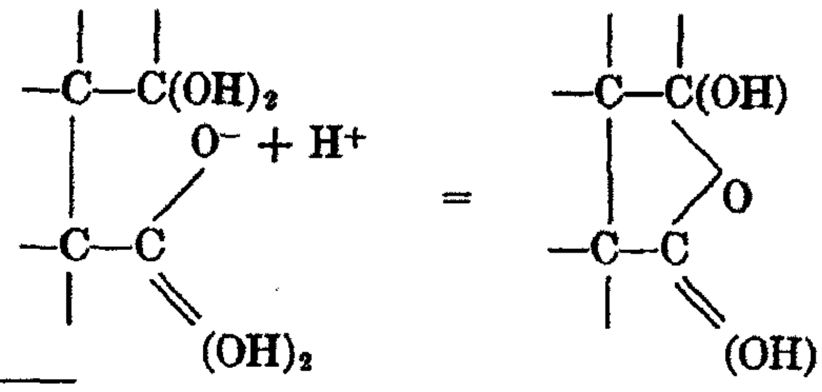
The secondary oxide, unlike the primary, possesses an acid nature, and with water it forms polyhydroxide compounds analogous to the orthoacids:



$$\begin{array}{l} -C-C(OH)_m \\ \;\;| \\ -C-C(OH)_m \end{array} + n\cdot O + n\cdot H_2O = \begin{array}{l} -C-C(OH)_{m+n} \\ \;\;| \\ -C-C(OH)_{m+n} \end{array}$$

basic acid

As to the adsorption of alkalies there are three possibilities depending upon the three possible different states of the charcoal surface. The first corresponds to the formation of an inner salt, or anhydrous oxide which is stable toward alkalies:



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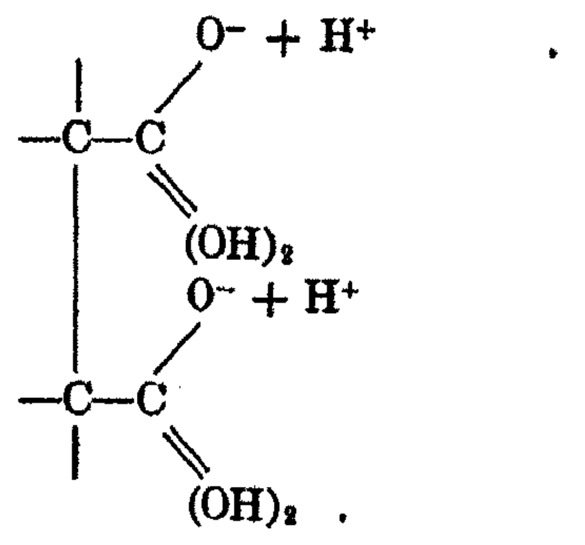
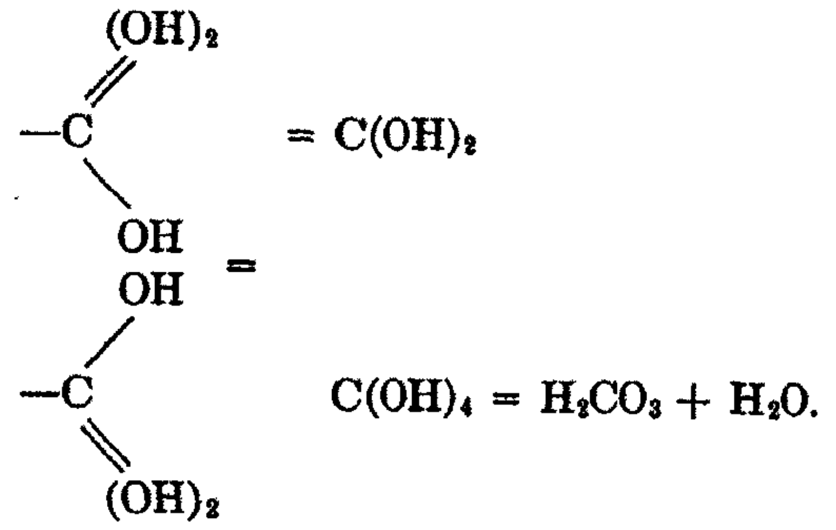
[1] Schilov: Kolloid-Z., 62, 107 (1930); Schilov and Tschmutov: Z. physik. Chem., 148, 233 (1930).

The second represents the typical case of surface saturation by hydroxyl groups:



In the presence of alkalies this behaves as an acid, neutralization follows and alkalies are adsorbed.

After autoxidation and reduction, or further oxidation by oxygen, carbon dioxide is split off and this reacts with the alkali to form a carbonate:



Thus, all phenomena resulting in alkali or acid adsorption can be explained by a simple assumption of the formation of hydroxyl groups upon the charcoal surface. The number of hydroxyl groups on each carbon atom determines the basic or acid nature of the oxide.

According to Bowden,[1] the significant area of a catalyst is not the arbitrarily defined maximum area, but it is that area which can be reached by the reactants. In the method of Bowden and Rideal[2] for measuring the areas of metallic surfaces by the electrolytic deposition of hydrogen from solution, the quantity measured is the amount of hydrogen which must be added to the surface to produce a definite change in the electrode potential.

Bowden and O'Connor[3] have applied the same method using cathodes of fusible alloys (Wood's Metal). In addition, they determined the relation between electrode potential and current density. This relation gives the rate at which hydrogen is being evolved at the surface and is, therefore, a measure of the catalytic activity of the surface for the reaction. They find that for a solid this increases with rise in temperature, decreases when fusion begins, and

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[1] Bowden: Nature, 122, 647 (1928).

[2] Bowden and Rideal: Proc. Roy. Soc., 120A, 59, 80 (1930).

[3] Bowden and O'Connor: Proc. Roy. Soc., 128A, 317 (1930).

increases again after complete fusion with further rise in temperature. Electrodes of metallic gallium rapidly catalyze the evolution of hydrogen and, therefore, relatively high current densities must be employed to produce a high hydrogen overvoltage. The accessible area of liquid gallium is about the same as that of mercury; on solidification the area increases to about 1.7 times the apparent area. According to the authors, the catalytic activity depends upon the accessible area and to a less extent upon the configuration of the surface metal atoms, but largely also upon the chemical nature of the metal.

Foresti[1] considers the surface covered by the adsorbed gas to be heterogeneous in that it is made up of active points of random distribution and different degrees of activity, and that this heterogeneous surface becomes homogeneous at low pressures. Using the data of Kistiakowski, Flosdorf and Taylor[2] for the adsorption of hydrogen on copper, he finds that the relation between the volume adsorbed and the pressure (0.03 mm to 0.3 mm Hg) is of the type, $V = K (p - m)^{1/2}$. If the constant m is neglected, the relation becomes quadratic, in which case, he contends, that the most active centers would be saturated by hydrogen atoms. This is not in harmony with the measurements of the differential heats of adsorption already made on the same samples of copper.

To become reactive, colliding molecules require a certain energy of activation. "The reducing factor for the case of three degrees of freedom is $-E/RT$, where E, the energy of activation is a magnitude of the order of some tens of thousands, (say 50,000 cal. per molecule. For a reaction at 1000° abs. the index is of the order of − 24.) Any cause which reduces the degrees of freedom by unity would reduce the index by one-third, a reduction of two degrees of freedom would reduce it by two-thirds of its value, and if all of the degrees of freedom were removed, the index would disappear entirely. With the above value of E the exponential factor in the several cases becomes (1) 3.77×10^{-11}, (2) 1.12×10^{-7}, (3) 3×10^{-4} and (4) unity, the first being the value met with in normal gas reactions.

Upon the basis of these relations, Porter[3] states that "an adsorbed layer of oriented polar molecules with their proper poles all pointing outward toward a surrounding gas will tend to swing the colliding molecules round so that instead of it being a chance, it may become a certainty that suitable poles for reaction to take place will be presented to one another; in this case, the rate of reaction passes from the first to the second of the above categories and it is therefore increased in a ratio of about 30,000 and we have a reasonable case of catalytic acceleration. If, further, the forces exerted by an oncoming molecule could swing it round the axis of approach so that it inevitably "fits" its future partner, a second degree of freedom passes into the category of certainties and we have case (3) and the catalytic activity is multiplied by 10^9, and so on."

"On the other hand, catalytic poisoning occurs when the wrong poles are made inevitably to present themselves. A single layer might be quite effective

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[1] Foresti: Gazz., **60**, 516 (1930).

[2] Loc. cit.

[3] Porter: Nature, **126**, 349 (1930).

in stopping a reaction; and a much smaller quantity might reduce the rate a few hundred or thousand times."

Elements lying near the maxima of the Biltz atomic frequency-atomic weight curve are as a rule good catalysts. Srikantan[1] has attempted to correlate catalytic activity with the energy of vibration of the atom by means of the function, $4\pi MVr^2$, where M is the atomic weight, V the frequency and r is the amplitude of the atomic vibration at the melting point of the solid. It is found, in general, that elements with high energies of vibration like nickel, iron, osmium, platinum and carbon are active catalysts; they give high values for this function. Low values were obtained, however, for weak catalysts and for poisons such as chlorine, bromine, mercury, sodium and zinc.

In contact with heated palladium hydrogen undergoes important changes which appear in the form of an enhanced activity. According to Poljakov,[2] the subsequent recombination of the thus activated hydrogen should proceed with an emission of light. This conclusion was substantiated experimentally. He concludes that at the cost of energy, provided the palladium is not saturated with hydrogen, we can not only activate hydrogen, but also expel it into space in an active state. He has also shown that heat is liberated in the recombination of the hydrogen atoms at the glass walls.

Srikantan[3] finds from a study of the interaction of carbon dioxide and hydrogen at various catalyst surfaces that a good catalyst support supplies the necessary energy at a lower temperature than a poor catalyst, and at the same temperature enables the reactants to attain an active state with a smaller quantity of energy.

Kröger[4] has studied the quiet union of pure detonating gas in the presence of various catalysts. The catalysts used were, (1) those which adsorb oxygen markedly, such as silver, and (2) catalysts that act chiefly chemically, in which the adsorption is retarded by the formation of intermediate compounds (oxides). Catalysis with antimony, nickel, copper and the oxides of nickel and copper, involves the alternate oxidation and reduction of the catalyst metal. Using silver having a particle size of from 0.05 to 1.0 mm., he finds that the reaction takes place at a lower temperature, the greater the mass of catalyst taken. Further, for any given mass of catalyst the transformation increases slowly at first with rise in temperature, then more rapidly and, finally, at higher yields it increases more slowly with further rise in temperature. Quite similar results were obtained with nickel and nickel oxide. With copper oxide, however, temperatures of complete reaction are higher the greater the mass of the catalyst employed. Variation in the amount of powdered antimony used is without effect, indicating no adsorption of either hydrogen or oxygen.

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[1] Srikantan: Indian J. Physics, **4**, 539 (1930).

[2] Poljakov: Ber., Ukrain. wiss. Forschungs-Inst. physik. Chem., **2**, 55 (1930); See Centrallblatt, **101**, 1822 (1930).

[3] Srikantan: Rec. Trav. chim., **49**, 1146 (1930).

[4] Kröger: Z. anorg. allgem. Chem., **194**, 73 (1930).

Adsorption

Schwab and Pietsch[1] have put forth a hypothesis to explain quantitatively not only the kinetics of catalysis, but also the phenomenon of activation and deactivation of the catalysts. The active points postulated by Taylor[2] are to be considered as homogeneous linear discontinuities of the catalyst surface, that is, as uni-dimensional boundaries of two-dimensional phases. These lines possess an enhanced heat of adsorption and, therefore, a diminished heat of activation. Adlineation implies an increased adsorption density on these linear structures. These lines may be due to crystal edges separating crystal surfaces of different crystallographic orientation, or to irregularities on the otherwise homogeneous surfaces produced either mechanically or by disturbances during crystal growth. The activity of these uni-dimensional phases may produce either orienting or deforming effects. That is, in the first case, they increase the speed of formation of the nucleus of the substance produced by decreasing the work required for the formation of the nucleus. In the second case, they make processes possible by decreasing the required heat of activation.

A number of experiments have been made recently[3] demonstrating adlineation on crystal edges and points. In all of these the reactions are localized initially on the crystal edges and then they encroach progressively upon the crystal surface. The crystal edges and surface irregularities are assumed to be actually capable of playing the same pronounced energetic rôle which is ascribed to them in consideration of the theory of contact catalysis. They are the seat of catalytic activity whether in unicrystalline material or in the boundaries of polycrystalline substances.

Just how and where the adsorption of a solute does occur on a crystal lattice is a question which so far has been somewhat evasive. France and his co-workers[4] have found that the growth ratios of potassium and ammonium alums are greatly modified when grown in the presence of dyes and other foreign substances. Thus, potassium alum grown in the presence of diamine sky blue grows into perfect cubes with no octahedral faces. Only the cubic faces are colored, and the growth ratio (100)/(111) changes from 1.60 to 0 in a dye concentration of 0.1 per cent. These effects are explained on the basis of the residual valency force fields of the crystal planes, of the interionic distances within the faces, and of the presence and distribution of polar groups in the adsorbed material. Further, the structure of the crystal is found to be a determining factor in the adsorption process. Only those faces covered by ions of like charge are colored by the dye. The cubic form of potassium alum crystals is made up of alternate layers of positive and negative ions,[5] whereas in the octahedral form the layers contain both positive and negative ions. It

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[1] Schwab and Pietsch: Z. physik. Chem., B **1**, 385 (1928); B **2**, 262 (1929); Z. Elektrochemie, **35**, 135 (1929).

[2] Taylor: Proc. Roy. Soc., **108A**, 105 (1925).

[3] Pietsch, Kotowski and Berend: Z. physik. Chem., B **5**, 1 (1930).

[4] France and his co-workers: J. Am. Chem. Soc., **46**, 540 (1924); J. Am. Ceramic Soc., **10**, 579, 821 (1927); **11**, 579 (1928).

[5] Wyckoff: Am. J. Sci., **205**, 209 (1923).

follows then that the dye should be adsorbed on the planes of the cube rather than on those of an octahedron. The position taken by the adsorbed dye molecules in the alum lattice is so far unknown.

Recently, Foote, Blake and France[1] have determined the lattice constants of pure potassium alum crystals and crystals grown in the presence of diamine sky blue. The lattice constants for the pure and dyed samples are found to be the same, showing that the adsorption of the dye does not measurably affect the plane spacings of the growing crystal. It appears justifiable to assume that the dye is adsorbed interstitially rather than as individual planes or by the replacement of ions of the unit cell.

Many investigations have been made in recent years dealing with the relation between adsorption from solution and the solubility of the substance adsorbed. In general, there appears to be an antibatic relation between adsorbability and solubility. In many cases these relations are quantitative.[2] Heyman and Boye[3] have extended these studies to include the relation between adsorption and dielectric constant. To this end they have studied the adsorption of certain aliphatic acids, benzoic and picric acids, pyridine and triethylamine by ash-free charcoal from solutions in polar and non-polar solvents and in their binary mixtures. Although strict antibasie between dipole moments, as well as molecular polarization of the solvent, and adsorption does not always exist, the relation does hold, in general, when the solvents used are not too different chemically. Thus, in the homologous series of alcohols the adsorbability of the solute (benzoic and picric acids) decreases with increasing molecular polarization of the alcohol. Very distinct relations were obtained in the investigations employing binary solvent mixtures. The adsorption curves (percent adsorbed plotted against solvent composition) are directly related to the molecular polarization curves, P_{12} and P_2, of the solvent mixture. Rectilinear adsorption curves are obtained not only when both solvent components are non-polar, but also when one component is polar, provided its specific polarization, P_2, is not, or only slightly, changed by the non-polar solvent. However, when the specific polarization of the polar component (P_2-curve) is strongly changed by the non-polar component, the adsorption curves are strongly curved. For example, when the P_2-curve shows a maximum, the adsorption curve shows a minimum. The general character of the adsorption curves is dependent for the most part upon the nature of the solvent and not upon the nature of the adsorbate. The position of these maxima and minima vary from adsorbate to adsorbate. In general, the minima of the adsorption curves do not occur in the same solvent mixtures as the maxima of the P_2-curves.

Alekseevskii[4] has attempted to explain adsorption phenomena upon the basis of the distribution of valence forces in the complex molecular complexes of the adsorbent. According to their character, four types of valence forces

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[1] Foote, Blake and France: J. Phys. Chem., 34, 2236 (1930).

[2] Freundlich, Kapillarchemie, IV, 1; Lundelius: Kolloid-Z., 26, 245 (1925); Angelescu and Comanescu: 44, 288 (1928); Sata: 49, 275 (1929); Herz and Levi: 50, 21 (1930).

[3] Heyman and Boye: Z. physik Chem., 150 A, 219 (1930).

[4] Alekseevski: J. Russ. Phys.-Chem. Soc., 62, 817 (1930).

are to be distinguished. These are: the homopolar type found in the molecules of elementary substances; the heteropolar stable compounds of different elements, like H_2SO_4, NaCl; the third type leading to molecular association, or crystalline hydrate formation; the fourth type represents the valence forces present in unstable compounds, that is, the forces in adsorption compounds. Only the last type of valence forces, which are distinguished by variable characteristics, are capable of solving adsorption phenomena. Upon the basis of these considerations, Alekseevskii has deduced constitutional formulae for active charcoal, silica gel, and clays.

Dohse and his co-workers[1] have applied their previous method to the hydrogenation of C_2H_4 at 0°, with nickel supported by activated charcoal as the catalyst. C_2H_4 and C_2H_6 are both strongly adsorbed, the hydrogen only weakly adsorbed by the catalyst. They applied equi-molecular quantities of C_2H_4 and H_2. By allowing the former to form a film upon the surface and then permitting the H_2 to enter they found the reaction to proceed specifically as a first order reaction, although two molecules are taking part. While the reaction velocity is independent of the C_2H_4 concentration it is directly proportional to that of the hydrogen. The reaction is of zero order when the concentration of the hydrogen is kept constant. They assume the existence of a two-dimensional gas layer on the support surface in which the ratio of C_2H_4 to H_2 is relatively large. When a molecule of hydrogen strikes upon a nickel point it becomes activated and reacts with the C_2H_4 molecule. Since its adsorption potential is practically the same toward nickel and charcoal, the C_2H_4 molecule formed moves laterally to the charcoal from which it vaporizes. Hitherto, the activity of the contact has been assumed to be dependent upon the magnitude of the active surface and the activity of the individual active points. According to the authors, the inactive support surface plays an important rôle in catalytic processes. It forms not only the reservoir from which the active points are supplied, but also a space into which the newly formed molecules are transported from the active points with little work. For, if the molecules had to be transferred directly to the gas phase, the reaction would take place much more slowly because of the much greater potential difference between the active point and the gas phase than between the active point and the inactive surface.

According to McBain and his co-workers,[2] the ordinary empirical sorption formula, $x/m = kp^{1/n}$, fails completely for the sorption of organic vapors by activated sugar charcoal. At the lowest pressures it gives a flat curve instead of the required straight line when plotted on a logarithmic diagram, the curve changing suddenly into a nearly horizontal line for all the higher pressure ranges. The authors assert that the only adequate expression for sorption results is that of Langmuir, namely $x/m = ab.p/(1+a.p)$, where a and b are constants. This, when rearranged gives $\frac{p/p_0}{x/m} = \frac{1}{ab} + \frac{p/p_0}{b}$, which is the

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[1] Dohse and his co-workers, Kälberer and Schüster: Z. Elektrochemie, 36, 677 (1930).

[2] McBain, Jackman, Bakr and Smith: J. Phys. Chem., 34, 1439 (1930).

equation of a straight line, if we plot $\frac{p/p_0}{x/m}$ against p/p_0. The Langmuir formula presupposes the validity of Henry's law at sufficiently low pressures, where $1/n$ should equal unity, and they found this to be actually true experimentally. Although the vapors are very similar in physical properties, their sorption by the same charcoal is very different. At the lowest pressures the non-polar hexane is the one most sorbed, and it approaches saturation, whereas the polar methanol does not. With change in pressure the sorption of methanol is more rapidly adjusted than that of hexane. They conclude also from their results that heats of adsorption cannot be calculated by means of the van't Hoff isochore, unless there is some certainty that in the isotherms at different temperatures the impurities present have exerted a precisely similar effect.

Improvements in evacuation have been found[1] to change not only the position of the adsorption isotherms, but also their form. Only by carefully and completely outgassing the charcoal at high temperatures, then admitting the vapor to be adsorbed and again outgassing at high temperatures is it possible to obtain a charcoal which is free from foreign materials. The adsorption isotherms obtained with this charcoal are of an entirely new type, in that almost all of the adsorption occurs at low pressures. There is practically no further adsorption with increase in pressure. The more drastic the preliminary treatment, the lower is the pressure necessary for complete saturation.

At very low temperatures and for a given pressure the adsorption of hydrogen on nickel is relatively large. It passes through a minimum between −200° and −175°, rising to a maximum at about −100° and then falls off gradually again with increasing temperature. The magnitude of the minimum is dependent upon the pressure. At 600 mm. the adsorption is independent of the temperature for temperatures between −110° and 0°, a fact which is explained by the assumption of a completely saturated surface layer. Except for the interval, −191° to −183°, where adsorption is discontinuous, the adsorption is, in general, reversible and reproducible. Benton and White[2] assume that the adsorption at the lower temperatures is of a "secondary" type, that is, more of a molecular nature, while at higher temperatures a relatively greater part of the nickel surface is capable of holding hydrogen by adsorption of a "primary" type, involving a marked activation of the gas.

Garner and Kingman[3] find that hydrogen or carbon monoxide is adsorbed reversibly on oxide surfaces at ordinary temperatures and adsorbed irreversibly at higher temperatures. The gas adsorbed at equilibrium pressures of 10^{-3} to 10^{-4} mm. on a $ZnO-Cr_2O_3$ catalyst is liberated at 100° to 120°, but is readsorbed within thirty minutes, giving a high vacuum. With further rise in temperature no gas is given off until 350° when water and carbon dioxide are evolved. Mixtures of hydrogen and carbon monoxide behave in a similar manner. The reduction of oxides by either of these gases is assumed to pro-

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[1] McBain, Lucas and Chapman: J. Am. Chem. Soc., **52**, 2668 (1930).

[2] Benton and White: J. Am. Chem. Soc., **52**, 2325 (1930).

[3] Garner and Kingman: Nature, **126**, 352 (1930).

ceed in three stages: an adsorption of the gas, then a combination with the surface atoms and, finally, the desorption of water, or of carbon dioxide, depending upon the starting gas.

When used alone, or mixed with other oxides, MnO_2 is a very active oxidizing catalyst. Its activity, however, appears to be influenced strongly by the alkalinity of the medium in which it is prepared and, hence, by the amount of alkali adsorbed by the oxide. Working with four differently prepared samples of MnO_2 and with a mixed catalyst containing 37 per cent of silver oxide, Lanning[1] finds that the adsorption curves for water vapor and carbon dioxide do not differ materially from the curves for oxides prepared in the absence of added alkali. He states that the effect of the alkali in depressing the catalytic activity of these oxides cannot be due to a change in the physical structure of the oxide, but must be due rather to catalytic poisoning by the adsorbed alkali.

Foote and Dixon[2] have studied the adsorption of water and benzene vapors on MnO_2. The isotherms for both vapors at low pressures indicate that these vapors are adsorbed in the same way that the permanent gases are adsorbed by charcoal. Pure surface adsorption is assumed within the range of pressures used. When the value of p/p_0 is about 0.5 the isotherms break rather sharply and the amount of vapor absorbed increases rapidly with a small increase in pressure. One part of the water isotherm corresponds to an adsorption, the other to condensation in the capillaries. Polanyi's adsorption theory is confirmed. Treatment of the outgassed oxide with CO or CO_2 diminishes strongly the surface adsorption, but does not alter the capillary adsorption. Both gases cover the active adsorption patches, reducing the surface adsorption of water vapor. Oxygen is without effect. Removal of these gases by heating restores the surface adsorption of water to its normal value.

Alekseevskii[3] finds that the optimum temperature of ignition of alumina for the adsorption of ethyl and isoamyl alcohol vapors is 400°-420°; for the adsorption of ethylene and ethylenic hydrocarbons and benzene is 600°-620°.

The catalytic activity of samples of similarly prepared cubic and rhombohedral ferric oxide (Fe_2O_3) toward the oxidation of benzidine or guajac resin by hydrogen peroxide is practically the same. It is not a function of the crystal structure of the two oxides.[4] Several hours heating at 550° practically destroys their catalytic activity toward these oxidations. As measured by the rate of combination of an oxygen-hydrogen mixture on their surfaces the activities are approximately the same, but in this case heating does not alter the activity of either toward this reaction. The decomposition of ozone at $-74°$ follows equally rapidly on both forms, but less rapidly on the highly heated oxides than on those dried at 300°. In their water sorption capacities, however, they exhibit distinct differences, that on the cubic Fe_2O_3 being from 10 to 60 percent less than on the rhombohedral form. The sorption capacity

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[1] Lanning: J. Am. Chem. Soc., 52, 2411 (1930).

[2] Foote and Dixon: J. Am. Chem. Soc., 52, 2170 (1930).

[3] Alekseevskii: J. Russ. Phys.-Chem. Soc., 62, 221 (1930).

[4] Emmett and Love: J. Phys. Chem., 34, 41 (1930).

of both forms is greatly diminished by heating to 550° and is not again restored by activation with hydrogen-oxygen mixtures. The most plausible explanation for the loss of catalytic activity of both forms is sintering.

When hydrogen-free naphthas are passed over initially sulfur-free nickel catalysts[1] at 300° the first portions passing the catalyst contain very little sulfur. The sulfur content of the product increases rapidly at first, then more and more slowly, finally attaining a constant sulfur content after a sufficient quantity of liquid has been vaporized through the catalyst. The reduction of the sulfur content is dependent upon the naphtha employed, the differences exhibited by the different naphthas being assumed as due to the nature and reactivity of the sulfur compounds present. Hydrogen-free naphtha vapors yield no hydrogen sulfide until the steady state of constant sulfur content is attained. It then increases slowly and finally reaches a constant state which then continues as long as the catalyst is used. All mercaptans are nearly completely removed in a single passage of the vapor through the catalyst at the steady state. Other sulfur compounds, like propyl sulfide, are also decomposed.

Sulfur-free nickel catalysts completely remove all sulfur from naphthas in the form of vapor. With continued use the nickel catalyst becomes less efficient in its action, but it finally reaches a steady state when its effectiveness in reducing sulfur compounds becomes constant.

Addition of hydrogen to the naphtha vapor increases the effectiveness of the catalyst in removing sulfur. The evolution of hydrogen sulfide begins at the beginning of the run. The evolution increases somewhat as the steady state is approached and then remains constant.

Although considerably less effective than nickel, the iron catalyst exhibits the same type of behavior. At no stage, however, does iron completely remove the sulfur.

Experiments made on the adsorption of sulfur from the liquid phase showed that the amount of sulfur removed is proportional to the quantity of catalyst added until the sulfur content of the naphtha has been reduced to a certain value. The sulfur is irreversibly adsorbed and it is not removed by benzene or sulfur-free naphtha. While all mercaptan sulfur is not adsorbed, other sulfur compounds are adsorbed.

The results of the work of Elgin, Wilder and Taylor show that the nickel sulfide surface catalyzes the removal of sulfur by catalyzing the decomposition of certain sulfur compounds with the evolution of hydrogen sulfide. The function of hydrogen in increasing the efficiency of the catalyst seems to be to maintain some fraction of the surface free from sulfur.

Employing the same technique with nickel contacts, Elgin[2] has continued the study of the action of a nickel catalyst on pure sulfur compounds when present individually in naphtha. Both butyl mercaptan and thiophene are at first removed when, in the absence of hydrogen, the vapors are passed over sulfur-free nickel at 300°. The catalyst reaches a state of constant activity in which it catalytically decomposes practically the entire mercaptan content

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[1] Elgin, Wilder and H. S. Taylor: Ind. Eng. Chem., 22, 1284 (1930).

[2] Elgin: Ind. Eng. Chem., 22, 1290 (1930).

with the liberation of hydrogen sulfide. It does not, however, affect the thiophene after the initial stages of the run. Nickel catalysts which have been carried to the state of constant activity with butyl mercaptan catalytically decomposed all of the other sulfur compounds used, (mercaptans and sulfides), except thiophene. Hydrogen sulfide is evolved when hydrogen is added to the naphtha solutions of all of the sulfur compounds. Even thiophene is removed at 300° when in contact with the catalyst at the steady state. Increasing the temperature to 400°, or increasing the proportion of hydrogen to naphtha increases the amount of sulfur removed. According to Elgin, the decomposition of the mercaptans follows the reaction,

$$C_4H_9SH = C_4H_8 + H_2S$$

From the results of a series of investigations of the adsorption of electrolytes by activated charcoal, Frumkin[1] is inclined to look upon active charcoal as a gas electrode. At the cost of adsorbed gases it sends ions into solution, thereby assuming a definite charge and attracting ions of opposite sign. In this way there is formed an electric double layer and the concentration changes in the solution resulting from the formation of this double layer are to be considered as adsorption. Ash-free charcoal activated at high temperatures adsorbs acids from neutral salt solutions, leaving the solution in contact with the charcoal strongly alkaline. The same charcoal adsorbs free acids intensively, but it does not adsorb the strong bases. Frumkin assumes in this case that the charcoal functions as an oxygen electrode.

On the basis of these considerations, it is obvious that if a charcoal is sufficiently heated at a high temperature to remove all traces of adsorbed gases, it cannot function as an electrode and send ions into solution. For this reason the adsorption observed on gas-charged charcoals will be impossible. Outgassed charcoal activated at 1000° in an atmosphere of carbon dioxide does not adsorb electrolyte material when brought in contact with dilute solution of hydrochloric acid or of sodium hydroxide. If air is admitted to the vessel containing the outgassed charcoal immersed in an aqueous solution of the acid or of a salt, the charcoal again assumes its original adsorption capacity. Further, if the proper quantities of acid and charcoal are used, the acid will completely disappear from the solution.

As pictured by Frumkin, the mechanism of the adsorption process consists of the formation of hydroxyl ions from the adsorbed oxygen; these pass into solution, leaving a positive charge upon the charcoal surface:

$$C_xO + H_2O = C_x + 2(+) + 2\,OH^-.$$

In an acid solution the OH^- ions combine with the H^+ ions of the solution while the positive surface attracts the anions of the solution and, thus, the acid disappears from the solution. Under similar conditions, neutral solutions become alkaline because the anions of the solution are replaced by OH^- ions. According to this view, alkaline solutions should not, and they do not,

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[1] Frumkin: Kolloid-Z., 51, 123 (1930); see also Bruns and Frumkin: Z. physik. Chem., 147 A, 125 (1930).

exhibit any appreciable concentration changes in contact with oxygenated charcoal. Under the conditions employed the amount of acid adsorbed is equivalent to the oxygen-content of the charcoal.

The oxygenated charcoal electrode is far from reversible, its potential being several decivolts less than that of a reversible oxygen-electrode. The oxygen potential of the charcoal may be increased to that of the reversible oxygen-electrode by platinizing the charcoal. The acid adsorption is strongly increased by the presence of the platinum.

There is a complete reversal of the adsorption behavior when the oxygen-charged charcoal is heated for some time in an atmosphere of hydrogen and then placed in an air-free electrolyte solution. The charcoal now adsorbs alkali, but no acid, and the neutral solution in contact with the charcoal becomes acid. The charcoal now sends hydrogen ions into solution at the cost of the adsorbed hydrogen, leaving the charcoal with a negative charge to attract the positive ions of the solution. Schematically, the mechanism is

$$C_x + H_2 + C_x + 2(-) + 2H^+.$$

The amount of hydrogen disappearing is equivalent to the amount of hydrogen ions formed, and, therefore, to the alkali adsorbed.

It is interesting to note also the application of Frumkin's views to the stability of charcoal suspensions. Oxygen-charcoal in alkaline solutions and hydrogen-charcoal in acid solutions are only weakly charged because of the presence of the opposing OH^- and H^+ ions, respectively; the corresponding suspensions coagulate rapidly. Oxygen-charcoals in acid solution and hydrogen-charcoals in alkaline solution are, on the contrary, highly charged and give stable suspensions. The influence of polyvalent ions is in accord with the demands of the theory. Polyvalent anions coagulate oxygen-charged platinized charcoal particles and polyvalent cations stabilize them. Exactly the reverse is true for the hydrogen-charged particles.

Sugar charcoal activated at 500° adsorbs[1] mineral acids from solutions of equivalent concentration in the order, $HCl > H_2SO_4 > H_3PO_4$, and organic acids in the order propionic > valeric > heptylic. Activating the charcoal at 800° reverses the order of adsorption of these acids. Activation in air decreases the adsorption of iodine from potassium iodide solution and increases the adsorption of alkali. Activation in carbon dioxide, on the other hand, increases the adsorption of iodine, but does not affect that of the alkali. Heating the charcoal in vacuo at 1200° removes carbon dioxide from the surface and thus destroys its ability to adsorb alkali. By this treatment the ability to adsorb acids is decreased, but the amount of iodine adsorbed is practically unchanged. Activation increases the pore size, allowing the larger molecules access to more surface. The amount of larger molecules adsorbed per unit mass of adsorbent is thereby increased in greater proportion than that of the smaller molecules.

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[1] Dubinin: Z. physik. Chem., A 150, 145 (1930).

According to Brouckère,[1] the adsorption of alkali iodides by barium sulfate is strictly reproducible only in the dark and in the absence of oxygen. The anomalies arising are due to the selective adsorption of the iodide ion. In experiments with solutions of potassium iodide containing free iodine, more atoms of iodine are adsorbed than of potassium, the ratio, I/K, being always approximately 3. It appears then as if the adsorption depends almost solely upon the KI_3 compound. The isotherms obtained in the iodine-free potassium iodide and in those containing no free iodine appear to indicate that, ceteris paribus, the KI_3 complex is more strongly adsorbed than is the simple iodide KI.

A polished brass foil immersed in a dilute solution containing sodium thiosulfate and lead acetate upon heating to boiling assumes a bright golden yellow color. The color then passes successively through a series of colors, namely, reddish violet, deep blue, bright steel blue and, finally, to gray. Copper, silver and iron show similar color changes. Beutel and Kutzelnigg[2] find that when the clear colorless solution of the complex lead thiosulfate is heated to boiling it becomes turbid and of a blue color. After a few minutes there is formed an apparently amorphous precipitate consisting of irregular granules. Upon longer boiling the lead sulfide is deposited as a mirror. The coloring of metals consists in the adsorption of insoluble compounds formed by the decomposition of the complex salt. Adsorption on metal surfaces can be considered as a special case of general surface adsorption. That it is of an electrochemical nature is shown by the following illustrations. Of the sixteen metals studied, Al, Mn, Zn and Cr, all standing above iron, did not color. All of those following iron, except cadmium and platinum did color during the treatment. Of the series, copper, silver, lead, and gold, the coloring is slower the more noble the metal. If a copper or zinc wire is used in place of the binding string, then the platinum also colors. The other metals also color more quickly and the time required to produce a given color is much shortened. The time required is much shorter with zinc than with copper wires. Further, the time required to produce a given color decreases with rise in temperature.

Kosakewitsch and Ismâilow[3] find that the adsorption of phenol from aqueous solutions and of benzoic acid from solutions in methyl and ethyl alcohol by charcoal is increased by alkali halides, the magnitude of adsorption increasing with the salt concentration. The activity of the adsorbate is increased by the salt. The relation between the adsorption of phenol and its activity in the solution is most clearly shown when the values of x/m are plotted against the activity of the phenol instead of the concentration. When this is done the adsorption curves for the pure water and the salt solutions coincide throughout. It is possible, therefore, to calculate the relative activity of easily adsorbable substances from adsorption data. By attributing the neutral salt effect to solvation they were able also to calculate values for the

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[1] Brouckère: Bull. Soc. chim. Belg., 39, 174 (1930).

[2] Beutel and Kutzelnigg: Z. Elektrochemie, 36, 523 (1930).

[3] Kosakewitsch and Ismailow: Z. physik. Chem., A 150, 295 (1930).

hydration per mol of salt which are in good agreement with values obtained by other methods.

Alekseevskii and Musakin[1] have studied the effect of a large number of acids upon the adsorptive power of various wood charcoals. Perchloric acid increases the adsorption of methylene blue and Congo red; it with chromic acid, nitric acid, and bromine water enhance the adsorption of phenol. The most active adsorbents for acetylene from the air were obtained by treatment of the charcoals with nitric and perchloric acids and bromine water. Treatment with nitric, perchloric, hydrofluoric, and chromic acids give the best adsorbents for benzene vapor. In general, the adsorptive properties of wood charcoal appear to be enhanced by the action of volatile oxidizing substances.

Heat of Adsorption

In a study of the relation between particle size and catalytic activity of three platinum blacks, prepared by different methods, Taylor, Kistiakowski and Perry[2] found that the two samples having the smaller particle size showed the greater catalytic activity. One of these was found to be superior in oxidation reactions, and the other slightly better for hydrogenation. The effect of extended heat treatment on the adsorption capacity of the three samples was quite marked. Heating to 350° gradually destroyed the adsorptive capacity of the sample of large size, reducing the adsorption of hydrogen practically to zero and that of oxygen nearly as much. The sample showed much sintering and was almost a metallic gray in color. The two samples of smaller size withstood a similar heat treatment much better, and, although somewhat sintered, they retained their black color practically unchanged. These sintering effects appear quite anomalous in view of the higher surface energy of the particles of smaller size. They found a distinct parallelism between catalytic activity and physical properties. The poorest catalyst has the coarsest structure and is the poorest adsorber. The quantities of hydrogen adsorbed and the heats of adsorption of hydrogen parallel the catalytic activity of this catalyst in the hydrogenation of ethylene.

Taylor, Kistiakowski and Perry[3] have also determined the differential heats of adsorption of H_2, O_2, SO_2, and CO on the same three differently prepared platinum blacks. The curves for the differential heats of adsorption show no minima. They state that the minima so frequently observed by others must be considered as a phenomenon specific for the adsorbent and adsorbate. The striking feature of their results is the magnitude of the heats of adsorption. These attain values of 30000 cal. and more for H_2, SO_2, and CO, and greater than 100000 cal. for oxygen. These values are, however, in harmony with those obtained by others. Langmuir[4] estimates the heat of adsorption of carbon monoxide to be of the order of 30000 cal. According to him, carbon monoxide begins to leave the surface in a vacuum at 350°-400°,

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[1] Alekseevskii and Musakin: J. Russ. Phys.-Chem. Soc., **62**, 205 (1930).

[2] Taylor, Kistiakowski and Perry: J. Phys. Chem., **34**, 748 (1930).

[3] Taylor, Kistiakowski and Perry: J. Phys. Chem. **34**, 799 (1930).

[4] Langmuir: J. Am. Chem. Soc., **40**, 1361 (1918).

whereas oxygen can not be removed below 1200°. Its heat of adsorption should, therefore, be much higher than that for carbon monoxide.

Flosdorf and Kistiakowski[1] have determined the heat of adsorption of hydrogen on zinc-chromium oxide, and of hydrogen, oxygen and water vapor on supported and non-supported platinum catalysts. While a fresh sample of the zinc-chromium oxide adsorbs very little hydrogen at 0°, it adsorbs large quantities at 100°. The adsorbed hydrogen could not be removed from the oxide surface by pumping at higher temperatures, except in the form of water. When heated in hydrogen at 100° or at 300° until no further gas was taken up there resulted a green material due undoubtedly to the reduction of the oxide. The green material obtained at 300° proved to be a reversible and strong adsorbent for hydrogen. The adsorption on the reduced sample was now stronger at 0° than at 100°, and on heating the sample to 400° the adsorbed hydrogen was recovered quantitatively. The heat of adsorption on the fresh, unreduced samples was 60000 cal. per mol of hydrogen, while that on samples reduced at 300° was 20000 cal. or less. These results seem only to emphasize the futility of attempting to measure heats of adsorption of hydrogen on easily reducible oxides. The higher value obtained represents largely the heat of reduction of the chromium oxide. They find that the heat of adsorption of water vapor on platinum measured directly is in good agreement with that calculated from the data on the adsorption of hydrogen and oxygen.

With the view of ascertaining whether the absence of a maximum heat of adsorption is dependent on certain conditions, including those employed by previous investigators, or whether with this metal the form is general, Maxted[2] has redetermined the heat of adsorption of hydrogen on platinum at 0° and 20°. He finds, in general, that the total heat evolved during the acquisition of a given adsorbed hydrogen content decreased with the age of the catalyst and finally approached a rather steady value. The differential heats of adsorption pass through well-defined maxima, the maxima becoming less pronounced with ageing of the catalyst. While the curves for the different series were found to be similar, the actual curve obtained for a given sample of platinum is dependent upon its history and degree of outgassing. Hence, the relatively high temperatures, 250° to 300°, employed by Taylor, Kistiakowski and Perry[3] may possibly account for the non-observance of a maximum. The adsorption isotherms were found to exhibit a gradual shift with time toward the pressure axis. "It would appear then that the heat of adsorption and the hydrogen isotherms are properties which, like catalytic activity, are specific not only to an individual specimen of a hydrogenating catalyst, but also to its condition and history." Maxted concludes that the possession of a high differential heat of adsorption and high primary adsorption should be intimately related to the possession of a relatively high catalytic activity. And this for the reason that it would be expected that a given point on the catalyst

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[1] Flosdorf and Kistiakowski: J. Phys. Chem., 34, 1907 (1930).

[2] Maxted: J. Chem. Soc. 1930, 2093.

[3] Taylor, Kistiakowski and Perry: Loc. cit.

surface must possess at least a certain critical free energy to bring about, by adsorption, the activation of hydrogen and, consequently, catalysis.

In a study of the adsorption of SO_2 by charcoal at 0° and 5° and in the region of small adsorbed masses, Polanyi and Welke[1] have found that the isotherms, as well as the curves for the differential heats of adsorption calculated from them, show a very peculiar and hitherto unrecognized course. The isotherms show two flection points, the molar heat of adsorption passing through a minimum at about 6500 cal. and then rising to over 10000 cal. Since such a course, if true should be of the greatest theoretical interest, Magnus, Giebenhain and Velde[2] have tested its reality by a series of new measurements. In this they determined the integral heat of adsorption of SO_2 on coconut charcoal for the concentration range of 13 to 17000 micromols, on 15.75 g. of charcoal (0.05 to 68 mg. of gas to 1 g.). They find that the molar heat of adsorption shows a regular retarded decrease with increase in the amount adsorbed. Approximate differential heats of adsorption were obtained by the admission of about 30 micromols to the already more or less charged charcoal. Only above an adsorbed mass of 2000 micromols to 1 g. of charcoal do the curves thus obtained agree within limits of experimental error with those calculated from the integral heats. For lower amounts adsorbed, the experimentally determined differential heats are much greater than those calculated. These deviations have been explained qualitatively on the basis of the time necessary for the adjustment of adsorption equilibria in the capillaries.

Dixon[3] has found that the heat of adsorption, q, in cal. per mol adsorbed, can be expressed in terms of the adsorption potential, ϵ, and the amount adsorbed, x, by means of the relation,

$$q = \int_0^{\text{total}} \frac{\epsilon dx}{x},$$

Hence, the calculation of the heat of adsorption at any desired pressure involves merely the plotting of ϵ against x, finding the area under the curve and dividing this by the amount of gas adsorbed. Basing his calculations on data previously obtained[4] he finds the differences between the calculated and observed heats of adsorption to range from 2600 to 3200 cal. per mol. These differences represent the heats of condensation of carbon dioxide.

The Polanyi theory accounts only for the heat liberated in compressing the gas from the free state to the state in which it exists upon the charcoal surface. The heat of condensation of carbon dioxide at 0° under its own vapor pressure is 2420 cal. per mol. As the temperature falls the space volume of the liquid diminishes and that of the heat of condensation increases. Since the major portion of the carbon dioxide adsorbed exists at a density greater than that of the normal liquid at 0°, Dixon assumes that the gas condenses to

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[1] Polanyi and Welke: Z. physik. Chem.. **132**, 371 (1928).

[2] Magnus, Giebenhain and Velde: Z. physik. Chem., A **150**, 285 (1930).

[3] Dixon: J. Phys. Chem., **34**, 870 (1930).

[4] Magnus and Kalberer: Z. anorg. allgem. Chem., **164**, 345 (1930).

a liquid whose density and heat of vaporization are greater than that of the normal liquid. In this pressure range the adsorption forces are very strong and, therefore, the equation of state employed in developing the theory no longer applies. It should be expected then that in the presence of the existing strong force fields the heat of adsorption should be higher than that calculated by means of the normal equation of state. The Polanyi theory postulates a compression of the gas on the surface of the adsorbent. The calculations of Lowry and Olmstead[1] and those of Dixon show that this theory agrees well with the experimental data obtained.

Unimolecular Films

Within recent years Lyons and Rideal[2] have made a critical study of the properties of unimolecular films. The force-area curves of palmitic acid on the surface of solutions of varying pH show that the high pressure region of the curves is practically independent of the nature of the underlying solution. It increases, however, very slightly in steepness with increasing alkalinity, although the area remains unchanged at zero compression. Spreading proceeds slowly on acid solutions, the rate of spreading increasing rapidly with increase in pH; in very strongly alkaline solutions equilibrium is practically instantaneous. They suggest that the attraction of the molecules for acid surfaces is very small.

The expansion of the film is believed to be due to a gradual tilting of the molecules from the close-packed formation of the solid state. The solid condensed film consists of molecules tilted to such an angle that the zig-zag chains interlock. It is assumed that in liquid condensed films the molecules are free tilted, but, in general, oriented parallel to one another, giving a two-dimensional structure analogous to the smectic state of mixed crystals. The expanded state is regarded as a two-dimensional liquid. The gradual transition from the solid condensed film through the liquid condensed and expanded films to the vapor film is due to the gradual increase in the angle of tilt of the film molecules as their mutual attraction becomes weakened in comparison with the attractive forces between the chain and the surface.

Upon solution the film area is reduced slowly at constant pressure. The rate of decrease is appreciably increased by increasing the alkalinity, by increasing the temperature, and to a slight extent also by increasing the pressure. If the film pressure is kept constant on solutions of pH 8.5-13.0, complete solution does not occur, but some form of relatively insoluble film is left. This new form of film is regarded as a bimolecular leaflet, like the elementary leaflet in a soap bubble; it contains palmitic acid and sodium palmitate. On weakly alkaline solutions the lower layer of the bimolecular film is less closely packed than the upper, but the closeness of the packing increases with increase in alkalinity. The solution of a unimolecular film begins at nuclei formed by the adsorption of soap molecules beneath the surface, so that when

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[1] Lowry and Olmstead: J. Phys. Chem., 31, 1601 (1930).

[2] Lyons and Rideal: Proc. Roy. Soc. 124A, 322, 333 (1929); 128A, (1930); Nature 125, 351, 455 (1930).

there is initially no soap in the bulk of the solution the process is autocatalytic.

Light reflected by soap bubbles shows at first the continuous color of the ordinary soap lamella, then the lamella begins to vibrate and the liquid collects in minute spheres. At the same time areas of unit color appear; these are separated by circles and give a mosaic appearance to the lamellae. That the areas are liquid is shown by the fact that their boundaries are perfect circles, and that these boundaries may be displaced without destroying the lamellae. The detached droplets also show the Brownian motion.

Perrin[1] believes that the thickness of each layer in the liquid lamellae is a whole-numbered multiple of the same elementary layer thickness. That is, the elementary structures are formed by the superposition of a number of identical lamellae having a thickness of 4.4 millimicrons. With increasing thickness of the film the order of color in white light increases, thus showing the discontinuous and periodic structure of the material. These films show black spots by reflected light. These spots consist of thin films of water molecules which are surrounded on all sides by adsorbed oleic acid or oleate molecules with their acid groups dissolved in the water. The structure forms are anisotropic lamella or liquid crystal layer.

It has been found[2] that in the formation of the adsorption film at the interface air-solution of a surface active substance the surface tension does not change, if the concentration of the substance is very small. According to Talmud and his co-workers, this corresponds to a state in which the polar molecules lie horizontally and unoriented upon the surface of the water. Hence, they assume that the polar groups of the surface active substances are only slightly hydrated because of the inhibition of the predominating hydration of the polar groups of the molecules by the non-polar chains. With further increase in concentration of the surface active substance, and simultaneous with the beginning of the decrease in surface tension, there is a partial orientation of the polar molecules in the adsorption layer which is accompanied by a greater hydration of the polar groups In the saturated adsorption film, where the molecules are completely oriented and the surface tension attains a minimum value, the polar groups are all hydrated. They conclude that in the layer consisting of non-oriented, horizontally lying molecules, the hydration of the polar groups is a minimum. Also, that the hydration of the polar groups is a minimum in the saturated film in which the completely oriented molecules stand perpendicularly to the surface. Consequently, the maximum hydration of the polar groups must occur at some intermediate concentration of the surface film. In this narrow range of maximum hydration of the polar groups the polar molecules are only partially oriented, that is, they are inclined at a certain angle to the surface. With respect to thermal agitation they behave not as a two-dimensional crystal of the saturated adsorption phase, but as a meso-phase,—a two-dimensional liquid crystal. Such

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[1] Perrin: Kolloid-Z., 51, 1 (1930).

[2] Talmud: Evolution of the Theoretical Views on the Nature of the Flotation Process, Non-Ferrous Metals, No. 1, 68 (1930) (In Russian); Talmud and Suchowoloskaja: Z. physik. Chem., (in press); Talmud, Suchowoloskaja and Lubman: A 151, 401 (1930).

considerations must lead to the view that in the region of maximum hydration the chains of polar molecules, by intertwining, must form a system analogous to a lyophile gel, a system which exhibits mechanical rigidity toward dislocation. The longer the chain and the greater its complexity, the greater will be the rigidity of the surface film. Further, the greater the solubility of the molecule the less will be the rigidity in the region of maximum hydration. In measure as the molecules assume a more vertical orientation and the molecules become less hydrated, the firmness of the adsorption film will decrease. It will reach a zero value for the liquid film and a definite constant rigidity for the adsorption film.

Monomolecular layers of fatty acids upon a water surface are analogous to a two-dimensional or "surface" gas. This gas exerts a definite pressure per unit length. For small concentrations the molecules are widely separated and obey the three-dimensional gas law, $PS = RT$, where P is the pressure and S is the surface. At greater concentrations the attractive force between the molecules becomes effective and there is formed finally a condensed film or two-dimensional liquid. According to Semenov,[1] the two-dimensional gas behaves like an ordinary three-dimensional gas and should, therefore, adapt itself to the van der Waals equation.

With increase in pressure, P, surface liquid formation occurs and the whole adsorbed layer separates finally, at high pressures, into a two-dimensional liquid and a saturated surface vapor phase. The liquid surface forms the more easily the greater the forces of attraction prevailing between the molecules. These are particularly large between metallic atoms, and, therefore, we should expect the formation of the surface liquid phase to occur easily with metal vapors.

Semenov's theory shows the existence of an inversion temperature, T_i, below which the critical condensation pressure exceeds, and above which it is less than the saturated vapor. In the temperature range, $T < T_i$ and at pressures below the critical, the amount of adsorbed gas increases with the pressure and forms a two-dimensional gas phase on the surface. When the critical pressure is reached a liquid is formed which quickly covers the whole surface; with this there is an accompanying decrease of the outer gas pressure to P_g. For the range $T > T_i$, and at pressures less than the critical, we find the same behavior, but in this case the unimolecular liquid layer formed when the pressure reaches the critical pressure, is stable, since it is less than p_g. As the pressure, p, is increased, the formation of a second liquid layer begins. At a certain pressure there is a stable bimolecular adsorbed layer. Thus multi-molecular adsorption occurs only when $T > T_i$ and $p_{crit} < p < P_g$.

Hydrogenation

Balandin[2] presents an empirical rule by which it is possible to predict the products of hydrogenation of organic substances. By assigning to the elements, halogen, oxygen, nitrogen, and carbon, the numbers 1, 2, 3 and 4,

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[1] Semenov: Z. physik. Chem., B 5, 471 (1930).

[2] Balandin, J. Russ. Phys.-Chem. Soc., 62, 703 (1930).

respectively, and letting π represent the product of the numbers assigned to any pair of these elements, he finds that the ease with which the linkage between the two elements is broken in the catalytic hydrogenation is inversely proportional to the value of π. This rule is found to hold for a large number of compounds. The most frequent exceptions to the rule are to be found among compounds containing the carbonyl group and among heterocyclic compounds containing nitrogen in the ring. He finds the order for the four elements to be the same as that of the ease of replacement of a given element from its compound with nickel by a different element in combination with hydrogen. "The readiness with which an atomic group is separated during the catalytic hydrogenation of a compound is greater, the greater its affinity to the catalyst; it is the smaller, the greater is its affinity to the remainder of the molecule. For this reason, the stability of a given linkage in the absence of a catalyst need not be the same as in its presence."

H. S. Taylor and Lavin[1] have attempted to determine the nature of the influence of specific surface on chain reactions involved in the oxygen-hydrogen system. In this they have assumed that hydrogen atoms, oxygen atoms, and hydroxyl radicals are the only atoms or radicals involved in the chain. Their results show that the nature of the surface is of fundamental importance in determining the velocity of atom-radical reactions. Potassium chloride is more efficient than clean glass in the H-OH combination. Alumina is also very efficient for the same reaction. Both, however, are inefficient catalysts in the recombination of hydrogen atoms. "Potassium hydroxide and carbonate, and especially, zinc-chromium oxide, are efficient agents for this reaction, as are also metallic surfaces." They have shown quite conclusively that a dehydrating catalyst, like alumina, promotes the H-OH combination, while the dehydrogenating catalyst, zinc-chromium oxide, promotes the H-H recombination.

Fine foam produced by forcing air through porous bodies into water containing a foam-producing substance, like saponin, has been successfully used in extinguishing highly combustible liquids. The relatively large volume of air which can be added to the burning hydrocarbon does not support the combustion of the burning gases, but it does take part in extinguishing the combustion already begun. Strange as it may seem, foam particles containing detonating gas or oxygen-acetylene mixtures do not explode when brought in contact with a flame or with the spark of an induction coil.[2] Burning benzin can be as easily extinguished by a detonating gas foam as by one containing carbon dioxide. It may be said in explanation of the behavior of explosive gas foams that not only does the highly developed liquid film influence to a high degree the behavior of the gas within, but it also hinders the propagation of the combustion. Conversely, these highly developed liquid films containing the proper catalyst enhance greatly the reactivity of gases. Biesalski finds that a colloidal solution of palladium containing 1/10 percent of saponin increases

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[1] H. S. Taylor and Lavin: J. Am. Chem. Soc., 52, 1910 (1930).

[2] Biesalski, Kowalski and Wacker: Ber., 63B, 1698 (1930); Biesalski: Z. angew. Chem., 41, 853 (1928).

enormously the speed of hydrogenation of ethylene, acetylene and salts of unsaturated fatty acids. It is essential that the foam-producing substance produce small stable homogeneous bubbles of high capillary activity. Through the use of fine bubbles the adsorptive power of the hydrogenating agent is increased two to three times that required by the laws of Gibbs.

Diphenyl ether in contact with nickel at 250° is reduced by hydrogen under 60 atms. to cyclohexane.[1] At 170° the products are cyclohexane, cyclohexanol, and traces of dicyclohexylester. Benzene, cyclohexane, phenol and cyclohexanol follow from the decomposition at 220°. Two possible explanations have been put forth for the mechanism of the reaction. The first involves the initial disruption of the carbon-oxygen linkage, followed by the hydrogenation of the benzene nucleus of the molecules decomposed. This view is favored by the isolation from the reaction product of benzene and phenol, along with their reduction products. The occurrence of benzene in abundance is ascribed to the difficulty of its hydrogenation, whereas phenol is easily hydrogenated. A second explanation of the formation of cyclohexane and cyclohexanol is given by the reaction

$$(C_6H_5)_2O \xrightarrow{H_2} (C_6H_{11})_2 \xrightarrow{H_2} C_6H_{11}OH + C_6H_{12}.$$

That is, since some benzene is obtained, they believe that the hydrogenation may occur after the ether has been split, rather than before.

Komatsu and Masumoto[2] find also that furfurol with nickel and hydrogen at 160° and 100 atms. gives furane, methyl furane and furfuryl alcohol. Tetrahydrofurfuryl alcohol is obtained at 180° and 85 atms. Dihydrofurfuryl alcohol is formed by partial hydrogenation at 144° and 80 atms. Furfurol is completely hydrogenated by heating at 150° and 100 atms. A depression of the pressure at a number of temperatures is taken to indicate that the hydrogenation proceeds in steps, depending on the temperature to which the reacting system is subjected. Tetrahydrofurfurylether is assumed to occur as an intermediate reaction product. This is transformed by heat to methylfurane, furane and n-butyl alcohol by disruption of the carbon-oxygen linkage.

The hydrogenation of acetoacetic ester over a nickel catalyst takes place readily[3] at 100° to 150°. The rate of reduction is about three times as fast in ether or methylcyclohexane as in the absence of a solvent. The rate of reduction in ethanol is intermediate between that of the pure ester and its solution in cyclohexanol, ethyl-β-hydroxy butyrate being formed practically quantitatively. The dehydroacetic acid, formed in small quantities in the reduction of the acetoacetic ester, is reduced in methylcyclohexanol at 185° to 190° under 108 to 305 atms., the reduction proceeding about four times more rapidly at the highest than at the lowest pressure. The chief product in the hydrogenation of dehydroacetic acid is 4-heptanone.

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[1] Komatsu and Masumoto: Bull. Chem. Soc. Japan, 5, 241 (1930).

[2] Loc. cit.

[3] Adkins, Connor and Cramer: J. Am. Chem. Soc., 52, 5192 (1930).

Nitrobenzene with hydrogen in the presence of reduced nickel at 100° and 50 atms. gives aniline. At 200° and 100 atms. the main product is cyclohexamine with small amounts of dicyclohexylamine and aniline. Aniline itself gives a similar mixture at 180° and 150 atms. Nitrophenols and nitronaphthalenes show similar transformations at high temperatures and high pressures.

In alcoholic solution, 2-4-dinitrophenol is reduced[1] to the diaminophenol in the presence of nickel and hydrogen under 500 pounds pressure. Maximum yields are obtained at 96°. Elevation of temperature produces a slight decrease in the yield of amine due to the formation of ammonia. A maximum yield of 91.5 percent is obtained with a concentration of 5 g. of nitrophenol to 20 cc. of alcohol, the yield decreasing with both higher and lower concentrations. An increase in the ratio, (g. catalyst)/(g. dinitrophenol), from 0.2 to 0.4 produces an increase in the diamine yield at all concentrations.

When heated with hydrogen at 80 atms. over copper at 200° to 230° benzene is hydrogenated to a product containing 15 per cent of cyclohexane. Under the same conditions, but at 200°, naphthalene is transformed quantitatively to tetrahydronaphthalene, and this in turn at 260° passes partially to dekalin. Under practically similar conditions phenol is changed to cyclohexane and a trace of diphenyl ether; the α- and β-naphthols are hydrogenated to the tetrahydronaphthols.

It has been found by Brown and his co-workers that the hydrogenating activity of lead, thallium, bismuth, and the lower oxides of iron, tin, molybdenum and vanadium give high yields of aniline from nitrobenzene. Under the proper working conditions, thallium and bismuth also give very good yields of azobenzene. Hartman and Brown[2] have recently studied the hydrogenating activity of cadmium from the reduced oxalate and hydroxide. At low temperatures slightly higher yields of aniline are obtained over the reduced oxalate; the reverse is true at higher temperatures. Both catalysts give maximum yields at 319°. Previous roasting of the catalyst before reduction seems to produce a more finely divided catalyst and thus increase its activity. Cadmium still retains its activity above its melting point so long as the nitrobenzene is continually passed through the catalyst. In the absence of the nitrobenzene there is a tendency for the cadmium droplets to coalesce. Although support materials, like pumice and asbestos, do not improve the aniline yields, they do prolong the activity of the catalyst by retarding the coalescence of the cadmium droplets near the melting point.

Hill and Kistiakowski[3] find that hydrogen and ethylene react when brought in contact with distilled cesium at 25°. The reaction proceeds much more rapidly at 200°. The rate of reaction at both temperatures, as indicated by the pressure drop, shows evidence of poisoning. A similar poisoning is observed in the reaction between carbon monoxide and hydrogen at room temperature. This reaction also begins very rapidly and then as rapidly diminishes

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[1] Bradt: J. Phys. Chem., 34, 2711 (1930).

[2] Hartman and Brown: J. Phys. Chem., 34, 2651 (1930).

[3] Hill and Kistiakowski: J. Am. Chem. Soc., 52, 892 (1930).

to zero. The reaction products of the first reaction contain ethane and cesium hydride, deposited as a white layer upon the cesium surface. While the mutual reactivity of the hydride and ethylene is very slight at room temperature, the reaction becomes quite rapid at 200°, and the hydride is removed. The resulting gases contain ethane and hydrogen, the latter being formed by the thermal decomposition of the hydride. Ethylene also poisons the surface of the cesium.

While hydrogenations catalyzed by alkali metals might appear to be explainable on the basis of the formation of intermediate compounds, the experiments of Hill and Kistiakowski seem to show that even over alkali metals only the adsorbed hydrogen is available for hydrogenation. Hydride formation serves only in diminishing the extent of free surface. Pease and Stewart[1] have previously shown also that while calcium hydride is an efficient catalyst for the reaction, the hydrogenation of ethylene over calcium does not proceed through the formation of the intermediate hydride.

Reduced rhenium and rhenium-copper catalysts catalytically hydrogenate the reactions;

$$CO + 3H_2 = CH_4 + H_2O \text{ and } C_2H_4 + H_2 = C_2H_6.$$

While the copper-free rhenium quickly loses its activity, it may again be regenerated by heating with hydrogen at 400°.[2] In the reduction of carbon monoxide rhenium possesses about the same activity as osmium. A 50 percent volume contraction is obtained when carbon monoxide is led over a rhenium-copper catalyst at 470°, indicating a quantitative decomposition of carbon monoxide to carbon and carbon dioxide. After a short time the reaction ceases completely. Externally the catalyst showed no change, but yielded 41 cc. of carbon dioxide on treatment with oxygen. The reaction proceeds only to the formation of a rhenium carbide, which, like the carbides of iron and nickel, does not catalyze the decomposition of carbon monoxide. After heating with air it is again capable of carbide formation.

With platinum oxide as catalyst, isoquinoline in acetic acid solution is readily hydrogenated to tetrahydroisoquinoline at room temperature.[3]

It has been more or less of a common belief that the sulfur in proteins would poison noble metal catalysts. For this reason no attempt has been made to catalytically hydrogenate the proteins. Bergmann and Michalis[4] have found that cystine, dialanylcystine and di-β-amino-ethyl sulfide are readily hydrogenated and almost quantitatively to the corresponding thiol compounds by palladium sponge in hydrochloric solution. Platinum catalysts, however, cannot be used for these hydrogenations.

Tetrahydrocarbazol in benzene is easily dehydrogenated by safrole to carbazole in the presence of palladium black.[5] Hydrocoumarin in anethol when heated with palladium gives a small amount of coumarin. Safrole does

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[1] Pease and Stewart: J. Am. Chem. Soc., 47, 2763 (1925).

[2] Tropsch and Kassler: Ber., 53B, 2149 (1930).

[3] Ranedo and Vidal: Anal. Fis. Quim., 28, 76 (1930).

[4] Bergmann and Michalis: Ber., 53B, 987 (1930).

[5] Akabori and Saito: Proc. Imp. Acad. Japan, 6, 236 (1930).

not reduce hydrohydrastinine in benzene when boiled with palladium, but dihydrohydrastinium salts are formed when treated with two mols of maleic acid in aqueous solution. Tetrahydroharman and tetrahydroharmine are dehydrogenated to harman and harmine, respectively, by heating with maleic acid and palladium.

Levulinic acid is easily reduced[1] to n-valerolactone in the presence of platinum oxide at room temperature. The speed of the reduction depends upon the solvent used. It is approximately 3.5 times faster in diethyl ether than in ethyl alcohol, and 4.5 times faster than in glacial acetic acid.

Conant and Hyde[2] find that the reduction of magnesium-free chlorophyl derivatives by the action of hydrogen and a palladium catalyst in alkaline solution does not lead to the formation of leuco compounds. They state that the reductions produced by hydrogen in the presence of palladized asbestos are not catalytic hydrogenations, but are reduction processes occurring at the potential level of the hydrogen electrode. They cite also in this connection the inability of palladized asbestos to add hydrogen to such double bonds as those which occur in allyl alcohol or in dimethylacrylic acid. The chlorophyl derivatives and the porphyrins, however, are easily hydrogenated catalytically to the leuco compounds in the presence of platinum oxide catalysts.

Coals containing no mineral constituents give only negligible quantities of oil on hydrogenation.[3] Of all the mineral constituents of coal only the iron compounds are of importance as hydrogenating catalysts, and of these FeS_2 is probably the best. Added Fe_2O_3 catalytically influences the hydrogenation and produces better oil yields, especially with older coals. Its catalytic influence on younger coals is less, and in general, these require more Fe_2O_3. Zinc chloride is still more active than the iron oxide and is good for coals of higher carbon content.

Dehydrogenation

Although the reaction products, hydrogen and naphthalene, exert no influence upon the speed of dehydrogenation of decahydronaphthalene in the presence of osmium, the products formed in the subsequent catalytic decomposition of naphthalene are poisonous to osmium.[4] Thus, osmium is not a suitable catalyst for this dehydrogenation. Its catalytic activity may be restored, however, by heating with hydrogen at 270°. With osmium the activation energy of dehydrogenation is 10,000 cal. per mol. In this respect the metal resembles nickel, on which the heat of activation of the decahydronaphthalene is 9,990 cal. per mol. After the catalyst had been used for some time its activity was abruptly increased and the heat of activation rose to 16,250 cal. per mol, a value about the same as that observed with palladium. Balandin attempts to explain this sharp increase in the activity of osmium on the basis of his "Multiplet Theory," according to which a catalytically active center is composed of several atoms of the catalyst substance. The sudden

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[1] Schutte and Thomas: J. Am. Chem. Soc., 52, 3010 (1930).

[2] Conant and Hyde: J. Am. Chem. Soc., 52, 1233 (1930).

[3] Hlavica: Brennstoff Chem., 10, 201 (1930).

[4] Balandin: Z. physik. Chem., B 9, 49 (1930).

change is then associated with a regrouping, or displacement of the metal atoms in the catalyst surface, whereby both the formation, as well as the adsorption of the poisonous substances is decreased, and thus the dehydrogenation catalysis of the decahydronaphthalene is favored. The failure of osmium to dehydrogenate other six membered ring systems is explained as probably due to the more rapid formation of the inhibiting substances.

Kodama[1] has studied the influence of added metallic oxides upon the copper-cobalt catalyst used in the reduction of carbon monoxide. MgO proved to be the most efficient promoter; it becomes active at 200°, but gives the best results at 240°. It was still sufficiently active after 16 hours use to bring about a 45 percent gas contraction. Petroleum and benzene are found among the products. With additions of TiO_2, ZrO_2 or CeO_2 liquid products are first obtained at 180°-200°. The gas contractions are about the same for the three promoters at the same temperature. All three catalyze the formation of hydrocarbon gases, and to a slight extent some liquid products. While ZrO_2 is the best promoter of the three, it is still not so good as MgO. Beryllium and zinc oxides are of little use as promoters, and cadmium oxide completely inhibits the activity of the cobalt.

Attempts to reduce carbon dioxide according to the reaction,

$$CO_2 + H_2 = H_2O + CO$$

have, heretofore, been carried out only at relatively high temperatures. The same reaction has been found to take place at moderate temperatures when the proper catalysts are employed.[2] With metallic copper the reaction is noticeable at 200°. Employment of $Cu\text{-}Cr_2O_3$, Fe-Cu, Fe-Co and Cu-Co-Zn contacts at temperatures between 200° and 450° and with mixtures of carbon dioxide and hydrogen in the ratio of 1:1 and 1:3, respectively, give yields of carbon monoxide up to 16 percent. With long contact, and especially with contacts containing cobalt, there is complete reduction of carbon monoxide to methane.

Molybdenum sulfide, MoS_2 is most efficient catalyst in the high pressure reduction of cresols at 460°-80° and pressures up to 240 kg./sq. cm. It gives a nearly complete reduction to hydrocarbons. While nickel, or its hydroxide, are good catalysts their efficiency is strongly influenced by the presence of sulfur. The phenols are reduced by a hydrogenation of the hydrocarbons formed more with nickel than with molybdenum catalysts. No cyclic alcohols are formed. Of the large number of catalysts employed $ZnCl_2$, $Al(OH)_3$, $(NH_4)_3VO_4$, $Cr(OH)_3$, UO_3, $Co(OH)_2$ and NiS were excellent catalysts; ZnO, basic copper chromate, WO_3 and $Fe(OH)_3$ are inactive.

Oxidation

In 1910 J. J. Thomson[3] called attention to the fact that combustion involves not only the molecules and the atoms, but also the electrons. He

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[1] Kodama: Sci. Papers Inst. Phys. Chem. Res., **13**, 93; **14**, 13 (1930).

[2] Bahr: Ges. Abhandl. Kenntniss Kohle, **8**, 219 (1930).

[3] J. J. Thomson: Brit. Ass. Rep., Sheffield, **1910**, 501.

stated that it was not improbable that the emission of charged particles from a surface is of primary importance in promoting combustion on hot surfaces. That these electrons might produce very important effects by union with oxygen, with moisture, or with the combustible material. Finally, that the action of surfaces might ultimately be found to depend on the fact that they form a support for layers of electrified gas in which chemical changes proceed with high velocity.

While the emission of electrons from tungsten is not affected by chemically indifferent gases, it is suppressed by the catalytic poisons.[1] The photoelectric emission from metals is also decreased by the catalytic poisons, HCN, H_2S and CO.[2] Thomson has also found that thermionic emission becomes perceptible when heated to the temperature at which it catalyzes the union of hydrogen and oxygen.[3] While variation of the proportion of hydrogen in the mixture does not alter the temperature at which the union takes place, an excess of oxygen does reduce the temperature of the combination below that of thermionic emission. Thus, oxygen becomes active toward hydrogen at a platinum surface at a temperature lower than that at which electrons are emitted from the surface. The activation of hydrogen occurs at the same temperatures as that at which thermionic emission becomes perceptible. Srikantan[4] has extended the experiments of Thomson to the study of reactions between hydrogen and carbon dioxide at the surfaces of filaments of platinum, of platinum coated with barium oxide, and of thoriated tungsten. The adsorptive capacity for carbon dioxide is greatly increased by using the coated platinum. The thoriated tungsten emits electrons with great ease at temperatures far below that required for dull red heat. Does the reaction between these two gases take place at the temperature at which thermionic emission becomes perceptible as in the case of platinum? It was found that while increase of hydrogen or carbon dioxide does not alter the temperature at which the reaction begins on the coated platinum, the temperature is far lower than that on the surface of plane platinum. The catalytic reaction on the thoriated tungsten begins at the temperature at which thermionic emission is just perceptible. These experiments clearly indicate that the activation of the gases on a catalyst surface is influenced to a large extent by the capacity of the surface to emit electrons at the temperature employed.

Thomson[5] has studied the condition of explosions of stoichiometric mixtures of carbon disulfide and oxygen. He finds that the reaction is very slow below 140°. It proceeds explosively, however, at a few degrees above 140°, if the pressure lies within certain limits. The transition from a slow reaction to an explosive combustion is sharp at the limiting pressures. Elevation of temperature widens the pressure limits within which explosion occurs. Upon crossing heated carbon disulfide and oxygen rays in the wall-free space the

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[1] Langmuir: Trans. Faraday Soc., **17**, 641 (1929).

[2] Kruger and Taege: Z. Elektrochemie, **21**, 562 (1915).

[3] Thomson: Physik. Z., **14**, 11 (1913).

[4] Srikantan: Indian J. Physics, **5**, 685 (1930).

[5] Thomson: Z. physik. Chem., B **10**, 273 (1930).

explosion was first observed at about 290°. It occurred at a much lower temperature when the rays were allowed to impinge upon a glass rod. These relations are not in agreement with the views of Alyea and Haber.[1] According to these authors, the upper pressure limit is the limit of ignition at the walls; the lower pressure limit is the limit of propagation of ignition through the free space. The chain reaction manifested in the combustion of carbon disulfide is analogous to that observed in the ignition of oxy-hydrogen gas at low pressures. In both cases the explosion begins at the wall.

The much greater influence of hydrocarbon concentration than of oxygen concentration on the rate of oxidation of ethylene and benzene has been found[2] to apply also to the oxidation of methane, methyl alcohol and acetaldehyde. While all of the reactions proceed by chains, the length of the chain and the methods by which it is ended vary considerably from reaction to reaction. With benzene the chains do not appear to reach the wall unless the free space of the reaction vessel is very small, while with methyl alcohol nearly all of the chains appear to end at the wall. The actual qualitative nature and condition of the wall, the extent of surface and dimensions of the vessel are found to exert a considerable influence upon the reaction rate. The variability of the nature of the wall and its ability to end a chain is assumed as due to variations in the adsorbed gas layers, and here in particular to adsorbed oxygen. If the reaction chains begin in the gas phase and end at the wall, the reaction will be much slower in a vessel of small than in one of large size. But, if the chains end for the most part in the gas phase, the dimensions of the vessel are unimportant. All three of the reactions studied were found by Fort and Hinshelwood to be slowed down considerably by a sufficient increase in wall surface. Thus, for example, with methane the reaction did not proceed at all in 30 minutes in a vessel filled with silica spheres. To explain their results with methyl alcohol they assumed that the efficiency of the walls in ending the chains depends upon the layer of adsorbed oxygen.

The mechanism of the oxidation of metals has been the subject of frequent investigations. Tammann and his co-workers,[3] and also Vernon[4] have studied the oxidation of copper at low temperatures. At high temperatures we have the comprehensive work of Pilling and Bedworth[5] and of Dunn.[6] While the results of all of these investigators lead to the conclusion that the speed of oxidation is conditioned by the speed with which the oxygen diffuses through the oxide layer formed, there is some disagreement as to the laws under which the diffusion takes place.

Pilling and Bedworth have shown that in so far as the kinetics of oxidation is concerned, metals may be divided into two classes, depending upon

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[1] Alyea and Haber: Naturwissenschaften, 1930, 441.

[2] Fort and Hinshelwood: Proc. Roy. Soc., 129A, 284 (1930).

[3] Tammann: Z. anorg. allgem. Chem., 123, 197 (1923); 128, 179 (1923); 152, 149 (1926); 169, 43 (1927).

[4] Vernon: J. Chem. Soc., 1926, 2273.

[5] Pilling and Bedworth: J. Inst. Metals, 29, 529 (1923).

[6] Dunn: Proc. Roy. Soc., 111A, 211 (1926).

whether the volume of the oxide is greater or less than that of the metal from which it is formed. If greater, the oxide formed will protect the remaining metal from oxidation; if the volume of the oxide is smaller, its porous nature can offer no protection to the metal below. Copper belongs to the first group. They have shown that when the oxide covers the metal completely the rate of oxidation is governed completely by the rate of diffusion of the oxygen through the oxide. Assuming the rate of diffusion of the oxygen to be inversely proportional to the thickness of the oxide layer, we may write

$$dx/dt = k/x. \qquad (1)$$

This upon integration becomes

$$x^2 = k \cdot t, \qquad (2)$$

where x is the weight of the oxide formed in time t and k is a constant. This equation was found to accurately describe the rate of oxidation of metals of the first group with the exception of copper.

Dunn[1] finds that the oxidation of commercial copper follows (2) over short intervals of time. However, if the copper has been previously activated by alternate oxidation and reduction, this law is not obeyed even for the shortest time intervals. In discussing the nature of the diffusion of oxygen through the oxide Dunn assumes that, (1) "the structural units of the oxide are in a state of vibration and that a random distribution of energies of vibration prevails; (2) that an oxygen molecule can only pass a structural unit, if this possesses at the moment energy greater than the critical energy, causing a loosening of the oxide at that point."

Whether or not oxygen can diffuse through the Cu_2O lattice will naturally depend upon the relative dimensions of the oxygen and the lattice. Taking the edge of the cubic cell[2] of Cu_2O as 4.28Å and the diameter of the oxygen ion[3] as 2.7 Å, and neglecting the size of the copper ion, Wilkins and Rideal[4] have shown that there is not sufficient room for the oxygen molecule of diameter[5] 3.62Å to pass through a stable lattice. While this may be true for low temperatures, the diffusion should be facilitated at high temperatures where the lattice is much less stable. Experimental evidence obtained at temperatures around 1000°, near the melting point of copper (1235°), appeared to support these considerations.

Wilkins and Rideal[6] claim that the rate of oxidation of copper must be dependent upon the rates of at least three processes: (a) condensation of oxygen at the Cu_2O-O_2 interface; (b) evaporation of the oxygen from this oxide-oxygen interface into the body of the oxide; and (c) the diffusion of oxygen through the oxide. They find at constant temperature that the low pressure oxidation of activated copper follows the simple relation:

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[1] Dunn: Proc. Roy. Soc., **111A**, 219 (1926).

[2] Greenwood: Phil. Mag., **48**, 653 (1924).

[3] Bragg and West: Proc. Roy. Soc., **114A**, 45 (1927).

[4] Wilkins and Rideal: Proc. Roy. Soc., **128A**, 394 (1930).

[5] Jeans: "Dynamical Theory of Gases," 327.

[6] Loc. cit.

$$\log p_o/p = kt, \qquad (3)$$

where p_o is the initial pressure of the oxygen, p is the pressure at the time t, and k is a constant. Relation (3) fails completely, however, when applied either to the oxidation of activated copper at high pressures, or to the oxidation of inactive copper at low pressures.

Feitknecht[1] finds that the speed of oxidation of copper at high temperatures does not exactly follow the parabolic law, $x^2 = K \cdot t$. Initially, the speed is too great and only after an initial oxidation of a few minutes is the validity of the law fulfilled. The oxide layer at all temperatures consists chiefly of Cu_2O, covered superficially by a thin film of CuO. The Cu_2O layer has a metallic-like structure, it shows crystal growth, and thus exhibits the same regularities as metals. According to Feitknecht, it is these observations on the crystal growth of Cu_2O that gives us a possible explanation for the deviations of the experimental results from the regularities demanded by theory. The diffusion of the oxygen takes place both through the lattice structure of the Cu_2O crystals and along their boundary edges. Since the extent of the crystal surface varies inversely with the square of the size of the crystallites, the proportion of oxygen diffusing along the boundary surfaces will increase strongly with decrease in the size of the crystals. Hence, if the Cu_2O layer is thin and the crystallite is small, the speed of oxidation is initially greater than that corresponding to the parabolic equation. Later, when the crystals become larger and cover the surface, almost all of the diffusion is through the crystal lattice and the law is obeyed.

Wilkins[2] takes issue with Feitknecht, and he maintains that the latter's conclusions deduced from experimental results are not justifiable for the following reasons. He states that equation (2) above is derived from (1), a relation which implies that the rate of oxidation is controlled by the speed of diffusion of oxygen through the Cu_2O layer. He claims that (2) follows from (1) only if the integration constant is zero. This can only be the case, however, if no oxidation has taken place up to the time from which measurements were made. For these reasons Wilkins advocates the use of the more general parabolic law:

$$X^2 = k \cdot t + c, \qquad (4)$$

where $\sqrt{c}$ represents the amount of preoxidation. This more general equation is found to be in agreement with Feitknecht's own data. Wilkins states that we must assume that the permeability of the oxide layer remains unchanged during oxidation. Also, that the diffusion occurring at the boundary of crystals plays only a slight rôle in the transfer of oxygen through the Cu-Cu_2O interface. Its contribution at high temperatures is small compared with lattice diffusion. In a study of the influence of pressure Wilkins[3] finds that the oxidation of copper obeys the relation: $d(p_o - p)/dt = k(p_o - p)$, down to pressures of about 10 mm. Activation of the copper increases the

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[1] Feitknecht: Z. Elektrochemie, 35, 142 (1929); 36, 16 (1930).

[2] Wilkins: Z. Elektrochemie, 35, 500 (1929).

[3] Wilkins: Proc. Roy. Soc., 128A, 407 (1930).

limiting pressure, that is, the pressure below which the oxidation ceases to be independent of the oxygen pressure, thirteen times, while sintering the surface increases it. He suggests that at the limiting pressure the grain boundaries of the Cu_2O crystals are just saturated with oxygen, and that the adsorbed gas diffuses laterally at 183°. At this temperature the parabolic law holds for long periods, provided that the copper is activated and the oxygen pressure is sufficiently high.

Lewis[1] finds that glass and pumice raise the ignition temperature of the hydrocarbons, the amount depending on the rate of heating and the concentration. Charcoal, however, raises the ignition temperature of the paraffins and lowers that of the olefins, the amount in each case varying with the nature of the charcoal. The effect of metals on the ignition point varies with the metal employed, with the extent and condition of the surface, with the concentration of the hydrocarbon, and with the speed of heating. They may raise the temperature or may have no effect at all; in some cases they may even prevent explosion. Thus, silver and platinum increase considerably the ignition temperatures; tin, zinc and aluminum show practically no effect. Lead raises the ignition temperature considerably and may even inhibit explosions. Copper also prevents the ignition of some hydrocarbons. The effect of the last two metals decreases as the molecular weight of the hydrocarbons becomes smaller.

Lewis suggests a three-stage mechanism for the combustion of paraffin hydrocarbons: (1) a primary dehydrogenation yielding unsaturated hydrocarbons, (2) the combination of these with oxygen to give unstable peroxides, and (3) the decomposition of these to aldehydes, etc., which are then oxidized to water and the oxides of carbon.

In the Haber-Bosch process water gas containing nitrogen, mixed with three to four volumes of steam, is passed over promoted iron catalysts. After scrubbing to remove the CO and CO_2 the effluent gas gives a 3 to 1 hydrogen-nitrogen mixture suitable for the synthesis of ammonia. Attempts to remove the residual CO from the hydrogen by preferential oxidation have met with considerable success provided the CO concentration does not exceed 0.5 percent. Lamb, Scalione and Edgar[2] have shown the possibility of preferentially oxidizing the 0.5 percent CO in the hydrogen by adding an amount of oxygen in excess of that required for complete oxidation of the carbon monoxide, then saturating with water vapor at 40° and passing it over hopcalite in small-bore copper tubes immersed in liquid baths. Water vapor poisons[3] the hopcalite toward the oxidation of both the carbon monoxide and the hydrogen, but more especially toward the latter. Lamb and Vail find that the water vapor concentration in the gas phase may be greatly increased since, as they found, the activity of the hopcalite depends not upon the concentration of the water in the gas phase, but upon the water content of the catalyst. Further, the activity is practically independent of the temperature.

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[1] Lewis: J. Chem. Soc., 1930, 34, 58.

[2] Lamb, Scalione and Edgar: J. Am. Chem. Soc., 44, 738 (1922).

[3] Lamb and Vail: J. Am. Chem. Soc., 47, 123 (1925).

Believing that the use of a large excess of steam in the gas phase and high temperatures should be efficacious in the oxidation of carbon monoxide, Keuntzel[1] passed water gas containing a large excess of steam over catalysts of CuO, MnO_2, and two hopcalite mixtures. The two oxides and a 5-component hopcalite were catalytically active but all three suffered reduction and loss of catalytic activity. Only the 2-component hopcalite (MnO_2 60: CuO 40) gave promise of preferential oxidation under the operating conditions employed. It gave a 96 percent efficiency for 37 hours. With a water gas of the initial composition: 1.3 CO, 1.5 O_2, 49.5 H_2, 28 CO_2 and 19.7 N_2 plus three volumes of water vapor over a commercial hopcalite 97 to 99 percent of the CO was oxidized to CO_2 in the temperature range of 160° to 195°. A "CWS" hopcalite in a copper chamber with the same mixture gave a 100 percent oxidation for several hours, then gradually falling to 96 percent after 69 hours of service. The loss of catalytic efficiency is apparently due to the reduction of the oxide by hydrogen and carbon monoxide, the loss of available oxygen through thermal decomposition of the oxides and to inefficient dissipation of heat. The steam serves to rapidly dissipate the heat of the reaction, preventing local overheating of the catalyst granules. It specifically inhibits the reduction of the catalyst and the oxidation of the hydrogen.

In the investigation of the decomposition of nitrous oxide on platinum at low pressures, Schmieschek[2] found evidence for an interesting low-pressure oxidation. The increase in pressure in the presence of platinum is less than we should expect if the oxide is to decompose according to the reaction:

$$2\ N_2O = 2\ N_2 + O_2$$

He explains this anomalous pressure effect as due to the disappearance of oxygen brought about by the formation of mercuric oxide. Independently, Leipunski[3] has studied the speed of oxidation of mercury in its dependence upon the partial pressure of the oxygen and mercury vapor in the presence of glowing platinum. He finds that the reaction speed is independent of the oxygen pressure and that it decreases with increasing mercury vapor pressure. Without a catalyst mercury combines with oxygen of atmospheric pressure at 300° to form the oxide:

$$2\ Hg + O_2 = 2\ HgO + 43000\ \text{cal.}$$

This reaction is reversible and, as we know, the oxide begins to decompose at 400°. Leipunski finds, however, that mercuric oxide is formed in contact with platinum when heated above 1300°. The evidence for this lies in the fact that mercuric oxide evaporates from the platinum surface and is deposited as a reddish yellow precipitate on the cool walls of the glass vessel. Thus, owing to the minimal vapor pressure at the temperature of the wall, the oxide is removed practically completely from the reaction and mercuric oxide continues to be formed on the heated platinum. Hence the reaction

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[1] Keuntzel: J. Am. Chem. Soc., 52, 437, 445 (1930).

[2] Schmieschek: Dissertation, Berlin, 1927.

[3] Leipunski: Z. physik. Chem., B 1, 369 (1928).

will go on with the disappearance of oxygen until the partial pressure of the oxygen in the vessel has fallen to the dissociation pressure of the oxide at the temperature of the wall, viz., about 5×10^{-19} mm. at 18°. In the presence of the catalyst, therefore, the reaction proceeds practically to completion.

Okayama[1] has attempted to find out if this decrease in pressure is due to the formation of mercuric oxide alone, or if there are other side reactions, such as the formation of ozone or of platinum oxide which may utilize part of the oxygen. He finds that on passing oxygen over heated platinum in the absence of mercury no ozone is formed. That platinum oxide is formed is shown by the gradual brownish coloration of the glass wall of the reaction vessel. Upon admitting oxygen the brown film becomes black and crystalline. The speed of formation of the platinum oxide was found to be so small in comparison with that of the mercuric oxide that its rôle in the removal of oxygen is negligible. Okayama states that while an increase in the mercury vapor pressure of 40-fold only causes an increase of 10 to 15 percent in the reaction speed, the influence of oxygen is considerable. This is directly contrary to the findings of Leipunsky. Okayama also finds that the reaction speed is independent of the pressure of the mercury vapor, but it follows the oxygen pressure according to the relation:

$$\frac{\Delta n}{\Delta z} = \frac{\sqrt{p}}{a + b\sqrt{p}},$$

where $\Delta n/\Delta z$ is the number of molecules of dissociated oxygen per sq. cm. of platinum surface.

It has been found[2] that the oxidation of ammonia to nitric acid is catalyzed best by those substances which emit radiation of the same wave lengths as those corresponding with the energy required for the dissociation of molecular to atomic nitrogen and oxygen. Calcium and silicon satisfy these requirements for oxygen; tin for nitrogen. A catalyst having the molecular composition 2.7 SnO_2, 2.7 CaO and 1 SiO_2 gives 81.5 to 86.2 percent of nitric acid from a seven per cent ammonia-air mixture. The efficiency of the catalyst at various temperatures is found to be closely related to the intensity of the radiation of the catalyst at the given temperature.

In so far as the reaction has distinctly begun, the catalytic oxidation of ammonia involves the disappearance of ammonia and the formation of nitric oxide and nitrogen in varying proportions, depending on experimental conditions. While the formation of intermediate labile compounds leading to nitrogen oxides or free nitrogen has always been assumed, opinions vary as to the nature of the intermediate compound. Some[3] assume the intermediate compound to be nitroxyl, HNO. Others[4] hold to the view that the oxidation of ammonia proceeds through the intermediate formation of the imid.

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[1] Okayama: Z. physik. Chem., B 6, 355 (1930).

[2] Andadurov and Weinschenker: Ukrain. Chem. J., 5, 1 (1930); see Brit. Chem. Abs., A, 1930, 1132.

[3] Andrussov: Z. angew. Chem., 39, 321 (1926); 40, 166 (1927); 41, 205, 262 (1928); Ber., 59, 458 (1926); 60, 536, 2005 (1927); Bodenstein: Z. angew. Chem., 40, 174 (1927).

[4] Raschig: Z. angew. Chem., 40, 1183 (1927); 41, 207 (1928); Hofmann: Ber., 50, 204 (1926); 60, 1190 (1927); 62, 2509, 3000 (1929); Neumann and Manke: Z. Elektrochemie, 35, 751 (1929).

Catalysts containing manganese have been found to be excellent catalysts for the oxidation of ammonia, since they bring about the oxidation at much lower temperatures. Employing mixed catalysts of MnO_2 and Bi_2O_3 at 300°, Nagel[1] was able to transform 90 percent of the ammonia used to nitrous oxide. He finds that catalysts capable of oxidizing ammonia at temperatures under about 500° yield nitrous oxide chiefly. Between 500° and 1000° nitric oxide and the higher oxides of nitrogen are formed, while at still higher temperatures nitrogen is the chief product. From the results obtained he assumes with Bodenstein that HNO is the intermediate compound. This decomposes at low temperatures to N_2O and water; at higher temperatures, however, it is oxidized to HNO_3 and NO. The formation of the free nitrogen is ascribed to a reaction between HNO and undecomposed ammonia.

Previous experiments[2] have shown that there is an upper limiting pressure above which the oxidation of phosphine proceeds with negligible slowness even in the absence of moisture, but below which explosion does occur. Working with perfectly dry gases, Dalton[3] finds that with oxygen in large excess the mixture does not explode until expanded to very low pressures. The pressures at which explosion occurs become rapidly greater with increase in the proportion of phosphine until the ratio of the two gases becomes unity, where the oxygen pressure begins to change more slowly and beyond this point becomes nearly constant. No explosion occurs at any pressure when the PH_3/O_2 ratio is below 0.1. The explosion pressure is found to be independent of the tube diameter and of the nature of its walls, but it is decreased by the admission of inert gases. These facts tend to show that the upper limit is subject to conditions quite different from those prevailing at the lower limit. Dalton assumes that the reaction occurs through a simple chain mechanism in which the deactivation of the chains is brought about by three-body collisions in the gas.

Syntheses

It has been shown by Dodge[4] that in the several attempts to calculate the free energy change involved in the synthesis of methanol all of the calculated free energy changes lead to values of $Kp = \left(\frac{P_{CH_3OH}}{P_{CO} \times P^2_{H_2}}\right)$ which do not agree at all with the published experimental results. Apart from the direct experimental method of determining the methanol equilibrium, some investigators have employed the Nernst approximation formula to calculate K_p. The results obtained are in fair agreement with the results on high pressure synthesis. Because of the unsound theoretical basis and its complete failure in many well-established equilibria, however, Dodge regards the agreement obtained as entirely accidental. This indirect method involves no equilibrium measurements, but does involve a knowledge of heat content, free energy

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[1] Nagel: Z. Elektrochemie, 36, 754 (1930).

[2] Hinshelwood and Dalton: Proc. Roy. Soc., 125A, 294 (1930).

[3] Dalton: Proc. Roy. Soc., 123A, 263 (1929).

[4] Dodge: Ind. Eng. Chem., 22, 89 (1930).

and entropy data for a series of reactions. The value of ΔF sought is the result of a difference of several much larger quantities, ΔH. A small percentage error in some of the larger values of ΔH is sufficient to make a considerable error in the calculated value of ΔF, much greater, in fact, than would the same error in the value of the absolute entropies. According to Dodge, the calculation of the free energy change for the methanol-synthesis reaction is far more dependent upon exact data for the various heats of reaction involved than upon entropy data. In support of his contention he states that an error of 0.1 percent in the heat of combustion of methanol will lead to an error of approximately 33 percent in the value of K_p for the reaction at 298.1°K.

It has been shown by Smith and Hirst[1] that carbon dioxide and hydrogen in the presence of a zinc oxide-chromium oxide catalyst at 304° react to form methanol, carbon monoxide and water. Likewise, carbon monoxide and water react to form carbon dioxide and hydrogen, and the equilibrium can be closely approached in the water gas reaction. However, owing to the fact that several reactions may occur through the action of this catalyst upon hydrogen-water-carbon dioxide mixtures at 304°, they did not find it possible to determine which reaction comes nearest to equilibrium. The suggestion is intimated that the formation of methanol from carbon monoxide and hydrogen may not be a direct process.

Wettberg and Dodge[2] have also studied the methanol equilibrium over a zinc chromite catalyst at 170° at 170 atmospheres and through the temperature range from 260° to 310°. A dynamic method was used and the equilibrium was approached from both sides. Their new data, however, differ considerably from results obtained by theoretical methods. The possibility of side reactions and the effect of these on the establishment of the methanol equilibrium is found to be difficult to estimate. It is obvious, so they state, that a true equilibrium cannot be established with respect to the methanol equilibrium when side reactions are proceeding simultaneously at a considerable distance from the equilibrium.

Lacy, Dunning and Storch[3] have determined the equilibrium constants for the reaction $2H_2 + CO = CH_3OH$ by approach from both sides at 250° and 300°, and also from the synthesis side at 200°. In all experiments the pressure was 50 atms. In this they employed a supported reduced catalyst consisting of copper, uranium and thorium. The average constants, $K_p = \frac{(p_{CH_3OH})}{(p_{CO})(p^2_{H_2})}$ at 250° and 300° are 0.00125 and 0.00019, respectively. They also calculated the equilibrium constants from measurements of equilibria in the two reactions.

$$2\,H_2 + HCOOCH_3 = 2\,CH_3OH, \text{ and}$$
$$CH_3OH + CO = HCOOCH_3.$$

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[1] Smith and Hirst: Ind. Eng. Chem., 22, 1037 (1930).

[2] Wettberg and Dodge: Ind. Eng. Chem., 22, 1040 (1930).

[3] Lacy, Dunning and Storch: J. Am. Chem. Soc., 52, 926 (1930).

Although both sets of constants are of the same order of magnitude, the lowest figures obtained by calculations based on the use of specific heat data and the estimated entropies of hydrogen and oxygen are about 10 to 50 times as large as those obtained experimentally. The data obtained at 300° and 50 atms. agrees very well with those obtained at 70 atms. by Newitt, Byrne and Strong,[1] but are only about 0.3 the value of those obtained by Smith and Branting[2] at atmospheric pressure.

Zinc oxide obtained from the basic zinc carbonate at temperatures below 350° is an active catalyst for the synthesis of methanol[3] from carbon monoxide and hydrogen. It soon loses its activity, however, when used alone unless promoted by certain other oxides. Of these Al_2O_3 and Cr_2O_3 by acting as protective colloids prevent the crystallization of the zinc oxide with its consequent loss of activity. Both of these oxides when heated above 500° begin to form spinels and, therefore, lose some of their protective influence. Oxides of the bivalent metals, (Mg, Ni, Cu, Co, Mn and Fe), having ionic diameters between 0.6 and 0.9 Å.U by entering into its lattice form solid solutions with the zinc oxide. The oxides of copper and nickel are reduced to metal, the former aiding, the latter hindering the catalysis. Natta finds that of the oxides entering the lattice structure those are most effective which cause the greatest deformation of the zinc oxide lattice. FeO is the most effective catalyst of this class.

Mixed catalysts containing iron, nickel or cobalt with molybdenum have been found to be especially active catalysts in the synthesis of ammonia. Nickel itself is a very poor catalyst, yielding less than 0.05 percent of ammonia. The activity of the mixed catalyst increases almost proportionally with the molybdenum content of the mixed catalyst, attaining a maximum activity at 70 percent of molybdenum. With higher molybdenum contents the activity again diminishes. Contacts rich in nickel are found to show a decided decrease in activity after 24 hours. Those having less than 62 percent of nickel become inactive in three weeks, while those containing a larger percent exhibit a permanent activity. Keunecke[4] finds at the beginning of the experiment that, with progressive reduction of the oxide accompanied by a simultaneous rise in catalytic activity, the contact mass takes up nitrogen. At the moment of greatest activity the amount of nitrogen taken up is nearly proportional to the molybdenum content of the catalyst. For long experimental periods the nitrogen content again decreased and after three weeks it is completely absent for all catalysts containing less than 62 percent of molybdenum. X-ray and magnetometric investigations of the used catalysts showed the presence of nickel-molybdenum mixed crystals and a nickel-molybdenum compound. Both are formed during the catalytic process and both are catalytically inactive. Contacts containing less than 30 percent of molybdenum and which at the beginning contain only nickel and molybdenum

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[1] Newitt, Byrne and Strong: Proc. Roy. Soc., **123A**, 236 (1929).

[2] Smith and Branting: J. Am. Chem. Soc., **51**, 129 (1929).

[3] Natta: Giorn. chim. ind. e applicata, **12**, 13 (1930).

[4] Keunecke: Z. Elektrochemie, **36**, 690 (1930).

nitride will at the end of the catalytic process show mixed crystals. A contact containing 62 percent will yield the nickel-molybdenum compound. Contacts with more than 62 percent give a mixture of the compound and permanent molybdenum nitride, and only these have permanent catalytic activity. Keunecke concludes that molybdenum nitride is the active constituent of the catalyst and that this is promoted by the compound, Ni · Mo.

Almquist and Black[1] first studied the poisoning action of water vapor and oxygen on pure and promoted iron ammonia catalysts. They found that appreciable amounts of oxygen are retained by the catalyst after the passage of 3:1 hydrogen-nitrogen mixtures, containing 0.016 percent or more of water vapor, over the catalysts at 444°. Additions of oxygen decrease the concentration of the ammonia produced to a constant value. The final ammonia concentration is lower, the higher the oxygen concentration and for equal concentrations of oxygen is lower for the less active catalyst. The poisoning action is accompanied by the formation of some oxide of iron, and the quantity of this formed is larger for the more active promoted catalysts. Since massive iron is not oxidized at this temperature,[2] Almquist[3] concludes that the catalyst takes up the oxygen in the form of a surface oxide, due to the interaction between the water vapor and the surface iron atoms possessing a high degree of unsaturation. Assuming that the active atoms taking part in the surface oxide formation are also responsible for the ammonia synthesis, and that the combination of active iron atoms and oxygen atoms occurs in the ratio 1:1, he calculated that in the pure iron catalyst approximately one atom out of every 2000 is active toward the ammonia synthesis, whereas in iron catalysts promoted by aluminum one atom out of every 200 is active.

Emmett and Brunauer[4] have extended these experiments to higher pressures. Their results show: "(1) The amount of oxygen taken up is approximately proportional to the ratio $\sqrt{P_{H_2O}}/\sqrt{P_{H_2}}$ throughout the range of P_{H_2O} and P_{H_2} values employed. (2) At high pressures promoted synthetic ammonia catalysts take up much more oxygen than do pure iron catalysts. (3) The oxygen content of the catalyst is present as oxide and not as adsorbed water molecules." That the oxide formed on the promoted iron catalysts is due to the formation of a surface oxide only and not to the formation of a solid solution is substantiated by two facts, namely, the rate of formation and removal of a large part of the surface oxide is very rapid, and the amount of oxide formed in the case of the promoted catalysts is ten times greater than for the pure iron catalysts. Except for a slight permanent injury, the poisoning of both doubly and singly promoted iron catalysts by water vapor is almost completely reversible. They suggest that the mechanism of the ammonia synthesis may consist in the reduction by hydrogen of the surface nitride, Fe_4N, formed by the reaction between the nitrogen molecules and the surface active iron atoms.

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[1] Almquist and Black: J. Am. Chem. Soc., 48, 2814 (1926).

[2] Evans and Eastman: J. Am. Chem. Soc., 46, 896 (1924).

[3] Almquist: J. Am. Chem. Soc., 48, 2820 (1926).

[4] Emmett and Brunauer: J. Am. Chem. Soc., 52, 2682 (1930).

Mixtures of an alcohol and ammonia or a primary amine when passed over heated nickel, or heated with nickel under pressure at 150° to 200° give almost theoretical yields of the corresponding primary or secondary amines.[1] Cyclohexanol and ammonia at 150° give cyclohexylamine, while dicyclohexylamine is exclusively formed at 190°. Guyot and Fournier believe that the mechanism of the reaction can be represented by three successive stages, namely

$$\text{(a)}\ RCH_2OH = RCHO + H_2,$$
$$\text{(b)}\ RCHO + R'NH_2 = RCH{:}NR + H_2O,$$
$$\text{(c)}\ RCH{:}NR' + H_2 = RCH_2NHR'.$$

Ethanol is dehydrogenated to aldehyde when passed over zinc oxide or zinc chromite at 300° to 400°. Practically no aldehyde is produced, however, if the reaction takes place under a sufficiently high hydrogen pressure; instead of aldehyde, substances of higher molecular weight are formed. Adkins, Kinsey and Folkers[2] have studied the aldehyde condensation reactions over zinc chromite and zinc oxide catalysts at pressures up to 500 atmospheres. In the passage of ethanol over zinc chromite under a pressure of 500 atmospheres several products are formed; among these are liquid ethyl acetate, n-butanol and a liquid boiling above 125°, but only traces of aldehyde. Upon replacing a part of the ethanol by aldehyde they found that the condensation products obtained in a given time to be greater in amount than if the reaction were dependent upon the aldehyde produced by dehydrogenation. The products obtained under high pressures from ethanol and aldehyde over zinc chromite at 360° was so complicated a mixture that fractional separation into its components was impossible. The product was, therefore, subjected to various forms of chemical treatment. The lowest fraction from the chromite catalyst contained aldehydes, alcohols, esters and water; that from the higher fractions contained alcohols, esters, and ethers, but no appreciable amounts of aldehyde, ketones or glycols. The alcohols and esters were both saturated and unsaturated in type. The nature of the products obtained indicate the occurrence of various reactions, namely, dehydrogenation, hydrogenation, dehydration, oxidation and aldol-like condensations. A summary of the reactions through which the simpler compounds may be formed is given below.

$$CH_3CH_2OH = CH_3CHO + H_2 \tag{1}$$
$$CH_3CHO + CH_3CHO = CH_3CO_2C_2H_5 \tag{2}$$
$$CH_3CHO + CH_3CHO = CH_3CHOHCH_2CHO \tag{3}$$
$$CH_3CHOHCH_2CHO = CH_3CH{=}CHCHO + H_2O \tag{4}$$
$$CH_3CHO + CH_3CHO = CH_3CH{=}CHCHO + H_2O \tag{5}$$
$$CH_3CH{=}CHCHO + CH_3CH_2OH = CH_3CH_2CH_2CHO + CH_3CHO \tag{6}$$
$$CH_3CH_2CH_2CHO + H_2 = CH_3CH_2CH_2OH \tag{7}$$
$$CH_3CH{=}CHCHO + H_2 = CH_3CH{=}CHCH_2OH \tag{8}$$
$$CH_3CH{=}CHCHO + H_2 = CH_3CH_2CH_2CHO \tag{9}$$

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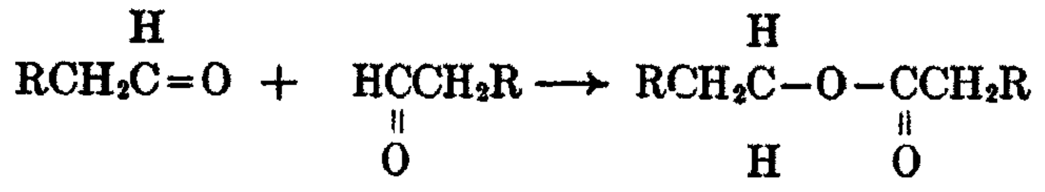
[1] Guyot and Fournier: Compt. rend., **189**, 927 (1929); Bull., (4) **47**, 203 (1930).

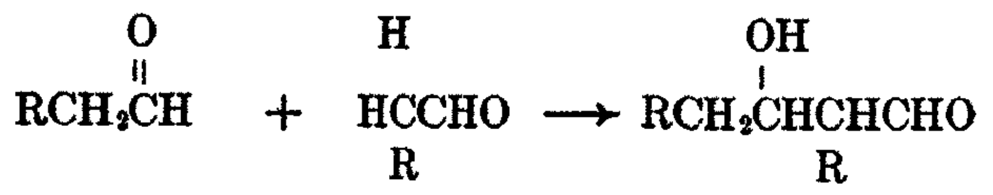
[2] Adkins, Kinsey and Folkers: Ind. Eng. Chem., **22**, 1048 (1930).

$CH_3CH_2CH_2CHO + CH_3CHO = CH_3CH_2CH_2CH{=}CHCHO$ (10)
$CH_3CHO + CH_3CH_2CH_2CHO = CH_3CH{=}C(C_2H_5)CHO$ (11)
$2\ CH_3CH{=}CHCHO = CH_3CH{=}CHCO_2CH_2CH{=}CHCH_3$ (12)
$2\ CH_3CH_2CH_2CHO = C_3H_7CO_2C_4H_9$ (13)
$C_3H_7CO_2C_4H_9 + C_2H_5OH = C_3H_7CO_2C_2H_5 + C_4H_9OH$ (14)
$2\ C_4H_9OH = C_4H_9OC_4H_9 + H_2O$ (15)
$2\ C_5H_{11}CHO = C_6H_{11}CO_2C_6H_{13}$ (16)

Among these two types of reactions are to be observed. The first involves the simple dehydrogenation of an alcohol, or the reverse reaction of adding hydrogen to an aldehyde, ketone or unsaturated compound. The second type of reactions occurring on oxide catalysts are those that involve an increase in the number of carbon atoms per molecule. According to Adkins and his co-workers, it appears more than probable that the synthesis of substances of higher molecular weight from ethanol or aldehyde is dependent upon two reactions both involving the addition to each other of two molecules containing carbonyl groups—that is,



$$\mathrm{RCH_2\overset{H}{C}{=}O} + \mathrm{H\underset{\underset{O}{\|}}{C}CH_2R} \longrightarrow \mathrm{RCH_2\overset{H}{\underset{H}{C}}{-}O{-}\underset{\underset{O}{\|}}{C}CH_2R} \qquad (1)$$



$$\mathrm{RCH_2\overset{\overset{O}{\|}}{C}H} + \mathrm{H\overset{H}{\underset{R}{C}}CHO} \longrightarrow \mathrm{RCH_2\overset{\overset{OH}{|}}{C}H\underset{R}{C}HCHO} \qquad (2)$$

"Direct evidence is lacking that the compounds containing chains longer than two carbon atoms are dependent upon the aldol reaction (reactions 3, 5, 10, 11). However, the nature of the products is such as to make it seem reasonable that the synthesis of the higher alcohols and esters is dependent upon the reaction. Whether aldols are actually formed and then dehydrated (reactions 3 and 4) or whether the condensation takes place with the simultaneous elimination of a molecule of water and the formation of an unsaturated aldehyde (5) is questionable. In no case has any glycol been found in the distilled reaction products, which is against the first assumption. Moreover, the catalyst is not active for dehydration of alcohols. A direct reaction, as in (5), seems more reasonable."

Manganese chromite and copper chromite behave similarly. The latter leaves almost no aldehyde in the reaction product, and produces about two and a half times as much of the esters of ethyl and butyl alcohols.

Decomposition

Although the equilibrium concentration of CCl_4 as calculated from its heat of formation (2543 cal.) is considerable, Bodenstein, Günther and Hoffmeister[1] were not able to synthesize it from its elements. Attempts to reach the equilibrium by the decomposition of CCl_4 showed that decompo-

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[1] Bodenstein, Günther and Hoffmeister: Z. angew. Chem., 39, 875 (1926).

sition is possible, but the reaction stops long before the calculated equilibrium was reached. Only 4% was actually decomposed at 400°, whereas according to the Nernst approximation formula 48% should be decomposed. Bodenstein and Günther[1] have passed CCl_4 in a very slow stream over activated charcoal in a quartz tube at 400° to 500°. They find that the decomposition approximates equilibrium at high temperatures without reaching it. Their observations clearly show that the reaction stops before equilibrium is reached and this deviation is greater the lower the temperature of the decomposition. The reaction is stopped by a poisoning of the catalyst which, they explain, may be due to a superficial film of carbon from the decomposition of the CCl_4, or by the adsorption of Cl_2 and CCl_4 which diminishes with rise in temperature. It is interesting to note that the density of C from the decomposition of CCl_4 ranges from 2.3 to 2.5,[2] whereas the density of ordinary amorphous carbon is 1.8.

Bahr and Jessen[3] find that while finely divided metallic cobalt does not decompose CO at 225°, the dissociation does take place on cobalt containing 9.24 percent of Co_2C. At temperatures above 225° the carbide gives free carbon. No carbide prepared from the dissociation of carbon monoxide on finely divided cobalt was found to give up its carbide carbon on treatment with hydrogen at temperatures as low as 240° to 250°. However, carbide formed from the free elements does form methane on heating with hydrogen above 400°.

In recent years the chemists of Japan have made extended applications of the use of a Japanese acid clay in many catalytic processes. Kashima[4] has studied the decomposition of ethyl, n-propyl, n-butyl, n-amyl and ethyl-n-butyl ethers over activated Japanese clay at temperatures between 200° and 400°. The chief decomposition products of the ethers are olefins, alcohols and water. There is formed also small amounts of aldehyde, gaseous products (CO_2, CO, O_2, H_2), and sometimes ester and a species of a petroleum hydrocarbon. A very slight amount of carbon is deposited upon the catalyst. That olefins and water are formed by the reaction:

$$(R \cdot CH_2 \cdot CH_2)_2O = 2\,R \cdot CH{:}CH_2 + H_2O, \qquad (1)$$

is confirmed by the fact that at temperatures above 300° the ratios of olefin to water are almost constant (2:1). Further, the yields of olefines from ethers are always greater than those from the corresponding alcohols. Kashima assumes that the alcohols produced in the decomposition of ethers may very probably arise through the reaction:

$$(R \cdot CH_2 \cdot CH_2)_2O = R \cdot CH{:}CH_2 + R \cdot CH_2 \cdot CH_2OH. \qquad (2)$$

The decomposition of ethyl-butyl ether gives rise to a mixture of ethylene, butylene, ethanol, butanol and water. Since the amounts of butylene and ethanol are larger than those of ethylene and butanol, the affinity between

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[1] Bodenstein and Günther: Z. angew. Chem., **43**, 423 (1930).

[2] Tammann: Z. angew. Chem., **115**, 145 (1921).

[3] Bahr and Jessen: Ber., **63B**, 2226 (1930).

[4] Kashima: Bull. Chem. Soc. Japan, **5**, 25 (1930).

the butyl group and oxygen must be less than that between the ethylene group and oxygen. At low temperatures (200°-250°) the ethers yield the corresponding alcohols, the amount of alcohol decreasing with rise in temperature. The ethylene yield, on the contrary, increases with rise in temperature and practically dominates the reaction above 300°. In general, the double bond of the olefin is formed on the carbon atom previously attached to the oxygen. With butyl ether, however, the butylene produced is found to be a mixture of the α and β isomers, with the latter in excess. The migration of the double bond through the action of the clay leads to the formation of the most stable isomer.

Ethylene, acetylene, propylene and trimethylene are unstable in the presence of copper or nickel at 200°. Acetylene spontaneously decomposes under these conditions, depositing carbon and forming various aromatic products and cuprene.[1] Mixtures of naphthalene with ethylene or acetylene, and of benzene with either of these two gases show no decomposition in the presence of nickel at 200°. The stability of the ethylene and the acetylene appeared to be due to dilution with benzene or naphthalene. When however, phenylethylene was passed over nickel, not the slightest decomposition was observed at 350°, it became apparent that the stability of the unsaturated linkages might be attributed to the influence of contiguous groups.

Goswana[2] has attempted to determine the influence of the contiguous groups attached to unsaturated linkages when the vapors of the compounds are passed over nickel at 350°. Phenyl-acetylene, sym-diphenylethylene and ethyl cinnamate do not decompose. Eugenol is only partially transformed to isoeugenol. While ethyl cinnamate, with its $CH=CH$ group attached to the phenyl and carbethoxy radicals, does not suffer decomposition, the case is very different with cinnamic acid, alcohol and aldehyde. Cinnamic acid decomposes in several steps:

$$\begin{aligned}
C_6H_5CH{:}CHCOOH &= C_6H_5CH{:}CH_2 + CO_2 \\
C_6H_5CH{:}CHCOOH &= C_6H_6 + CH\equiv CH + CO_2 \\
C_6H_5CH{:}COOH &= C_6H_5C\equiv CH + H_2O + CO_2 \\
C_6H_5CH{:}CH_2 + C_6H_6 &= C_6H_5CH{:}CHC_6H_5 + H_2 \\
CH{:}CH &= C + H_2 \\
4\ H_2 + CO_2 &= CH_4 + 2\ H_2O.
\end{aligned}$$

At 350° the alcohol and aldehyde yield phenylethylene:

$$\begin{aligned}
C_6H_5CH{:}CHCH_2OH &= C_6H_5CH{:}CH_2 + HCHO \\
C_6H_5CH{:}CHCHO &= C_6H_5CH{:}CH_2.
\end{aligned}$$

Their results show that the phenyl and the carbethoxy groups have a stabilizing influence on unsaturated linkages. Whereas the COOH, CHO and CH_2OH groups do not protect the unsaturated portions. It is interesting to note in this respect that the enolic ethyl-acetoacetate decomposes to acetone,

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[1] Sabatier and Senderens: Bull., **21**, 530 (1899); Compt. rend., **130**, 250 (1900); **134**, 1127 (1902).

[2] Goswana: J. Indian Chem. Soc., **7**, 647 (1930).

carbon dioxide and ethylene. Although one stabilizing carbethoxy group is present, the hydroxyl group renders the molecule unstable and it decomposes.

When heated with thoria at 400°, diethylacetal decomposes[1] giving 22 percent of acetaldehyde, 13 percent of ethyl vinyl ether, 30 percent of alcohol, 3 percent of water, a gas containing 30 percent of ethylene, 42 percent of hydrogen, 6 percent of carbon monoxide, 14 percent of carbon dioxide and 8 percent of methane. The corresponding methyl, propyl, butyl, isobutyl and isoamyl acetals over thoria decompose in a similar manner. While alumina, blue tungstic oxide and manganous oxide give similar results, the yield of the vinyl alkyl ether is smaller. Alumina and tungstic oxide give a gas containing about 95 percent of ethylene; with manganous oxide the gas contains 52 percent of hydrogen.

According to the resonance theory, catalysts with wave-lengths of 4114-2576 Å induce the dissociation of $CaSO_4$ to CaO and SO_3; those with wave-lengths of 2576-1546 Å cause dissociation to SO_3, SO_2 and O_2, while those with wave-lengths less than 1545 Å give rise to SO_2 and O_2, particularly at high temperature. Experiments[2] made with a large number of salts as catalysts confirm this theory. By using MnO_2 at 600° the yield of SO_3 can be increased from 0.18 to 25.85 percent, while the yield of SO_2 is kept as low as 54 percent. When the wave-lengths characteristic of an element and of the catalyzed substance are the same it is a sure indication that the element is a catalyst. The catalytic activity decreases with increase in wave-length. Each wave-length has a definite minimum temperature at which it begins to show its activity, and each must possess sufficient energy to decompose the molecule. It is, therefore, possible to calculate beforehand not only the direction of a reaction and its character, but also the catalyst to be used and the approximate temperature conditions.

The nature of the starting material and the temperature of reduction has been found[3] to influence considerably the catalytic activity of cobalt in the decomposition of formic acid to hydrogen and carbon monoxide. The effect of temperature is not very noticeable between 200° and 300°. The activity is greatly reduced, however, when the reducing temperature is raised to 1000°, and especially so, when raised to 1200°. The activity of hydrated cobalt oxides reduced at 300°-500° is higher than for the non-hydrated oxides reduced at these temperatures.

Ruiz[4] finds that the speed of decomposition of hydrogen peroxide in the presence of a platinum foil is inversely proportional to its potential. Previous heating in an oxy-hydrogen flame decreases the potential below the normal. The glowing of the foil thus permits its use at higher current densities without the formation of platinum oxides which exert a deactivating influence. Poisoning of the foil by CS_2 or KCN also alters the potential. Platinum exhibits its maximum catalytic influence in solutions whose pH lies between 12.2 and 12.7.

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[1] Mlle. M. Cabanac: Compt. rend., **190**, 881 (1930).

[2] Adadurov, Deribas and Kraini: Zhuri. Prikladnoi Khim., **3**, 509 (1930).

[3] Hüttig and Kassler: Z. anorg. allgem. Chem., **187**, 24 (1930).

[4] Ruiz, Z. Elektrochemie, **36**, 149 (1930).

THE COLLOID CHEMISTRY OF THE NERVOUS SYSTEMS. V[1]

BY WILDER D. BANCROFT, ROBERT S. GUTSELL,[2] AND JOHN E. RUTZLER, JR.[3]

> *"My first proposition, therefore, amounts to this—that the process of weaning one's-self from the deep bondage of opium, by many people viewed with despairing eyes, is not only a possible achievement, and one that grows easier in every stage of its progress, but is favored and promoted by nature in secret ways that could not, without some experience, have been suspected."*
>
> Thomas DeQuincy: "Confessions of an Opium Eater."

The cure for morphinism and other habit-forming drugs requires a well-blended knowledge of medicine, logic, psychiatry, chemistry, pharmacology, sociology, and physiology. It is not an undertaking in which one man alone can hope reasonably for success; the by-ways are far too numerous, and the main path is too obscure. It is only by clinging tenaciously to a definite idea, and constantly viewing that idea with a fresh perspective that any measure of reward has been obtained. Toil and tribulation never must cloud the road to the goal, no matter how rough it may be.

Up to the present time no one has devised a practical cure for morphinism based upon sound, scientific premises that has come into general use. That is because there has not been a generally accepted rationale for the action of morphine on living tissue. Even today the fact that morphine is both a stimulant and a depressant[4] bewilders some good pharmacologists;[5] because depression and stimulation have come through usage to have opposite meanings. The lack of a clear understanding of how a drug can be both a stimulant and a depressant has befogged the issue in the study of drug addiction; although it is by no means the sole reason why an eminently successful treatment has not been evolved. The purpose of this paper is to elucidate the most useful theory of drug addiction and to show that it both accounts for the facts of drug addiction and provides a rationale for the treatment of morphinism. Cases will be presented to uphold the theoretical considerations and demonstrate the validity of the theory.

There are several theories of drug addiction that are defended by various authors. Tatum and Seevers[6] recently outlined most of them in a paper on morphinism. McGuigan and Ross,[7] and Loofs[8] believe that the drug is

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[1] This work is done under the programme now being carried out at Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[2] M.D.

[3] Eli Lilly Research Fellow.

[4] Sollmann: "A Manual of Pharmacology," 217 (1917).

[5] Barbour, Gregg, and Hunter: J. Pharm. Exp. Therap., 40, 433 (1930).

[6] Physiol. Review, 11, 108 (1931).

[7] J. Am. Med. Assoc., 64, 1494 (1915).

[8] Z. ges. Neurol. Psychiat., 79, 433 (1922).

destroyed rapidly or inactivated by combination, thus giving the addict tolerance. It appears to be true that the addict has developed an increased power to destroy morphine.[1] The views of McGuigan and Ross are based upon their observation that morphine sensitizes animals to strychnine if time is allowed to elapse between the two injections, and that oxidized morphine tetanizes more rapidly than morphine. They explain the usual absence of tetanus in animals by assuming that the tetanizing substance is destroyed rapidly. This explanation accounts only for the tolerance that is developed to morphine; it does not provide a useful working hypothesis. Even with the increased power of destruction of the drug the blood of the animal contains enough morphine to be toxic to normal animals.[2] This supposed increased power of destruction of morphine will be explained on a colloidal basis. Finally, it neglects entirely the phenomenon of abstinence symptoms during which there is a mild form of tetanus. DuMez[3] says: "It has not been proved that the destruction of morphine in the organism, if it does take place to an increased degree, is a causative factor in the production of tolerance." A theory that is really usable will account for all of the facts that are observed.

Hirschlaff[4] and others have proposed the theory that anti-bodies form after the pattern proposed by Ehrlich for proteins. These immune bodies make the cells respond to the absence of morphine and protect the cells from its action. These results generally have not been substantiated.[5] Furthermore, we do not know of any case in which a substance, not in colloidal suspension, produces antibodies in the living organism. This theory thus can be discarded *per se.*

Light[6] considers that the state of addiction is essentially one of imagination or wilful manifestations which are conjured up in order to enlist sympathy or to obtain more of the drug. This author believes drug addiction to be other than somatic in nature. This automatically throws the whole thing into the realm of the psychic which is erroneously considered to be apart from the brain. A complete enigma thereby is made of drug addiction. This theory is tantamount to the admission that nothing is known of drug addiction; and it bears the marks of an effort not to face the facts.

One does not imagine one's-self into a condition of complete collapse, and even death, which may be brought about by the abrupt withdrawal of morphine.[7] So, while drug addiction and withdrawal are accompanied unquestionably by many psychotic manifestations of varying degrees of severity, there is a physical basis for the whole thing that must be faced and worked out. No amount of evangelism can evade the fact that drug addiction is a disease. Sollmann[1] says: "To the physician he [the drug addict] should appeal as a

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[1] Takayanagi: Archiv exp. Path. Pharm., **102,** 176 (1924).

[2] Wells: "The Chemical Aspects of Immunity," 270 (1929).

[3] J. Am. Med. Assoc., **72,** 1069 (1919).

[4] Berlin Klin. Wochenschr., **1902,** 1149, 1177.

[5] Pellini and Greenfield: Archiv. Int. Med., **26,** 279 (1920); **33,** 547 (1924).

[6] "Opium Addiction." Published by the American Medical Association (1929).

[7] Lambert et al: Am. J. Psychiatry, **10,** 433 (1930).

sufferer, as afflicted by a form of insanity; one who, like any other insane patient, should be treated with unflinching firmness, but with the most considerate kindness." Mr. Koepfgen of the Narcotic Educational Association of Michigan, says:

"Had the organizers of this association been willing to accept the consensus of public opinion, including governmental and medical science's findings, it is doubtful if any program of relief would have been entered into. Addicts have been catalogued as social misfits and outcasts, as hereditary mental cripples, and it is generally accepted as a fact that if they were not addicts they would occupy some other anti-social sphere. They are considered degenerates, and as leeches upon the whole social structure, sucking the life blood at every opportunity from the social, moral, and economic life. Incurable social lepers, debauched by their own viciousness.

"Society's attitude toward its addict population is reflected and magnified by the addicts' attitude toward society, an attitude equally as destructive, but founded perhaps on more reliable and understandable premises, than those of society toward the addict. We find the addict readily admitting to himself and not seldom to others, that he is a physical, mental, and spiritual wreck; admitting stealing, lying, cheating, and, if occasion demands it, being a major criminal. He is not, however, ready to agree with society that he was 'born that way.' In many, many instances, he realizes that he came from as good stock and as fine a home environment as those who condemn him. He lays claim to having possessed at one time the same physical and mental attributes as his condemners; of having had the same loves, hates, desires, ambitions and aspirations as his scorners. One thing he is sure of is that without his drug he will be sick—physically sick—with an intensity that puts to shame man's ordinary whinings over usual ailments. Let society call it a vile habit if they care to, he knows that if it is a habit it is the only habit known that causes not only mental anguish, but real physical, excruciating pain. His is the paradox of seeing organized society planning and building and caring for other sick members of society, regardless of whether or not the patient contracted his disease legitimately or illegitimately, and almost completely ignoring its addict population; extending their sympathy and charity to its animal kingdom, and yet saying to its human addict population 'So you are sick are you? Well, lie down and die and prove it, but provide your own proving ground.' If, sometimes, they do just that, it isn't too bad for the addict, it is just a blessing to society.

"The addict lives each day and dreams each night just one thing—fear. Fear, first and paramount, that he will be unable to obtain his drug to allay his illness; fear that he will be caught stealing; fear that he will be found with his medicine in his possession; and fear of the police, his associates and of himself. Society has pronounced addicts incurables and has turned the problem over to the police departments for solution; substituting a prison cell for a hospital and a warden for a physician. Society looks into its mirror and smiles with satisfaction and pride at the image reflected there, and fails to recognize itself as the real culprit in this deplorable situation. A culprit guilty of thoughtlessness, carelessness and indifference.

"Many medical cures have been attempted. Nearly all of them have failed. Science recognizes it as a habit only and fails to look upon it as a disease, not only a physical disease, but as a mental, moral, and spiritual disease. Governments, likewise, have failed to look upon addiction as a disease, but only as a crime, the violation of a revenue act. The addict is punished for being sick, or actually for trying not to be sick.

"The addict is given a forced physical cure and at the same time inoculated with the germs of antisocial conduct. He has instilled into him the virus of that green eyed monster hate and misunderstanding; he is vaccinated with a Christian Code and returned to society with a straw hat and a Merry Christmas wish in the dead-of-winter months; chained to the North Pole by public opinion and prison stigma, and prevented from working his diamond mine in South Africa filled with faith, hopes, and desires and ambitions.

"When will society learn that drug addiction is a disease; when will they learn that it is impossible to cure addiction by imprisonment, locks and bars, handcuffs and clubs; that it is no more possible to kick a drug habit out of one's system than it is to kick out Bright's disease or Scarlet Fever?

"The addict has been 'tried by fire' so often that all that remains is the charred corpse of a one-time human being which should be placed on a pinnacle at the entrance of society's alabaster gates as a monument to and constant reminder of society's stupendous ignorance, listlessness, and inhuman treatment of its addict population."

The etiology of the disease is not fixed, nor yet is the etiology of neuritis, which is recognized as a disease.

The theory sponsored by Wuth,[2] Barbour,[3] and Tatum, Seevers, and Collins[4] gives us a working basis and fixes the site of the disturbance, so that some progress can be made in the study of the problem. Tatum and Seevers[5] say of this theory: "Wherein the many manifestations are referred to abnormalities of the central nervous system which may or may not be demonstrable by cytological technique, and due to the chronic state of poisoning." A more complete and detailed picture than this must be drawn in order to open a successful attack on the general problem.

Bancroft and Rutzler,[6] following Claude Bernard's theory of anesthesia proposed an explanation of drug addiction. By this theory morphine agglomerates reversibly certain of the protein colloids of the brain and central nervous system. Given this rationale the phenomena encountered in drug addiction can be explained.

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[1] "A Manual of Pharmacology," 235 (1917).

[2] Münch. Med. Wochenschr., 70, 1266 (1923).

[3] J. Pharm. Exp. Therap., 36, 251 (1929).

[4] J. Pharm. Exp. Therap., 36, 447 (1929).

[5] Physiol. Rev., 11, 108 (1931).

[6] Proc. Nat. Acad. Sci., 17, 186 (1931).

Abe[1] goes even more into detail about what happens in chronic morphinism. His ideas furnish a definite working basis for the study of drug addiction both from the theoretical and practical points of view. It seems worth while to consider the work of Abe in detail at this point. In the case of animals that exhibit the greatest natural tolerance to morphine, the tissues adsorb less morphine than the same tissues of animals that exhibit less natural tolerance. Just the reverse of this is true for the blood serum. In some animals such as the rabbit and the dog, the blood serum adsorbs less morphine than the serum of the cat. However, in these cases the tissues of the rabbit and the dog adsorb less morphine than the corresponding tissues of the cat.

If we assume that the action of morphine on the organism depends on the ratio: $\frac{\text{affinity of tissues for morphine}}{\text{affinity of serum for morphine}}$, and that the morphine that is adsorbed by the tissues is wholly responsible for the toxic effect, the smaller the coefficient the greater will be the tolerance to the drug. There are, therefore, two types of natural tolerance to morphine. The first case is that in which the serum adsorbs morphine to a large extent and the tissues adsorb only a small amount. In the other type of natural tolerance the serum adsorbs only a small amount of morphine, and the tissues only a minute quantity. Here again the ratio is small. In the first type of tolerance the ratio is smaller than in the second.

Abe goes on to explain acquired tolerance on a colloid-chemical basis. Work was done first on the adsorbing power of the tissues of various organs, and of the blood serum of animals accustomed to morphine. These results were compared with those on normal animals. It was found, in the case of the addicted dog, that divers tissues adsorbed less of the drug; at the same time the adsorbing power of the serum was greater. This is due probably to the presence of a greater concentration of morphine, under which condition the serum might well take up more morphine. In the case of the addicted rabbit, the adsorbing power of many of the tissues as well as of the blood serum was found to be lower than for the normal rabbits. He proceeds from this to distinguish two types of acquired tolerance. The first type is that of the dog, in which the ratio mentioned above is lowered because the tissues take up less and less morphine and the blood serum more and more morphine. The second type is that of the rabbit in which the amount of morphine taken up both by the tissues and the blood serum is lowered as the addiction proceeds. This type of acquired tolerance corresponds to the second type of natural tolerance; and the first type corresponds to the first type of natural tolerance.

The excised bladder, uterus, and small intestine of rabbits that were given morphine were excited when immersed in fresh Ringer's solution. The excitation is due to the washing out of adsorbed morphine; it is an effect upon the parasympathetic nerves, for the effect can be obliterated by atropine which is a paralysant for parasympathetic nerves, and also by morphine. Abe likens this excitation to the withdrawal symptons seen in human beings.

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[1] Revue d'Hygiène, 52, 356 (1930).

Barbour, Gregg and Hunter[1] say: "From smooth muscle experiments, Abe has introduced evidence that morphine stimulates *as it leaves the cells*, and thus gives rise to the withdrawal symptoms. Morphine cannot, however, be thought to stimulate only as it passes out, for the same object tests as used by Abe (smooth muscle of intestine, uterus, etc.) exhibit an immediate and persistant stimulation when morphine is first applied. The drug thus falls into Straub's class of substances which exhibit their effects either while entering or leaving the cell but never during chemical equilibrium with the cell environment. On the metabolic side this concept can be illustrated by Plant's demonstration in dogs of a wave of hyperglycemia on the initiation of withdrawal, similar to that which the initial dose of morphine induces. Again sweating in man commonly appears in both instances. Another example is the edema of the brain in rats which Flowers, Dunham and Barbour found most marked early in addiction and on the first day of withdrawal."

There is no question that the stimulating action of morphine as it enters the organism must be a part of the picture.[2] So far as "chemical equilibrium with the cell environment" is concerned, everyone knows that morphine does exert an effect when it is in equilibrium with the cell environment, though not necessarily a stimulating one.

Abe goes on to say that the intensity of the excitation produced by morphine leaving the excised organs is proportional to the rapidity with which the morphine is carried away, to the dosage of morphine that was administered, and finally to the length of time that the drug has acted on the tissues. He says: "In the same way, the gravity of the withdrawal symptoms is proportional to the rapidity with which the withdrawal takes place, to the dose used, and to the time during which the patient has been accustomed to the drug.

"The excitation produced by morphine leaving the excised organ can be completely suppressed by putting back the morphine. By administering morphine one can also make the abstinence symptoms disappear.

"The excitation produced when morphine is washed out is due to the excitation of the parasympathetic system. In the abstinence symptoms we can also observe parasympathetic symptoms (vagatonics)."

Probably it is not strictly true that the severity of the withdrawal symptoms is proportional to the amount of drug used and to the length of time it has been used. Lambert[3] says: "The amount of suffering during the withdrawal period is often an individual idiosyncrasy, but the amount of drug used, length of addiction, and physical and mental condition have some bearing. The emotionally unstable types tend to exaggerate their symptoms. The greater the amount of drug used, the longer the period of addiction, also the older the addict, the more marked is the secondary cachexia apt to be and consequently the withdrawal period can reasonably be expected to be more stormy, and the recuperation or convalescence slower. However, this does not always follow, as their statements are often misleading." Again, Plant and

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[1] J. Pharm. Exp. Therap., 40, 434 (1930).

[2] Bancroft and Richter: J. Phys. Chem., 35, 215; Bancroft and Rutzler: 1185 (1931).

[3] Am. J. Psychiatry, 10, 491 (1930).

Pierce[1] have found that there is no relation between the size of the dose, the length of time that it has been used, and the intensity of the withdrawal symptoms in dogs. In this case the psychic factor is ruled out. On the other hand, tolerance to the depressant action of morphine develops more rapidly on increasing doses of the drug than on small constant doses.[2]

After the tissues become saturated with morphine it is probable that larger doses of the drug or administration over a longer period of time will not make the withdrawal symptoms anything like proportionally worse. The factor in the case of human beings is a psychic one; they depend on morphine more and more, and fear withdrawal more as time goes on. Many people agree that there is an upper limit to the dosage of morphine that any given patient needs; this upper limit is very roughly eight grains per day. It is only natural to assume that reversible agglomeration takes place when the tissues and the serum proteins adsorb morphine. The colloids are peptized again when the morphine leaves the tissues and serum. In the case of the nervous tissue we are probably dealing with jellies, and the whole thing may well be a question of more and less bound water; the former is equivalent to peptization, and the latter to agglomeration.

Barbour[3] and his co-workers have demonstrated that the livers, kidneys, and brains of dogs addicted to morphine are dehydrated; while the blood serum tends to show hydration. Along the same line, Binz[4] observed the agglomeration produced when morphine acted upon the isolated cerebral cortex. Barbour and his co-workers have done some interesting work on brain-water movements in morphinism and anesthesia. Unfortunately no distinction is made between water which may be present due to syneresis, and water that is adsorbed by the protein colloids. The interpretation of experiments on edema must be withheld until this distinction is made. In another paper Barbour, Hunter, and Richey[5] say: "Withdrawal of morphine induces hydration of the blood and probably of the tissues in general. In view of this (and of empirical relief by saline purging and the like) the distressing symptoms of withdrawal in man appear closely related to tissue hydration."

In brief review the theory of chronic morphinism as it stands at present is that the drug goes into the blood stream, and thence to the protein colloids of the nervous systems and the blood serum; the central nervous system is apparently affected first. The ratio of morphine taken up by the tissues to morphine adsorbed by the blood serum is small. The adsorbing capacity of the serum proteins is large; and, as the concentration of morphine rises, the serum proteins adsorb more of it, thus keeping the ratio small. The proteins of the nervous system become saturated first. The morphine which is adsorbed by the protein colloids causes reversible agglomeration, or its equiva-

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[1] J. Pharm. Exp. Therap., 33, 329 (1928).

[2] Tatum, Seevers, and Collins: J. Pharm. Exp. Therap., 36, 452 (1929).

[3] Barbour et al: Am. J. Physiol., 90, No. 2, October (1929); Barbour: Science, 73, 346 (1931).

[4] Gwathmey: "Anesthesia," 34 (1914).

[5] J. Pharm. Exp. Therap., 36, 251 (1929).

lent, the loss of bound water. Above a certain concentration, different for each individual, the tissues and serum do not adsorb appreciably more morphine. There is a period of excitement corresponding to the initiation of agglomeration. Upon withdrawal, morphine leaves the tissues and blood stream slowly and peptization takes place gradually, or the equivalent, more water is bound, giving rise to excitement which is manifested by withdrawal symptoms. In the course of time the peptizing agents normally present in the body return the nervous systems to their correct degree of dispersion; and the patient recovers. Endocrine or other disturbances that either preexisted morphinism, or were brought about by it, may call forth agglomerating agents which will retard materially the return to normal.

There are roughly thirty different ways that have been used to treat drug addiction, all of which aim at amelioration of withdrawal symptoms. The after-care is generally considered to be a different problem. Lambert[1] has studied many of the methods of treatment; and has made a very complete report on the subject. Some of the methods that have been used can be considered here in some detail. It is not either useful or necessary to take up the use of magnesium sulphate (as an anesthetic), allonal, ravenin, bromides and chloral, sodium luminal, alcohol, paraldehyde, veronal, trional, and pyramidon in the treatment of drug addicts. Each of these is an agglomerating agent for the protein colloids of the nervous systems, and as such can only act in the same direction as morphine, thus making the problem harder. Sodium bromide has been given with chloral under the mistaken impression that they are both sedatives. Sodium bromide merely quiets the nerves by peptizing the colloids out of their irritable state, and allows one to go to sleep; whereas chloral hydrate puts one to sleep by agglomeration. Lambert found that none of them were of any particular benefit during the withdrawal period, as one would expect from the theory.

The treatment by the use of Narcosan, a mixture of lipoids, non-specific proteins, and water-soluble vitamins, apparently aggravates the withdrawal symptoms. This drug is apparently of very little benefit[2] since it generally increases the suffering of the patient. Atropine and aspirin were both found wanting so far as the alleviation of suffering is concerned.

Hyoscine treatment is designed to allay the discomfort of withdrawal by throwing the patient into a delirium. However, addicts claim, and Lambert found, that this drug does not help the patient, despite the delirium. It was found that codeine, which is in the morphine series of alkaloids, can be substituted for morphine during the gradual withdrawal of the latter. Codeine does lessen the withdrawal symptoms. Since codeine undoubtedly works in the same direction as morphine, this form of treatment is merely a leap from the fire into the frying pan, although one does not become habituated to codeine so easily as to morphine.

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[1] Lambert et al; Am. J. Psychiatry, 10, 433 (1930).

[2] Lambert et al: Am. J. Psychiatry, 10, 433 (1930); Nellans and Massee: J. Am. Med. Assoc., 92, 1153 (1929).

Sodium amytal has been used in the treatment of drug addicts; the thought being that the patient could be rendered almost unconscious by the drug due to its anesthetic action. In this way withdrawal symptoms might be obliterated. This should not be the case unless the patient is deeply anesthetized, because sodium amytal and morphine are both agglomerating agents, and act in the same direction. Lambert, p. 525, says: "Seven of the twelve patients showed considerable irritability both during and after treatment. It was also found that where the patients became disturbed under the use of amytal further doses accentuated this restlessness, rather than diminished it. . . .

"The disturbed cases thrashed about in a state of motor restlessness and mental confusion and delirium. The typical symptoms of barbituric acid intoxication were apparent in the ugly, irritable frame of mind of the patient, the staggering gait, and slurring and ataxic speech, and mental haziness.

"In a few cases marked psychomotor excitement manifested itself." It was found that the withdrawal symptoms were not ameliorated by sodium amytal and that recuperation was slightly delayed.

These findings were quoted because it is worthy of note that the effects found can all be predicted on the basis of the theory of reversible agglomeration in living tissue.

In other cases Lambert's Committee used psychotherapy to some avail. This will be discussed under another heading. Potassium permanganate was found to be of no use in treating drug addicts. Strychnine and parathyroid extract in different sets of experiments did not alter the withdrawal picture.

Concerning alkalies Lambert's report, p. 529, says: "As mentioned previously, sodium bicarbonate in 30 grain doses every four hours is often beneficial to patients undergoing abrupt withdrawal treatments, as the marked gastro-intestinal symptoms incidental to these methods of withdrawal and the semi-starvation often produce a condition resembling acidosis with acetonuria [which condition is probably an aid to the agglomeration that has caused the addict all of his trouble] and the alkali also reduces the subjective sensations of 'heartburn' and abdominal cramps." They found that sodium bicarbonate was more effective than magnesium oxide.

Abrupt withdrawal, when the patient can stand up under it, or seven or fourteen day reduction treatments are recommended by Lambert as a result of his exhaustive study. None of the drugs studied helped materially in making the withdrawal period easier.

Nellans and Massee[1] mention three other methods for the treatment of drug addiction. The Pettey treatment uses forced fluids, vapor baths, atropine, scopolamine, and other sedatives along with spartein sulphate and sodium thiosulphate. Spartein is apparently also an agglomerating agent, since it has a strong curare action, paralyzes the respiratory center, and has a weak local anesthetic effect.[2] The Jennings treatment consists of the use of ethylmorphine hydrochloride in the place of morphine and spartein sulphate. The Sceleth method of treatment is by the administration of a mixture that

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[1] J. Am. Med. Assoc., 92, 1153 (1929).

[2] Sollmann: "A Manual of Pharmacology," 318 (1917).

would scare anyone: scopolamine, pilocarpine, ethylmorphine hydrochloride, cascara sagrada, and alcohol. Strychnine is used for good measure. Nellans and Massee recommend the abrupt withdrawal treatment.

E. H. Williams and co-workers[1] have used alfalfa protein by injection in the treatment of drug addiction, the method being called the proteal treatment. It is designed to replace Narcosan in withdrawing drug addicts. In this report the statement is made that: "We disagree with this clinical deduction [that there are toxic substances of a definite character in the blood as a result of chronic morphinism or withdrawal] because it seems to us that the evidence presented by the clinical picture of addiction, and certain chemical features, indicate primarily rather a disturbance of the endocrine system—either primarily or secondarily to the sympathetic nervous system. There is no question about the endocrine hypo-function in these cases, as indicated by the lowered blood pressure, low basal metabolism, and generally weakened condition which may be improved by direct action of endocrine substances." Undoubtedly the above statement forms an important part of the picture of drug addiction. Further on they say: "In addition to this treatment primarily, we found it expedient to keep the patient alkalinized with sodium bicarbonate, and, to combat the inevitable nervousness, we administered strychnine. . . . as suggested by Lambert and Tilney in their narcosan treatment. Strychnine was the sheet anchor of the treatment given by the late Dr. Bishop and its value is recognized by everyone who attempts the treatment of drug addiction." Williams found orchitic substance to be useful in his treatment. The paper does not point out clearly that the proteal treatment has a very definitely better effect on the patient than does Narcosan, which is worse than nothing.

Strychnine seems to be quite widely used in one way or another in the treatment of drug addicts. Lambert pointed out that it does not help the patient. Sollmann[2] says that the bitter and tonic effects of strychnine make it useful in the treatment of chronic alcoholism and other drug habits. He also says that morphine is theoretically objectionable as an antidote to strychnine because its action on the spinal cord is synergistic to strychnine. "It has been employed, however, and its analgesic action at least would be useful." It seems best, for the time being, to assume that strychnine merely soothes the gastro-intestinal tract to a small degree during withdrawal.

In another method of treatment[3] profuse catharsis, very hot baths and salicylates are used during a ten to fourteen day withdrawal period. Bancroft and Rutzler[4] have discussed MacLeod's use of the peptizing agent sodium bromide in the treatment of drug addicts.

Poppe[5] succeeded in mitigating the withdrawal symptoms by the use of ephedrine hydrochloride in three addicts who were given abrupt withdrawal.

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[1] Med. J. and Record, September 7, 1927.

[2] "A Manual of Pharmacology," 194, 197 (1917).

[3] Sollmann: "A Manual of Pharmacology," 236 (1917); Drysdale: Clev. Med. J., 14, 353 (1915).

[4] Proc. Nat. Acad. Sci., 17, 186 (1931).

[5] Klin. Wochenschr., 7, 775 (1928).

Since ephedrine is a good peptizing agent[1] and acts upon the sympathetic nervous system,[2] which is disturbed during withdrawal, its successful use, barring side reactions, is to be expected. Undoubtedly it will be used more as time goes on.

In résumé, many of the treatments devised for use on the drug addict during withdrawal make use of agglomerating agents which are worse than useless in an already agglomerated condition. The only treatments that have merit from the view-point of the present theory are those that employ sodium bicarbonate, sodium bromide, ephedrine, or withdrawal without drugs. As yet, the real problem that is involved has not even been touched upon. It matters not by what method withdrawal is accomplished, or whether or not a severe reaction occurs. The important and pressing thing is to bring about normal nervous, physical, and mental stability. It appears that people have been too busy trying to devise means for painless withdrawal.

Mr. Koepfgen, who probably has the best treatment that there is in this country for drug addicts, says:

"In administering treatment for addiction, this Association has always recognized the problem as more than a habit problem. We have looked upon it as a problem requiring not only medical treatment, but as one requiring also a physical, mental, moral, and spiritual rehabilitation; a problem that cannot be solved in a few short weeks, but one that requires months; medical treatment over a short period and a long time rehabilitation period conducted under thoughtful, conscientious, and sympathetic administration; a treatment administered under conditions as near ideal as possible where the sufferer can be removed from his usual environment and tempations; a treatment which can be conducted in the open where outside labor and recreation can be furnished and where a normal routine of activity and methods of living can be had, and where the mental and spiritual life can be studied and administered to. Society does not attempt the cure of blood poisoning in a room infested with scarlet fever. Why then should attempts be made to cure drug addiction under less favorable conditions?"

It seems advisable to consider the mental condition of drug addicts from the point of view of reversible agglomeration.

Jelliffe and White[3] say: "The habitual use of opium in some form has become common among all classes in society. The same thing may be said with reference to the reasons for taking opium as has been said with reference to alcohol." Under the psychology of alcoholism they say: "People drink because of definite returns which they get from drinking. . . . When the individual is confronted by situations to which he cannot adjust adequately, when the world of reality makes demands which are too great for him to meet, one of the ways in which the individual reacts to such a condition is by narcotizing himself and so withdrawing from the whole situation. . . . The moment the individual, harassed by the absolutely inacceptable demands of

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[1] Bancroft and Rutzler: J. Phys. Chem., 35, 3189 (1931).

[2] Chen and Schmidt: "Ephedrine and Related Substances," (1930).

[3] "Diseases of the Nervous System," 1073 (1929).

the world, finds an avenue of escape in which he can rest from their harassings, finds the possibility of peace, of repose, he finds it equally impossible to resist the temptation to avail himself of it. He is rendered more and more incapable of meeting the conflict efficiently. Therefore a vicious circle is established and the individual is hopelessly involved."

Further on they say: "Aside from the class of individuals described above, it must be constantly borne in mind that indulgence in alcohol is oftentimes the expression of a neurosis or a psychosis. For example, the recurrent attacks of manic-depressive may be ushered in by alcoholic indulgence, and if one is not keenly observant he may easily suspect that he is dealing with an alcoholic psychosis rather than with a manic-depressive. The same thing of course may be said of dementia precox."

"It is these[1] less well differentiated types of emotional and volitional deviations which are to be designated, at least for statistical purposes, as psychopathic personality. The type of behavior disorder, the social reactions, the trends of interests, etc., which psychopathic personalities may show, give special features to many cases, e.g., criminal traits, moral deficiency, tramp life, sexual perversions and various temperamental peculiarities.

"In accordance with the standpoint developed above, a psychopathic personality with a manic-depressive attack should be classed in the manic-depressive group, and likewise a psychopathic personality with a schizophrenic psychosis should go in the dementia praecox group."

In discussing constitutional inferiority, Jelliffe and White say: "This type not infrequently suffers psychotic episodes where for any reason, such as conscription or imprisonment, they are prevented from slipping from under responsibility or running away from reality. Often at the slightest stress, such as a strong effort to make good, business reverses or loss of a loved object they develop paranoid symptoms, deep depression, or take to alcohol or drugs." These authors say that when a psychosis develops as the result of the use of opium it is characteristically a hallucinated state; and there are usually paranoid symptoms. In view of the theory of reversible agglomeration in living tissue, it is worthy of note that alcohol and morphine, both of which are agglomerating agents, may bring about paranoid conditions. Also, in general paresis and dementia praecox paranoid, which are accompanied by agglomeration,[2] there are delusions of grandeur. According to Dr. Lang[3] the hypomanic state is an imbalanced, agglomerated one. The hypomanics frequently become drug addicts in civil life because morphine has a definite sedative action. Their first response to sedative drugs, which act by agglomeration, is usually an improvement, because they then can concentrate better on a lesser number of stimuli received. Because of the psychomotor hyperactivity and flight of ideas that one often observes, in some salesmen for instance, it is felt that they have a tendency to be in a condition akin to the hypomanic state of the manic-depressive psychosis. In the rehabilitation of drug addicts it is very important

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[1] "Statistical Guide, New York State Department of Mental Hygiene," 22 (1930).

[2] Lang and Paterson: J. Phys. Chem., 35, 3425 (1931).

[3] Private Communication.

to recognize tendencies toward one type of psychosis or another in order that the proper kind of treatment (mild peptization or agglomeration) may be used during rehabilitation.

It can be seen that in the case of the drug addict there are all sorts of possibilities; the drug may have been taken originally in response to: a schizoid type of personality with or without a definite psychosis, a cycloid type of personality with or without a definite psychosis. In other words, the individual may have had a mental condition that involved either over-dispersion or agglomeration of certain of the protein colloids of the brain. In each case, the type of post-withdrawal treatment is necessarily different. Of course, the first thing that must be accomplished is peptization; for in either case morphine will cause abnormal agglomeration if it is used for any length of time. By the time that the nervous systems are returned approximately to normal by peptization, the decision must be made as to whether the patient was originally over-dispersed or agglomerated. Mental rehabilitation can then be carried out by the use of the proper drug.

Lambert[1] says: "As we have mentioned, as a class drug addicts are very suggestible, and many of their real or imaginary symptoms are often relieved by suggestion properly applied. Sterile hypodermics containing saline or plain water were given to twenty-five patients at various times with frequent quieting effect."

Dr. Stolper[2] says that those suffering from dementia praecox paranoid are extremely suggestible. This is probably a well-known fact. At any rate, the comparison is interesting.

So, here we are in 1932 with no drug that is generally recognized as being of real value in alleviating the suffering during the withdrawal of narcotics from addicted persons. Worse still, with the exception of the work of Dr. Stokes in his colony at Warwick, New York and Mr. Koepfgen in his colony near Detroit, no intelligent plan known to us has been devised for the mental rehabilitation of drug addicts. And it should be emphasized that the only really important thing is mental rehabilitation; it makes little or no difference how the drug is withdrawn.

The theory of reversible agglomeration in living tissue, including particularly the work of Drs. Lang and Paterson, makes it possible to use certain drugs during the post-withdrawal treatment that theoretically and practically aid mental rehabilitation. If the patient merely wants morphine when he has recovered from the withdrawal, and has no physical need for it, the problem is a serious one to which much time, thought, and energy must be given. This type of patient must be given institutional care and the proper drugs along with "brain drill" for a period of several months in order to change his mental habits; he must be taught to face reality and depend on himself. The problem is a simple one if the patient is merely in a state of nervousness and is bothered by insomnia; because in this case the proper dosage of a peptizing agent will restore him to normal. If the individual took drugs originally because of some

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[1] Am. J. Psychiatry, 10, 528 (1930).

[2] Private Communication.

mental condition that was accompanied by over-dispersion, treatment with a peptizing agent should help him through the withdrawal period. Continued use of the dispersing agent should then cause him to resume the drug because of a return to his original mental condition, even perhaps to an aggravated form. Where there is a manic-depressive psychosis or tendency, or a paranoid coloring to be dealt with, peptizing agents will tend to restore the patient to normal both as regards the mental upset and the after effects of drug addiction. The individual who is best described as a "pathological thrill-seeker" presents another difficult colloidal problem.

In this study no attempt has been made to standardize the treatment of drug addicts with a peptizing agent; no effort has been made to use the best possible peptizing agent. The main purpose has been to employ a drug that must act primarily as a peptizing agent for agglomerated protein colloids, and to show that it can be used successfully, thus supporting the general theory.

Cases will be reported in chronological order including both successes and failures. Even the failures have taught us much regarding the application of the theory.

Case 1, J. H.

Early in the year a brief report[2] was made on this particular patient. Since a detailed report is desirable, and since much has transpired since that time, the case must be considered here.

The patient was a male nurse, forty-nine years of age. He had been addicted to the use of morphine for a period of sixteen years. The reason given for his initial addiction was that he was given morphine for several weeks to allay the pain of an abscessed kidney. Before coming to us he had been withdrawn from the drug about six times by various methods: insensible withdrawal, rapid withdrawal, abrupt withdrawal, and the Towns-Lambert treatment. The patient returned to the use of morphine every time but once within a period of one to two weeks because of weakness, insomnia, and nervousness. After one of his withdrawals the patient abstained from morphine for a period of about four months. The interesting thing here is that he used large quantities of sodium bromide during that time. The peptizing action of the sodium bromide undoubtedly kept the patient from returning to the use of morphine. The sodium bromide produced a rash which caused him to discontinue its use, with the result that he again began to use morphine.

The patient was not a good risk from the start because after withdrawal he had no prospects of employment, little money was available to him; and he had an aged and ill mother to care for in surroundings that were not of the best. The natural prospect was that the combination of circumstances would prove to be too much for him. In addition he was a manic-depressive depressed.[1] During the time that he was under observation in connection with this study, hypomania was the only indication of a psychosis that was observed.

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[1] Bancroft, Gutsell, and Rutzler: Proc. Nat. Acad. Science, 18, 8 (1932).

[2] Private communication from Willard State Hospital.

The patient was admitted to the Ithaca Memorial Hospital[1] on November 30, 1931, at which time he claimed to be using twelve and one-half grains of morphine a day by intravenous injection. Upon admission to a private room, the patient's clothing and belongings were thoroughly searched before being placed under lock and key. A hypodermic syringe and needle were removed and disposed of. No morphine was found. He was put to bed at this time, and not allowed to be up except for short intervals, during which time he did not leave his room, until three days after morphine was discontinued. No visitors, except members of his immediate family, were allowed to see the patient. When visited by members of his family, the nurse in attendance was present all of the time with rigid instructions to prevent any drugs from being given to the patient. He was not allowed to have any packages; and the two or three letters that came were scrutinized carefully before delivery to him.

Physical examination revealed retracted gums which accompanied gingivitis. The prostate gland was slightly boggy and slightly enlarged in the left lobe. There was no tenderness. The skin was smooth, white, and dry with numerous discolorations of the arms and thighs where hypodermic injections had been made. The knee jerks were active and equal. The patient was thin but not emaciated; there was only a small amount of subcutaneous fat. The other physical findings were negative.

It was learned that the patient had a severe constipation while taking morphine. He had nocturia about twelve times a night.

The following plan was made for the experiment. The patient was to be studied for two or three days prior to the initiation of withdrawal of morphine. The drug was then to be withdrawn as rapidly as consistent with physical comfort, at the same time using enough sodium rhodanate, administering it in a water solution by mouth, as needed, to allow the withdrawal to be accomplished rapidly without too much discomfort.

December 1, 1932.

The patient slept only at intervals and between 1:00 a.m. and 6:00 a.m. His appetite was very good in the morning. He smoked cigarettes incessantly; he was calm with an apparent substratum of nervousness and apprehension. The patient quieted down during the evening. He had a fairly comfortable day; he was rather restless before midnight. The nocturia of which he complained was manifested. During the twenty-four hour period he was given six grains of morphine sulphate by subcutaneous injection. It would appear from his restlessness that he has been used to a larger quantity of the drug than this.

December 2, 1931.

The patient was very restless during the early morning hours. When given morphine he quieted down and slept fairly well from 2:00 a.m. to 6:00 a.m. He had a fairly comfortable day, being more quiet and less apprehensive. He did not concentrate so well as he did on December 1. These changes prob-

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[1] The Hospital placed at our disposal a limited number of beds for a limited length of time, for which we are duly grateful.

ably resulted from the twelve grains of morphine that were administered during the last twenty-four hour period. During the afternoon the patient was given an enema; and at night two Alophen tablets were administered. He was uncomfortable during the forepart of the evening.

December 3, 1931.

Morphine reduction was started on this date. The patient passed a fairly comfortable night. His appetite was very good during this day. The day was an easy one for him; he was only slightly nervous, and not apprehensive at all. He concentrated better than before. He talked incessantly when given the opportunity. At times he would, without provocation, try to convince those attending him that his family was respectable, he was honest and not murderous, even though he was an addict. At times he became argumentative. The manic-depressive characteristics of the patient were beginning to come to the surface. It did not require close observation to see that the patient was very jealous of his own personal comfort. He was quiet, friendly, cooperative, and popular.

The patient slept a little during the day, and for a long time during the evening. At this time it was decided to administer equal quantities of morphine by hypodermics at regular intervals during each twenty-four hour period. They were given at 5:00 a.m., 11:00 a.m., 5:00 p.m., and 11:00 p.m. Sodium rhodanate was given at 6:00 a.m. and 10:00 p.m., and as needed. Table I shows the daily dosage of morphine, and of sodium rhodanate during the withdrawal period.

TABLE I

Date	Grains Morphine	Grams NaCNS	Date	Grains Morphine	Grams NaCNS
12-1-31	6	0	12- 6-31	2.5	1.33
12-2-31	12	0	12- 7-31	1.0	1.10
12-3-31	7.5	0.67	12- 8-31	0.62	3.00
12-4-31	6	1.33	12- 9-31	0	3.8
12-5-31	4	1.33	12-10-31	0	1.5

December 4, 1931.

The patient slept well all night. His appetite continued to improve. When visited at 11:00 a.m. he was very much relaxed; he was neither nervous nor apprehensive. The patient made the remark that some of the wrinkles had gone out of his face. There was a definite change in this respect which was probably due to the nervous relaxation afforded by the sodium rhodanate. The relaxation persisted throughout the day. During the afternoon he slept off and on; he yawned a great deal. The yawning was not a withdrawal symptom. It was due in all probability to the fact that when truly relaxed he found that he was tired.

The pupils were contracted; and there was no change to date. The patient was somewhat uneasy before his hypodermic at 5:00 p.m. After the injection the patient said that he could not feel the morphine "take hold." It goes without saying that in this case, and each of the others, the patient was not told how much morphine was being administered. They always received the same volume of solution from the hypodermic syringe. The five o'clock injection did not quiet the patient very much; he was only very slightly restless. The secretions from his nose and eyes increased somewhat. The patient did not complain at any time during the day. One hour before the morphine was administered in the evening, ten grains of sodium rhodanate were given. The patient said that the 11:00 p.m. hypodermic "took hold." Thirty minutes after the sodium rhodanate was given the patient was very definitely more quiet. The increased secretions subsided. He was given two Alophen tablets during the evening. By 11:30 p.m. the patient was asleep.

December 5, 1931.

The patient slept well after 11:30 p.m. last evening. His appetite was good again on this date. During the basal metabolism test at 8:00 a.m. the patient was kept awake only with difficulty. Sodium rhodanate was given one hour before morphine was administered on this date. The patient was more composed than he had been at any time since entering the hospital; he was somewhat less talkative and appeared to be mentally and physically normal. He was much quieter than formerly, and was not at all apprehensive. At noon he was extremely comfortable.

During the afternoon he slept a great deal. At 4:00 p.m. he was very relaxed and quiet, as compared to slight nervousness at that time on December 4. During these five days the patient slept more each night. The pupils of his eyes remained contracted. At night he was given two Alophen tablets; the physic had not worked to date. The patient put in a very comfortable day. He slept from nine o'clock in the evening to twelve o'clock.

December 6, 1931.

Except for short intervals, when he was awakened to be given medicine, the patient slept from midnight until 6:30 a.m. He had a comfortable night, and slept soundly. Relaxation and quiet were the order of the morning. At noon the patient complained of cramps; it was thought at first that this was a withdrawal symptom. He then said that he had not had a bowel movement for three days. At 1:00 p.m. a good bowel movement made the patient feel better; and the cramps disappeared.

Abour 3:00 p.m. the patient became somewhat nervous. He said that there were darting spots before his eyes. The patient stated that he could tell during past withdrawals to within one-sixteenth grain how much morphine he was being given. On the assumption that he could tell perhaps to one-eighth grain[1] how much drug was being administered, he was asked to guess the amount being given at each dose. The patient was unable to tell anything about how much morphine was being administered per dose. He could not even form an opinion. At various times, as the reduction continued, the patient was asked to guess how much morphine there was in each

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[1] Sollmann: "A Manual of Pharmacology," 236 (1917).

hypodermic. Each time that he was asked his guess was 100%, or more, too high. The patient was not told whether he was right or wrong.

Because of nervousness the patient did not concentrate his attention well at times during the afternoon. Each time such a condition was observed, the patient became markedly more nervous a short time afterward. Although he was not perspiring actively, it was noticed on this date that the patient's skin was becoming softer. The action of the sphincter urethrae was much improved from this time on. There was no retention of urine; the patient voided easily, in a good stream, and emptied his bladder. The nocturia had decreased quite markedly. From this time on none of these troubles were manifested. Instead of an increase in the number of cigarettes smoked per day, there was a steady decrease.

At 6:00 p.m. the patient was resting quietly after what the nurse described as a "good day." From 9:00 p.m. to 11:00 p.m. he was quite nervous, and slightly depressed; the patient perspired a little, and could not stay in bed for long spells. His leg muscles and back ached somewhat. The hypodermic of morphine at 11:00 p.m. quieted him down and obliterated the symptoms. The symptoms were not in any sense of the word severe; yet the patient only received 2 1/2 grains of morphine in twenty-four hours. One hour after morphine was administered the patient was asleep. He was given two Alophen tablets during the evening.

Many times during the treatment it was observed that sodium rhodanate quieted the patient without the administration of morphine; for instance, less restlessness was observed after sodium rhodanate was given.

December 7, 1931.

The patient slept well, and passed a fairly comfortable night from midnight until 5:00 a.m. At five o'clock he was slightly nervous. Again at 8:00 a.m. the patient was somewhat restless and nervous. At 11:00 a.m., before being given morphine, he was distinctly more comfortable. This is ascribed to the sodium rhodanate which was given one hour before. There was a good bowel movement at noon. From 2:00 to 4:00 p.m. the patient dozed lightly; at six o'clock he was resting quietly. The actions of the patient during the daytime were essentially the same as on December 6.

Without telling the patient anything about how much morphine he was getting, it was ascertained that at a dosage level of one grain per twenty-four hours during former treatments, he was possessed with a feeling of great depression, accompanied by suicidal thoughts. No evidence of depression or suicidal thoughts could be detected on this date. At 8:00 p.m. the patient was given two Alophen tablets. He appeared to be rather nervous; he climbed in and out of bed several times. When he settled down in bed there was almost continuous motor activity; but the patient was mentally very calm and collected. This motor activity may have been due to a more rapid diminution of the amount of morphine in the sensory nerves than in the cord. That is, the rhodanate ion may have forced morphine off of the protein colloids in the one place more rapidly than in the other.

A slight incoordination was noticed in the patient's speech. The pupils of his eyes were normal in size during the evening for the first time. At no time before or after that were the pupils dilated. The patient guessed that he was being given one-half grain doses of morphine; whereas one-quarter grain doses were being administered. During the evening the patient was very talkative. It was quite difficult to break in on his conversation. In order to combat the restlessness sodium rhodanate was given earlier than usual in the evening. This quieted the patient down markedly. His speech became slower, and periods of silence longer.

Thus on one-twelfth of his usual dose of morphine, the patient passed a fairly comfortable day. By 11:15 p.m. he was asleep.

December 8, 1931.

During the night the patient slept for more than five hours, which shows that he probably was not suffering much. At 4:30 a.m. he complained of severe nausea, but was unable to raise anything. The nausea passed away in about an hour. When seen at 9:30 a.m., the patient was depressed; he talked slowly and not often, as compared to his usual volubility. By merely talking with him and engaging his attention he went over into the hypomanic condition. The depressed condition of the patient brought on a brief wave of discouragement. During the morning the patient was nervous. He perspired a little for a short time, and had a slight backache. As the day progressed he became steadily more nervous. Seven and one-half grains of sodium rhodanate did not quiet the patient down at 1:30 p.m. He was so nervous that he could not stay in bed, in a chair, or walk around the room for more than five minutes at a time. This was the only withdrawal symptom that bothered the patient to any extent.

At 3:05 p.m. six grains of sodium amytal were administered in capsules by mouth. The patient took this medicine sullenly, saying that morphine was the only thing that would help him. He was more excited, restless, and nervous one-half hour later. It is quite natural that such a reaction should be observed, because sodium amytal, being an agglomerating agent, should prolong the effect of the morphine which is also an agglomerating agent. However, the use of sodium amytal was justified, because an attempt was being made to anesthetize the patient for a few hours. At 3:05 p.m. three grains more of sodium amytal were administered. Twenty-five minutes later the patient was thrashing about wildly on the bed. He was irrational and delirious. His sense of balance and memory were lost; the patient was ataxic, confused, intoxicated, did not know where he was, and exhibited hypermotor activity. He mumbled, twisted sentences up, and did not know people's names. The sodium rhodanate probably acted to reapportion the two agglomerating agents in the brain, so that some centers were adsorbing proportionately a great deal more of them than others. This stormy period was ridden out by the investigators because they felt secure in the knowledge that the peptizing agent both clears and causes transient psychoses, and that it would clear this condition. It should be emphasized that the patient was not mean or difficult to handle at any time.

The patient was given one-eighth of a grain of morphine at 4:20 p.m. This cleared him quite a bit mentally, but left him quite intoxicated. He was slightly irrational, and quite restless. This restlessness was almost entirely a motor reaction so far as could be determined. There seemed to be a strychnine-like action on the cord. In fifteen minutes the patient was much clearer and not so restless. He refused food at 5:00 p.m., although he had taken little nourishment all day. At 6:20 p.m. he was given fifteen grains of sodium rhodanate; the patient was still agitated at seven o'clock, at which time he ate toast and jello, and drank tea. A two cc. sterile saline hypodermic containing a few drops of a 5% solution of novocaine was administered. The novocaine was added so that the local anesthetic effect of morphine would be simulated. This quieted the patient for about fifteen minutes, which demonstrated that a large part of his trouble was mental.

The patient became restless and nervous again at 8:10 p.m.; he was in and out of bed a good deal. Petrolagar was given at this time. At nine o'clock he pled for an injection of morphine to be given instead of at eleven o'clock. A saline hypodermic was administered as before. This made him easier for a few minutes; the patient then insisted that the injection did no good. At 9:30 he was given seven and one-half grains of sodium rhodanate; he was very restless at that time. One-eighth grain of morphine was administered at 11:00 p.m. The patient expressed the fear that there were many days of suffering before him, as had usually been the case. He guessed, shortly afterward, that he was being given one-quarter of a grain of morphine at a dose; whereas, he was only getting one-eighth of a grain. He was told that one-eighth grain doses were being given; at first the patient refused to believe this. When he was convinced that that was the case, a wide grin came over his face, he turned over in bed, and said that we would not hear another word out of him. The patient quieted down markedly and dozed for about ten minutes after volunteering the information that a difficult time is in order when the last one-half grain of morphine is withheld. Upon wakening, the patient had a good appetite which was satisfied. It seems perfectly fair to assume that much of the restlessness that the patient exhibited was due to the fear that he was faced by many days of discomfort before the morphine was completely withdrawn. He volunteered the information that had it not been for the sodium amytal he would have had a fair day.

Later on it was learned that the afternoon and evening of this day were a blank in the patient's mind. Only very slight gastro-intestinal symptoms were observed; they took the form of nausea during a part of the morning.

December 9, 1931.

Just after midnight, the patient appeared to be somewhat depressed; he was uncommunicative. He did not want to be bothered, for he desired to sleep. At 2:00 a.m. the patient was awake, restless, and very talkative. He was in the hypomanic state again. An hour later, he was up and about; he perspired a little for a short time. It should be borne in mind that the patient perspired only at such times as are mentioned in this record, and then only for fifteen to twenty minutes. Between 3:30 and 4:30 a.m. the patient slept for brief intervals. Ten grains of sodium rhodanate were administered at 4:30 a.m. Although he continued to be restless, the patient slept better from that time on. Petrolagar was given at 6:00 a.m.; this was used in an attempt to keep the bowels open and at the same time avoid diarrhea.

At eight o'clock the patient ate a hearty breakfast. He was not depressed; and his mental condition was much improved. He was restless for short periods of time; his elbows and buttocks were red from the friction of contact with the bed. The patient complained of feeling as though worms were crawling around in his abdomen. No tremors were found. This sensation was relieved by ten grains of sodium rhodanate, given at 10:00 a.m. The peptizing agent quieted the patient definitely. At about this time his face became flushed—vasomotor instability—which reaction subsided in fifteen minutes.

Definite auditory hallucinations, mental discontinuities, and hallucinations of sight were exhibited each time that the patient was on the verge of sleep, either just as he was dropping off, or upon awakening. These symptoms, and those that some of the other patients exhibited, will be discussed in detail further on.

A brief wave of restlessness passed over the patient at 10:30 a.m. At 5:00 a.m. and again at 11:00 a.m. the patient was given a sterile saline hypodermic containing a few drops of novocaine solution. He did not ask for these injections. At noon the patient ate a good-sized dinner; he was fairly quiet all afternoon. At 5:00 p.m. the patient protested that he did not want the hypodermic, despite the fact that he believed that it contained a little morphine. He slept from seven to eight o'clock in the evening.

By nine o'clock in the evening the patient was very quiet; he did not talk a great deal, except when he was addressed. He gave the appearance of being mentally drowsy and relaxed. He was incredulous when told that no morphine had been administered for twenty-four hours. The patient slept lightly from 10:30 p.m. until midnight. During his nervous spells on this date, the patient experienced no difficulty in staying in bed. It was somewhat difficult to fix his attention during the daytime. The patient exhibited slight muscular twitching during a large part of the day; this did not seem to bother him. Since, according to Sollmann, morphine has a strychnine-like action on the cord, the assumption is made that the rhodanate ion threw the morphine off of the protein colloids of the sensory nerves before those in the cord. The sedative action of the morphine was counteracted thereby, the result being the strychnine-like action. In the usual case when there is twitching, the morphine has merely left the sensory nerves more rapidly than it has the cord.

December 10, 1931.

Shortly after midnight, the patient exhibited a wave of depression which soon passed off. At no time did these periods of depression last for more than twenty to thirty minutes; furthermore, they were not observed to occur often. There was never any severe depression. The patient was very quiet all night long, although he only slept at intervals. No request was made for morphine. In the morning his appetite was better; he was rational. The patient was absolutely calm, comfortable, and collected during the whole day; he stayed in bed, and did not exhibit any signs of nervousness or restlessness. The nervous tension was gone from his face. He was not depressed. So absolutely quiet was he that several physicians who saw him refused to believe that no morphine was being administered. That was the first of a series of grave mistakes that certain physicians made where this case was concerned. The patient had six bowel movements during the day. He slept during the evening. No hypomanic symptoms were seen during the last twenty-four hour period; thirty grains of sodium rhodanate were given in this time.

From this point on a very brief clinical summary will illustrate the reactions that the patient underwent.

December 11, 1931.

Shortly after midnight the patient vomited an emesis basin full of dark vomitus. A hot water bottle was applied to the epigastric region; this made the patient feel better and he fell asleep almost immediately. He had a comfortable night, and slept well. At no time during the course of this study did the patient become hyper-sensitive to heat or cold. Under all other treatments the patient did become hyper-sensitive to heat and cold. The patient was quiet and composed all day long. Thirty grains of sodium rhodanate were administered in the last twenty-four hours. No withdrawal symptoms were noticed. The bowels were normal.

December 12, 1931.

The patient slept soundly for eight hours. In the middle of the morning he was taken outside, away from the hospital, for two hours. During this time he vomited bile once. He felt nauseated after supper. Because sodium rhodanate may upset the stomach at times, administration of the medicine was changed so that it was given before meals. The patient was not nauseated thereafter. He passed a comfortable, quiet day. Twenty-five grains of sodium rhodanate were given during the twenty-four hour period.

December 13, 1931.

The patient slept at long intervals during the night. The hypomanic condition was observed less and less as the days progressed. The clinical observations for the day were negative, except for a rise of nervous tension during the late afternoon and evening. The patient was not uncomfortably nervous. The nervousness is accounted for by the fact that the patient was only given fifteen grains of sodium rhodanate, five of which were given at 6:00 a.m. and ten at 10:00 p.m. He needed more of the medicine than this to keep him comfortable.

December 14, 1931.

That he did not have enough sodium rhodanate on December 13, was shown again by the fact that the patient did not sleep well during the night. He complained bitterly about not sleeping well. That brings up a very important point which must be considered carefully. Insomnia leads many addicts back to the drug that they were using. This patient returned to morphine on several former occasions because of insomnia, after having been withdrawn. The patient slept less as the dosage of sodium rhodanate was decreased. This means that he did not stay peptized sufficiently. Certain of the sensory nerve colloids bordering on a state of agglomeration gave rise to irritability which kept the patient awake. If, at this time, the patient had been given an agglomerating hypnotic, it would have tended to cause more agglomeration of the protein colloids of the nervous systems. This would have started him back almost surely on the road to morphinism, because his original addiction was due partly to nervousness and hypomania, which are generally agglomerated conditions. Sodium rhodanate, in the correct amount, will quiet the sensory nerves by peptization and *allow the patient to go to sleep;* whereas, such drugs as chloral hydrate, allonal, veronal, sedormid, and sodium amytal put one to sleep by agglomeration. That is where mistakes have been made in the past. At the same time, it should be emphasized that too much sodium rhodanate will keep one awake due to over-peptization of certain protein colloids in the brain. In such cases either the peptizing agent can be discontinued temporarily, or an agglomerating drug used. It is very important to determine in any given case which kind of sleeplessness one is dealing with in order to employ the correct medication.

Since the patient was not being given enough sodium rhodanate, especially at night, none was given until 10:00 p.m., when thirty grains were administered. He slept lightly for two hours thereafter. He was neither depressed nor nervous. Using the ferric chloride test, sodium rhodanate could not be demonstrated in the blood serum. This may be of very great importance, indicating, as it does, that the tissues took up most of the drug. A slight nervous cough was noticed during the day.

December 15, 1931.

A very uncomfortable night was passed by the patient. He was neither restless nor nervous; but he was very much upset mentally, because he did not sleep well. Having decided from the theory that the patient was not being given enough sodium rhodanate, the only thing to do was to continue the larger dosage until the desired result was accomplished. It was quite evident that if this problem was not solved satisfactorily, the patient would soon return to the use of morphine. At 1:30 p.m. five grains of sodium rhodanate were given. He was then taken for a long walk in an attempt to tire him. The desired results were accomplished; he had an excellent appetite and felt like sleeping. At this time, he began to complain of feeling weak. He was extremely jealous of his own comfort.

The patient was given twenty-five grains of sodium rhodanate at 9:00 p.m. He fell asleep immediately thereafter, and slept soundly until midnight.

December 16, 1931.

The patient slept soundly for seven hours. He spent a quiet, comfortable day; he was taken for a walk during the afternoon. His appetite was fair, but not voracious. Five grains of sodium rhodanate were given at 2:00 p.m., and twenty-five grains at 9:50 p.m.

December 17, 1931.

The patient slept soundly during the night. The problem of sleeping apparently was solved. He spent a quiet, comfortable day. He still complained of feeling weak when taken out for a walk. Twenty-five grains of sodium rhodanate were given at 8:00 p.m. The patient slept soundly from nine o'clock until midnight. There were no signs of nervousness.

December 18, 1931.

A good night's sleep was had by the patient. In the evening, he complained of feeling weak and tired. The day was a quiet, comfortable one. Twenty grains of sodium rhodanate were given at 8:00 p.m. He slept from 8:45 until midnight.

December 19, 1931.

The patient passed a comfortable night, and slept well. During the rest of his stay at the hospital, it was impressed upon him daily that alcohol, sedatives, nervous exhaustion, and the like would lead him back to morphine. He was informed that in times of distress, no matter what its nature, he should come immediately to those who treated him.

In the afternoon the patient was shown a list of the common withdrawal symptoms. He looked the list over, and became very nervous. Perspiration broke out all over him; he became flushed and felt it necessary to lie down. The reaction subsided in fifteen minutes. This was a good illustration of the extreme suggestibility of the patient.

At 8:00 p.m. twenty grains of sodium rhodanate were administered; an effort was being made to reduce the amount of the drug administered daily. The patient slept from 9:00 p.m. until midnight.

December 20, 1931.

Twenty grains of sodium rhodanate was not quite enough to afford the patient a long sound sleep. Considering his relative inactivity seven hours of sleep should have been adequate. During the latter part of the treatment, the patient was taken out for a short walk every day. Fifteen grains of sodium rhodanate were given at 8:00 p.m., after the patient had had a comfortable day.

December 21, 1931.

The patient slept well during the night. Except for a short period of nausea at 10:30 a.m., this day was uneventful. Ten grains of sodium rhodanate were administered at 8:00 p.m.

December 22, 1931.

After a comfortable night during which he slept well, the day was uneventful. Seven and one-half grains of sodium rhodanate were administered at 8:00 p. m.

At this time during the treatment the hypomanic characteristics of the patient had practically disappeared. The psychomotor hyperactivity and flight of ideas had subsided. The patient smoked very little as compared to almost continually in the beginning. He had lost his taste for cigarettes. The sodium rhodanate made them taste bad. He still complained of feeling weak.

December 23, 1931.

The patient was somewhat restless during the night; this was probably due to the smaller amounts of sodium rhodanate that were being used. The smaller amount was continued, however, in order to avoid having the patient depend upon the drug too much, seven and one-half grains being given at 8:00 p.m.

December 24, 1931.

After a night of sound sleep, the patient passed a comfortable day. During the ten days before this date the patient several times volunteered the information that he did not think about morphine. This statement is probably true despite the untrustworthiness of this type of person, because he was in no particular hurry to leave the hospital, and was not in need of any drug. So far as could be determined, the patient had no desire for drugs.

The patient was discharged from the hospital on this date. After being told how much sodium rhodanate had been given to him at different times during two weeks previous to this, he was instructed to administer to himself the quantity that would be effective in all times of stress. Arrangements were made for a periodic check-up on the condition of the patient. Lack of funds made it impossible to hospitalize him for a longer period of time; this would have been very desirable.

January 4, 1932.

It was learned that the patient would not be able to take a position for quite a while because it was necessary for him to be constantly with his aged, infirm mother. The task was arduous in the extreme for a man in his condition. At night, when his mother did not need him, he slept within two feet of a stove, in order to keep the fire burning. At this time the patient was instructed to take five grains of sodium rhodanate and fifteen grains of sodium bromide, a poorer peptizing agent, each night. The feeling of weakness, of which the patient formerly complained, was gone.

January 8, 1932.

The sodium bromide proved not to be efficient enough to give the patient his sleep and allay all nervousness. So, five grains of sodium rhodanate at 4:00 p.m. and ten grains at 9:00 p.m. daily were ordered. The patient was gaining weight slowly at this time. His problems at home were becoming more acute.

January 16, 1932.

The patient was doing well despite the strain that he was under at home. He was told to take sodium rhodanate as needed, in an effort to reduce the amount to a minimum.

February 9, to February 21, 1932.

About this time it was noticed that the facial expression of the patient was not very frank. Further, rumors came from many sources that the patient was using morphine again. Then a packed committee of local doctors vouchsafed unscientific, baseless information to the effect that the patient was not only taking morphine, but was never entirely withdrawn while in the hospital. In the better judgment of more qualified people, this information was incorrect. The circumstances surrounding the treatment of the patient in the hospital made it quite certain that morphine was completely withdrawn. Upon being questioned, the patient named an unscrupulous physician who had supplied him with several grains of morphine with the knowledge that he (the patient) had been treated with sodium rhodanate. It was found that the patient had also secured some pantopon, which is habit-forming.[1]

He used the morphine and pantopon for a period of about four days as a result of five successive sleepless nights, which were brought about by the necessity of caring constantly for his mother. Then, struck by remorse, the patient withdrew the morphine in his own home without anyone knowing that he was either using the drug or going through withdrawal. To do this he used large doses of sodium rhodanate; it was not possible to learn the size of the doses of sodium rhodanate that he used. The patient said that he suffered slight withdrawal symptoms during one night. He also said that the first of the one-quarter grain doses of morphine that he used stimulated him much more than that-sized dose ordinarily would. Sodium rhodanate, by its peptizing action, must have prevented the morphine from exerting its full agglomerating action.

While there was every reason to believe that the above chain of events was substantially correct, scientific proof that the patient was not still taking the drug was desirable. To that end, arrangements were made to have the patient spend several days in the Strong Memorial Hospital[2] of the University of Rochester under close observation, under morphine-tight conditions. The room occupied by the patient was kept locked; all of his possessions except a toothbrush were taken from him before entering the room; cigarettes were furnished by Dr. McCann; the required clothing, handkerchiefs, toilet articles, etc. were furnished by the hospital. The food on his tray was inspected by the nurse in charge at every meal time. No visitors were allowed. The patient was not given toilet privileges. In other words, everything that could be done, was done to prevent the patient from access to morphine. The patient was admitted to the Strong Memorial Hospital on February 21, 1932. Nothing abnormal was found in the behavior of the patient on that day.

February 22, 1932.

Dr. McCann's report says: "In a short interview, I (Dr. Akelaitis) could find no symptoms of withdrawal. Patient was composed, there was no de-

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[1] Kunkel: Clifton Med. Bull., 18, 6 (1932).

[2] Professor William S. McCann, of the University of Rochester Medical School kindly conducted this experiment and made available a report of the results, thereby adding very valuable data to this study.

pression or psychomotor retardation, no sudorrhea, and no tremor. He talked spontaneously, relevantly, and coherently. No preoccupations or distortions of content. Patient was well oriented, memory for remote and recent events apparently good. Patient is very enthusiastic about sodium rhodanate treatment.

"Dr. Goldstein and I (Dr. McCann) had a long interview with the patient. No symptoms of withdrawal can be detected as yet, and I believe the drug has been pretty well excluded."

February 23, 1932.

No withdrawal symptoms were detected.

February 24, 1932.

"I (Dr. McCann) can see no evidence of withdrawal symptoms. I do not think that there has been any leak in our system of excluding morphine.

February 25, 1932.

"Behavior most exemplary. No signs of withdrawal or of morphine. Pupils medium size. No lachrymation, salivation, or any evidence of distress."

February 26, 1932.

No evidence of withdrawal symptoms was seen. "The measures which we have used to exclude his access to morphine have been very rigid, and included digital examination of the rectum and daily enemas. It is my (Dr. McCann's) opinion that he has had no morphine during his stay here of five days and that no symptoms of withdrawal have been noted.

"The patient made several interesting statements. He said that sodium rhodanate did not entirely alleviate his suffering during the withdrawal experiments at Ithaca. He was so ill at one time that he received enough amytal to produce a stuporous condition.

"Since the 'cure' he admits having received several quarter grain doses of morphine and some 'pantopon' tablets. His comment on this is as follows: 'That ordinarily these small relapses would have brought back immediately all of his former terrible cravings.' He attributes the fact that this did not occur to his continued use of sodium rhodanate."

February 26, 1932.

No symptoms of withdrawal were observed on this day. The patient told Dr. McCann that his period of illness during withdrawal under sodium rhodanate was part of one day; whereas, it was always of three or four days duration on previous withdrawals. "He feels that he was benefited definitely by the rhodanate."

When the patient was left at the Strong Memorial Hospital, he was instructed to tell the doctors there nothing but the truth, even if it did not agree with what he had told us.

From this there seems to be no doubt but that the patient withdrew himself at home after using morphine for several days. It was an experiment that we would have liked to have tried but would not have dared to. Such an experiment as this should prove beyond a question of doubt that sodium rhodanate is beneficial in the treatment of drug addiction.

February 29, 1932.

The patient was gaining weight rapidly at this time. He appeared to be quiet and on an even keel.

March 18, 1932.

This day provided another interesting study of the patient. He came to us in the worst hypomanic condition in which we had ever observed him. He had been drinking whiskey all of the week. Investigation revealed that he had not had any sodium rhodanate during the week previous to that of March 18. He was dirty, disheveled, and intoxicated; his speech was not well coordinated. He was oblivious to those around him; his face was gray, and exhibited nervous tension. He claimed to have used a quart of whiskey during the day. The patient was thoroughly disgusted with himself.

Twenty grains of sodium rhodanate were administered at 9:30 p.m.; at this time he was also given "Bisodol" and psychotherapy without hypnosis. By 10:00 p.m. he was out of the hypomanic state, and much quieter. Ten grains more of sodium rhodanate were given at this hour. The grayness and lines soon left his face; he became more quiet; and by 10:30 he was completely sober; he talked and acted sober, in every respect. "Bisodol" was administered again at this time. The sight of whiskey sickened him so that he vomited. He returned home sober with instructions to take ten grains more of sodium rhodanate before retiring. He slept well during the night.

It was not difficult to see that the patient could not be trusted to administer sodium rhodanate to himself only when needed. When he did not need it, he would not take it. This generally resulted in sleeplessness, nervousness, and a return to the hypomanic condition. He would then use sodium rhodanate in too large quantities. This upset him on the over-dispersion side. Except for the intervals in between, the patient was feeling upset. As a result he went on an alcoholic spree.

March 25, 1932.

The patient was quiet and in excellent condition, when seen on this date.

March 30, 1932.

At this time the patient was in one of his quiet intervals after having used too much sodium rhodanate. He was in good condition, quiet, and relaxed. He said that he had not felt better in years; the pupils of his eyes were normal in size. He claimed that he never thinks of morphine; he was sleeping about ten hours each night.

In order to try to keep him on an even keel two sets of capsules were made up for him. One of them contained ten grains of sodium rhodanate with one-quarter of a grain of saccharin to act as a disguise. The other contained one grain of ephedrine sulphate, and ten grains of sodium bicarbonate. The sodium bicarbonate was to keep his stomach settled; and the ephedrine to keep the blood pressure up, and as an added peptizing agent. One capsule of each was to be taken every other night.

April 1, 1932.

The ephedrine, in addition to the psychic effect of a change to an unknown medicine, brought about a slight sympathetic nervous upset. The patient refused to use the capsules, and requested sodium rhodanate. He was quiet and fairly well relaxed when seen on this date.

April 6, 1932.

The patient was intoxicated again. Sodium rhodanate was administered; and it straightened him out within two hours. The twofold problem then presented itself. In the first place, the patient had learned from experience that he could use either morphine or alcohol for short periods of time and rely upon sodium rhodanate to stop their use. Secondly, it was difficult to make him use a constant small amount of the peptizing agent. At this time he was instructed to take ten grains of sodium rhodanate every night, with the hope that he would do so.

April 19, 1932.

The patient was looking and feeling very well on this date. Evidently he had been using the sodium rhodanate as he was instructed.

April 23, 1932.

When seen, the patient was in a hypomanic condition. Still, he was feeling well. He had gained quite a bit of weight.

From various sources, it was learned that during previous withdrawals the patient was: ill for three or four days, depressed, cranky, "a mean customer," whiney, paranoid, subject to severe gastro-intestinal upset, with cramps, diarrhea and nausea, bothered by hot and cold flashes, tremors, inability to satisfy his craving for food, twitches, profuse perspiration, yawning, a craving for the drugs, sneezing, and a crawling sensation in the lower abdomen. His bones and joints ached; he was restless. One doctor said that the patient suffered severely all of the common withdrawal symptoms, and was a "mean customer."

In contrast with this, it was found that under the sodium rhodanate treatment the patient exhibited a slight gastro-intestinal upset of short duration, short periods of yawning, a very little muscular aching for a few hours, and restlessness. There was delirium, which has not been reported as being a factor in other withdrawals that the patient went through.

A good many data of a physical nature have been accumulated during the study of this case. It is of advantage to present it here. Table II gives the variations in blood pressure and weight of the patient from the start of the experiment. The data show that the blood pressure at the start of the experiment was low, as is common with drug addicts. During the whole time that the patient was under treatment the systolic pressure rose slightly. The definite upward trend did not begin until nearly the end of the withdrawal period. The statement is made in the report of Lambert's committee, p. 490, that there is often a fall in the systolic and diastolic readings during withdrawal. The opposite was found here. The diastolic readings did not vary much at any time; although there was a slight upward trend during withdrawal. These blood pressure data do not bring to light any vasomotor instability.

TABLE II

Date	Blood Pressure	Weight in Pounds	Date	Blood Pressure	Weight in Pounds
12- 1-31	115/70	—	12-14-31	—	135
12- 2-31	105/65	139	12-15-31	—	135½
12- 3-31	120/70	140	12-16-31	122/70	—
12- 4-31	112/60	141	12-17-31	122/75	140
12- 5-31	115/70	141	12-18-31	—	140
12- 6-31	113/68	142	12-22-31	105/70	—
12- 7-31	115/68	141	12-23-31	—	140¾
12- 8-31	122/68	138	1-16-32	—	153
12- 9-31	120/74	139	2- 9-32	—	149½
12-10-31	130/75	139	2-21-32	120/75	—
12-11-31	135/78	135½	2-29-32	—	157½
12-12-31	135/74	135	4-23-32	140/85	164
12-13-31	—	135			

The changes in weight that the patient underwent are of interest. During the early part of the withdrawal he gained weight. He did not lose weight until two days after withdrawal. This can be attributed to the six bowel movements on December 10, in addition to the fact that his appetite was not hearty from the eighth to the twelfth of December. After the withdrawal, the patient did not gain weight rapidly, as is usually the case. This is ample proof of the absence of severe withdrawal symptoms, in the first place, and the non-appearance of the "chuck horrors," in the second place.

Table III shows the volume of the urine for twenty-four hour periods during hospitalization. While there was not a constant water intake during the study, the general trend of the output figures is of great interest. The initial increase in the volume may be due to a decrease in the amount of water adsorbed by the blood serum and nervous system proteins. Morphine is carried to the liver or intestines by the blood for destruction or elimination. The peptizing action of the rhodanate ion throws morphine off of the particles on which it is adsorbed. This will tend to increase the amount of free morphine in the body fluids. If, then, this available morphine goes to tissues that have not taken up much of it before, and have not taken up much sodium rhodanate, dehydration will take place. This, in turn, may increase the water output.

TABLE III

Date	Volume in Ounces	Date	Volume in Ounces
12-3-31	46	12- 9-31	17
12-4-31	51	12-10-31	15
12-5-31	58	12-12-31	15
12-6-31	30	12-14-31	30
12-7-31	80	12-22-31	30
12-8-31	30		

The sharp decrease in water output (the values are well below the average)[1] from the ninth to the twelfth of December inclusive is interpreted as being due to adsorption of water by the colloids of the body that were then being peptized by the rhodanate ion. From the fact that a large decrease in water output occurred on the next day after the patient was given his last dose of morphine, one can surmise that the sodium rhodanate was forcing the morphine out of the system at greater than the normal rate. Other evidence will be cited which sustains this view.

The phenolsulphonephthalein test for kidney function[2] was performed on the patient at intervals. The results are given in Table IV.

TABLE IV

Date	cc. Urine First Hour	cc. Urine Second Hour	% of Dye Eliminated First Hour	% of Dye Eliminated Second Hour	% of Dye Total
12- 1-31	240	100	72	21	93
12- 7-31	65	115	18	5	23
12- 8-31	90	20	71	2	73
12- 9-31	95	65	72	18	90
12-11-31	128	30	76	14	90

The data show that the patient had a high renal function at the start of the experiment. The function became very poor, and then recovered. The dye was injected intravenously; this brings up the possibility that the low function found on December 7, may have been due to the transfixation of the vein. However, the kidney function was lower than would be expected on the next day. That 23% was a real value is supported by data obtained on another case. Were the kidneys adsorbing large amounts of morphine at this time?

Table V is given merely to show that the patient did not exhibit any upset that can be gauged by changes in rate of pulse or respiration.

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[1] Starling: "Principles of Human Physiology," 893 (1930).

[2] Hawk and Bergeim: "Practical Physiological Chemistry," 675 (1926).

TABLE V

Date	Rate Pulse	Rate of Respiration
11-30-31	70	22
12- 1-31	70	22
	70	20
12- 2-31	72	20
	76	20
12- 3-31	68	20
	60	20
12- 4-31	70	18
	62	18
12- 5-31	60	20
	60	20
12- 6-31	68	22
	70	20
12- 7-31	72	20
	70	20
12- 8-31	72	20
	72	22
12- 9-31	70	22
	74	20
12-10-31	72	20
	70	20
12-11-31	92	30
	78	32
12-12-31	70	18
	68	18
12-13-31	80	20
	88	20
12-14-31	70	20
	70	20
12-15-31	72	20
	70	18
12-16-31	72	18
	72	18
12-17-31	70	20
	88	20
12-18-31	92	20
	92	20
12-19-31	90	20
	80	20
12-20-31	70	18
	80	18
12-21-31	76	20
	80	20
12-22-31	72	18
	84	20
12-23-31	90	22
	80	20
12-24-31	76	20
	80	22
2-21-32	84	20

Through the kind cooperation of the Tompkins County Laboratory, the data in Table VI were secured. The values for the 22d of February were taken from the report of Dr. McCann. The data show that until nearly the end of the withdrawal period the patient had a relative lymphocytosis. After withdrawal the basophiles and eosinophiles dropped out of the picture largely;

and the condition became one of polymorphonuclear leucocytosis. The leucocytosis which developed upon withdrawal is generally encountered in this type of case.[1] This leucocytosis began to subside; and the original lymphocytosis reappeared. When the number of white blood cells increased again, the percentage of polymorphonuclear leucoytes increased more than the percentage of lymphocytes. Since Takacs[2] showed that sodium rhodanate may produce a leucocytosis, it seems a fair assumption that the second rise in the number of white blood cells was due to that drug. The final blood count was normal. Throughout the study, the monocytes were somewhat below normal in percentage.[3]

TABLE VI

Hematology

Date	W.B.C.	Polys.	Lymps.	Monos.	Eosins.	Basos.
12- 1-31	7,850	66.0%	30.5%	1.0%	2.0%	0.5%
12- 2-31	9,750	64.5%	29.5%	2.0%	3.0%	1
12- 3-31	10,300	73.5%	23.5%	0.5%	2.0%	0.5%
12- 4-31	8,525	61.5%	34.5%	0.5%	2.0%	1.5%
12- 5-31	9,000	64.0%	33.0%	2.0%	0	1.0%
12- 7-31	10,600	66.0%	31.5%	1.0%	1.0%	0.5%
12- 8-31	13,200	77.0%	20.0%	3.0%	0	0
12- 9-31	14,600	73.5%	24.5%	1.5%	0	0.5%
12-10-31	14,900	77.5%	20.0%	2.0%	0	0.5%
12-11-31	11,550	74.5%	23.5%	2.0%	0	0
12-12-31	10,000	62.0%	36.0%	2.0%	0	0
12-14-31	11,300	69.0%	29.0%	2.0%	0	0
12-15-31	13,000	74.5%	23.0%	2.0%	0	0.5%
12-16-31	14,250	76.0%	22.0%	2.0%	0	0
12-17-31	16,550	80.0%	18.0%	1.0%	1.0%	0
12-18-31	14,475	78.5%	19.0%	1.0%	1.0%	0
12-19-31	16,800	77.5%	21.5%	0.5%	0.5%	0
12-21-31	11,300	76.0%	22.0%	1.0%	1.0%	0
12-23-31	13,250	77.0%	21.0%	2.0%	0	0
2-22-32	8,200	75.0%	20.0%	—	—	1.0%

Routine urinalyses were made almost every day while the patient was confined to the hospital. The data are given in Table VII. There was a definite increase after an initial decrease in specific gravity with the progression of time; the higher figures are somewhat above normal. In all probability, this is due to the presence of sodium rhodanate, which is eliminated by the kidneys. An added factor is that sodium rhodanate doubtless forces sodium chloride out of the body, because the rhodanate ion is more strongly adsorbed by the proteins than the chloride ion. No sugar was found in the urine at any time during the study.

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[1] Lambert et al: Am. J. Psychiatry, 10, 433 (1930).

[2] Z. ges. expt. Med., 50, 430 (1926).

[3] Starling: "Principles of Human Physiology," 657 (1930).

TABLE VII

Date	Appearance	Reaction	Sp. Grav.	Albumin
12- 1-31	Cloudy amber	Alkaline	1.025	Trace
12- 3-31	Clear straw	Acid	1.021	"
12- 4-31	Cloudy straw	Acid	1.021	"
12- 5-31	Cloudy straw	Acid	1.016	"
12- 6-31	Cloudy amber	Acid	1.025	—
12- 7-31	Cloudy amber	Acid	1.027	Trace
12- 8-31	Cloudy amber	Alkaline	1.019	"
12- 9-31	Cloudy amber	Alkaline	1.031	"
12-10-31	Cloudy amber	Alkaline	1.032	"
12-12-31	Cloudy amber	Acid	1.035	"
12-14-31	Cloudy straw	Alkaline	1.030	"
12-15-31	Clear amber	Alkaline	1.031	"
12-17-31	Clear amber	Neutral	1.030	Ft. Trace
12-18-31	Clear	Acid	1.030	Ft. Trace
12-19-31	Straw	Alkaline	1.030	Ft. Trace
12-21-31	Clear amber	Acid	1.036	Trace
12-22-31	Cloudy straw	Alkaline	1.036	Ft. Trace
12-23-31	Cloudy amber	Alkaline	1.031	Ft. Trace
2-22-32	Clear amber	Acid	1.034	None

It is interesting to note that the urine became alkaline toward the end of the withdrawal period. If there was a true alkalosis, it undoubtedly played a useful part in the peptization therapy; because the hydroxyl ion is even a better peptizing agent than the rhodanate ion. This does not mean in any way that the rhodanate ion was not responsible largely for the suppression of the abstinence symptoms. The data show that sodium rhodanate did not bring about a condition of albuminuria. This negative finding is of value only as it points out the safety of sodium rhodanate in this respect when used in large doses.

Table VIII shows the variations in basal metabolic rate at intervals during the course of the treatment. The data show that the patient's basal metabolism was within the normal limits of plus or minus ten percent. On the eighth of December, when the dosage of morphine was very low, the basal metabolic rate was low. If there was much nervousness, one would expect the metabolic rate to be higher, barring complicating factors. Thus, yet another physical test demonstrates that the patient was not greatly upset during withdrawal. The data also show that sodium rhodanate, in large doses, does not affect the thyroid gland.

TABLE VIII[1]

Date	Metabolic Rate	Date	Metabolic Rate
12-2-31	+ 1%	12-12-31	+8%
12-5-31	−10%	12-19-31	+3%
12-8-31	− 1%		

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[1] The staff of the Tompkins County Laboratory kindly secured these data.

Tests of the rate of sedimentation of the red blood corpuscles, using citrated venous blood, showed a high rate which exhibited no definite trends, one way or another. Experiments showed that, by adding sodium rhodanate to the blood samples, the sedimentation rate of the red cells can be decreased tremendously.

Two psychological tests were performed at frequent intervals during the treatment. The first was a dictation-writing test, in which an eighty-four word section of an article was read to the patient, a phrase at a time. The patient was required to take down the dictation as rapidly as he could. The time to accomplish this was recorded. The test was performed at the same time each day; this rules out the factor of the relationship between the times that morphine was given and the test was made. According to Dr. Lang[1] this provides a measure of the involvement of the hearing and the projection system from the ear, to the writing center, to the hand. In Table IX the data obtained on giving this test are set down. The data show that the patient was not seriously upset until December 7th, and that he made a rapid recovery.

TABLE IX

Date	Number of Words	Time needed	Number of Mistakes	Remarks
12- 3-31	84	5 min. 45.8 sec.	2	
12- 4-31	84	3 " 48.0 "	1	
12- 4-31	84	2 " 52.2 "	1	Well person, same dictation, writing illegible.
	84	3 " 0.0 "	1	Well person.
12- 5-31	84	3 " 41.6 "	1	Writing less legible.
12- 6-31	84	3 " 14.2 "	0	Writing more compact and legible.
12- 7-31	84	3 " 40.6 "	6	Writing poor.
12- 8-31	84			Delirium, no test.
12- 9-31	84			No test. Delirium on awakening.
12-10-31	84	3 " 49.4 "	3	Handwriting not steady.
12-22-31	84	4 " 1.8 "	1	Handwriting better than at start.

The other test, which was performed until the last day that the patient was given morphine, consisted of crossing out the letter "O" whenever it occurred in a given paragraph. The paragraph was different each day; but it was from the same magazine, so that the letters were all in the same size type. The patient was timed with a stop-watch while performing the task. The number of "O's" that he crossed out divided by the total number in the paragraph was taken as the accuracy. The data that were obtained are given in Table X. The test was performed just before the preceding one each day. It appears from this that there was no serious fatigue or attention defect until the final day of withdrawal. On the 9th of December this test, and the preceding one, were attempted just as the patient was awakening. At such times during that day, the patient was irrational.

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[1] Private Communication.

TABLE X

Date	Number of O's	Time required	Number missed	Accuracy
12-3-31	44	1 min. 12.4 sec.	7	84.1 %
12-4-31	41	1 " 26.2 "	4	90.25%
12-5-31	41	1 " 5.2 "	2	95.1 %
12-6-31	41	1 " 9.0 "	4	90.25%
12-7-31	43	1 " 41.0 "	3	93.1 %
12-8-31	Test not done.			
12-9-31	Patient could not do test.			
Normal Subjects	41	1 " 22.8 "	2	95.1 %
	32	43.2 "	0	100. %
	48	1 " 6.8 "	1	97.9 %
	41	51.0 "	0	100. %

By comparison with the few controls that are given at the bottom of Table ~~X, the patient was somewhat slow and inaccurate in performing this task.~~ This test did not bring the nervousness of the patient to light, as the dictation test did.

Since this patient shows evidences of a manic-depressive psychosis, he should not return to the habitual use of morphine, if he will consistently take sodium rhodanate for a period of months. The peptizing action of the rhodanate ion should relieve him of the hypomania, nervousness, and sleeplessness, and thus perhaps counteract an inadequate personality. When the administration of the medicine was supervised, it was observed to accomplish these ends.

Case 2, H. A.

The patient was a white male, aged 48, who had been taking four grains of morphine sulphate per day for not less than two years. He was admitted to the hospital on the 18th of January, 1932. No attempt was made to study him during that evening. The same precautions were taken to exclude morphine as were followed in Case 1.

A physical examination revealed that with a few exceptions the patient was normal. The knee jerks were equal but hyperactive. His weight was well maintained. His expression revealed some nervousness and tenseness; there was a definite substratum of apprehension. His skin was dry.

A general survey of the patient left the impression that he was very jealous of his own comfort, and extremely impatient. On a careful observation, one could detect delusions of grandeur. Further investigation revealed the fact that for years he had had hypochondriacal tendencies. This was his first experience in the withdrawal of morphine; he was a man of good standing in his community. The patient, while not psychotic, tended toward hypomania; he was a salesman. He claimed that morphine depressed him.

Table XI shows how the dosage of morphine was reduced, and the amounts of sodium rhodanate that were given during the withdrawal period. The data in this table play an important rôle in the elucidation of some of the later events.

TABLE XI

Date	Grains Morphine	Grams NaCNS	Date	Grains Morphine	Grams NaCNS
1-19-32	4	0.00	1-23-32	5/8	4.00
1-20-32	3½	1.00	1-24-32	0	0.00
1-21-32	2	2.33	1-25-32	0	0.33
1-22-32	1	3.33	1-26-32	0	0.67

January 19, 1932.

During the night the patient had a chill which lasted but a few seconds. After sleeping poorly, he awoke in an irritable frame of mind. He had a low fever, and was somewhat delirious. In the morning he refused a bath and refused nourishment. Throughout the morning the patient complained of feeling chilly. At 10:00 a.m. he complained that he ached all over his body.

At noon he had worked up a fever of 102°F. Upon examination his chest was normal. He was somewhat apprehensive during the day. These observations are given in order to demonstrate the great degree of suggestibility, and impatience of the patient. Nothing more was seen of the chill reaction. He was nervous and restless when the administration of morphine was delayed for one hour, in the evening.

January 20, 1932.

The patient slept better during the night than he had through the previous night. He was nervous and irritable when he awoke, although he was brighter than he had been. The administration of morphine was regulated so that it was given at 6 a.m., 11 a.m., 4 p.m., and 10 p.m. He was irritable and restless when he was taken to the basal metabolism room instead of being given his breakfast. The basal metabolic rate was +13%. Like many morphine addicts, the patient smoked incessantly. In the evening he became restless and irritable again; but, on the whole, the patient passed an easier day. Fifteen grains of sodium rhodanate were given at 11:00 p.m.

January 21, 1931.

During the night, the patient slept more soundly and longer than he had in years. He was given eight ounces of magnesium citrate solution at 6:00 a.m. An hour later ten grains of sodium rhodanate were administered. Slight nervousness and yawning were observed during the morning; the patient was comfortable, nevertheless. The pupils of the eyes were not so contracted as they had been. It was obvious that he was used to being waited upon, and expected it. Five grains of sodium rhodanate were given at 11:00 a.m.

Except for some nervousness and excitement at 3:30 p.m., one-half hour before his dose of morphine was due, the day was uneventful. During the early evening the patient slept at intervals. From 9:00 until 10:00 p.m. he was slightly nervous. At 11:00 p.m. fifteen grains of sodium rhodanate were administered; fifteen minutes later the patient was sleeping soundly.

January 22, 1932.

At 2:10 a.m. the patient awoke, and complained of feeling chilly and of a pain in his abdomen. His skin was covered with perspiration. Ten grains of sodium rhodanate were given at 2:30 a.m. to combat these symptoms. At 2:40 a.m. the patient was sleeping soundly. He passed a comfortable night. Five grains of sodium rhodanate were given at 8:00 a.m., at which time the patient was irritable, and refused to have a basal metabolism test.

Relatives of the patient gave out the information that he always had to be humored even during very minor physical upsets; at the least sign of a physical disturbance he was prone to consult a doctor. The patient said that care must be taken that he should not vomit during the withdrawal; for it would be impossible to stop if it once got started.

In the fore-noon the patient said that he ached slightly all over, the most pronounced ache was in the back. The pupils of his eyes were dilated somewhat, for a brief period around ten o'clock. At noon he said that he felt badly all over; he smiled broadly as he made this statement. There was not a great deal of hyper-motor activity. The patient claimed that he could feel distinctly the quieting effect of sodium rhodanate.

At noon five grains of sodium rhodanate were administered. The patient slept from one until two o'clock. Several times during the afternoon he complained of pains in the legs, back, and neck. Five grains of sodium rhodanate were given at 5:00 p.m. The impression was that any suffering that there was, was largely mental.

The patient was restless and irritable during the evening. To combat this ten grains of sodium rhodanate were used at 8:10 p.m. At eleven o'clock the patient was given fifteen grains of sodium rhodanate; he slept from that time until 2:20 a.m.

January 23, 1932.

At 2:30 a.m. the patient awoke, and complained of feeling cold. When given sodium rhodanate (five grains) he vomited immediately. The patient then proceeded to try to make good on his prediction that there would be trouble should he start vomiting. Amidst a good deal of hyper-motor activity which resulted in various gyrations he tried to vomit without result. These antics lasted for about one-half hour, following which one-eighth of a grain of morphine at 3:10 a.m. quieted him somewhat. At this time he refused sodium rhodanate, claiming that it made him sick. During the early hours of the morning, he was rather disconsolate. He talked constantly and loudly; he did not complain of pain. The patient was quite determined to have his own way. Fifteen grains of sodium rhodanate were administered at 6:30 a.m.; he became quieter then. The patient's appetite for breakfast was very poor.

At eight o'clock he complained of pain in the back, legs, and back of the neck. There was no evidence of suffering. At times he felt nauseated. The patient slept at intervals throughout the morning. Eight ounces of magnesium citrate were given at 11:30 a.m. When sterile hypodermic injections were made at the hours that morphine was due, a little novocaine was dissolved in the water. Fifteen grains of sodium rhodanate were given at 12:30 p.m.; at the same time ten grains of sodium bicarbonate were administered in order that the sodium rhodanate should not upset the stomach so much. His appetite was poor at noon.

During this day, and the day before, the patient smoked less than he did previously. In each one of these cases it has been noticed that the patients smoke progressively less for a period of about two weeks. There are considered to be two factors involved in this. In the first place the sodium rhodanate quite evidently makes the cigarette smoke taste bad. Secondly the patients become less nervous, except for about a day, which brings about a reduction in the amount of smoking.

Between one and two o'clock the patient was very irritable and restless; there was a good deal of hyper-motor activity. The last administration of sodium rhodanate, when viewed in retrospect, appeared to excite him somewhat. He walked madly up and down the corridor, refused to listen to reason, and declared that he wanted either to die or continue taking morphine. He said that the treatment was not helping him. Careful observation by several people failed to detect any signs of physical suffering; at no time, from this date on, was physical suffering a part of the picture, so far as could be determined. On the other hand, there is no question but that he was mixed up mentally to quite a considerable extent.

The patient's back was rubbed for one-half hour between 2:00 and 2:30 p.m. This quieted him so that he dozed for about one-half hour. Had there been much physical distress, that effect probably would not have been produced. At 3:30 p.m. fifteen grains of sodium rhodanate were given. This precipitated delirium within an hour; the patient became very restless and nervous. At times he screamed, largely to attract attention to himself. He threw himself around, and refused to stay in bed.

Between six o'clock and midnight he vomited yellow fluid four times. The patient was not maniacal or hard to restrain; he became quiet when spoken to authoritatively. At the same time he attempted to demonstrate that he was uncontrollable, which was not the case. At 6:00 p.m., and again at 7:20 p.m., he was given one-eighth of a grain of morphine. The quieting effect was noticed. At 10:30 p.m. ten grains of sodium rhodanate were given. The delirious condition lasted throughout the night.

January 24, 1932.

Two compound cathartic pills were administered at 12:30 a.m., immediately following which the patient had a liquid bowel movement. Later in the morning, there was another liquid bowel movement. During the early morning, the patient was very noisy. Twice he complained of tenderness in the abdomen. At 5:00 a.m. tetanic twitches began, and became pronounced. This phenomenon has been explained already. It is worthy of note that none of the patients treated by sodium rhodanate were bothered by the twitches; none of them ever complained about it. He vomited again at 8:00 a.m.

Except at short intervals, the patient was not rational all day long. From noon until two o'clock he slept in very short naps. After that, until seven o'clock, he became progressively quieter. Several times during the day and evening he told those attending him to leave him alone, and not bother him. From 9:00 p.m. until 10:00 p.m. and from 11:00 p.m. until midnight the patient slept at short intervals. These periods were interspersed with periods of restlessness. During the evening he was more rational than he had been. No sodium rhodanate was administered during the twenty-four hour period.

January 25, 1932.

During the early morning, the patient slept for four hours. He was less irrational and restless than he had been. He vomited again at 8:30 a.m., and then slept soundly for an hour. After being more or less irrational all morning, he quieted down and cleared at about 2:00 p.m. The patient was rather quiet all afternoon.

The patient was given five grains of sodium rhodanate at 8:10 p.m. He was restless after that, and complained that he was very ill and going to die. He jumped up and down, and moved about a great deal in the bed. He was disagreeable; in a half-hearted attempt to find his way out, he ran up the hallway. Except for brief intervals, the patient was irrational all night long. It should be emphasized again that no physical suffering was observed by those attending the patient. Twice before midnight he asked for morphine. He and one other patient were the only ones who asked for morphine after the withdrawal.

January 26, 1932.

He did not sleep much during the night; he was very restless, and at times disagreeable. The delirium persisted. Around eight o'clock in the morning the patient became rational. During the rest of the morning he was quieter than he had been. He continued to be quiet all afternoon. He was given five grains of sodium rhodanate at 12:40 p.m.

In the afternoon the patient complained of feeling weak all over. All of the patients that have been treated by this method have complained of feeling weak. This is not due to loss of weight, lack of nourishment, or lowering of the blood pressure; because there generally has not been an excessive loss of weight, lack of nourishment, or drop in blood pressure. It may be due to a rapid reversal of the colloids of the nervous system.

At 10:00 p.m. the patient was given five grains of sodium rhodanate. He passed a quiet night.

January 27, 1932.

The patient slept practically all night long. In the morning he said that he did not care to talk because he had had a nervous disease. He was given five grains of sodium rhodanate at 7:00 a.m. and again at 2:00 p.m., and ten grains at 10:00 p.m.

Aside from short periods of restlessness, nervousness, and forgetfulness the day and evening were uneventful. His appetite was good.

January 28, 1932.

There was no lack of sleep during the night. The patient complained of aching legs at 6:00 a.m., and asked for sodium rhodanate ahead of time.

Five grains were given. His appetite continued to improve. Five grains of sodium rhodanate were given at 2:00 p.m. He was slightly nervous and restless at times during the day. Physiotherapy was employed to combat the ache in the legs of which he complained. For three days, despite the report of nervousness, the patient was able to hold his arm and hand extended with less tremor than could those attending him.

Fifteen grains of sodium rhodanate were given at 10:00 p.m. There followed six hours of practically uninterrupted sleep.

Thus, nine days after entering the hospital the patient appeared to be in pretty good condition. The mental reaction to the withdrawal was more severe than in Case 1; but the physical symptoms were no more marked, despite the fact that this patient was less stoical than Case 1. It seems evident that he was withdrawn somewhat too rapidly for the maximum ease. Perhaps the delirium, in this case particularly, can be regarded as an expression of the irritability through which living tissue goes upon agglomeration, and again upon return to normal. Since the rhodanate ion probably forces the morphine off of the tissues more rapidly than it would come off in gradual withdrawal alone; an accentuated irritability might result. Much the same thing has been observed with rabbits in their reactions to sodium amytal and ether.[1] The rabbits were much more intoxicated when forced rapidly out of the anesthesia by sodium rhodanate.

January 29, 1932.

After passing a comfortable night, the patient complained of a backache. He was uneasy and his appetite was poor. Five grains of sodium rhodanate were given at 7:00 a.m.

At this point, the reactions of the patient again assume real importance; for later events showed that he was forced into a psychosis as a result of over-dispersion with sodium rhodanate. At 10:00 a.m. he expressed dissatisfaction with hospital life. Five grains of sodium rhodanate were given at 2:00 p.m. Shortly thereafter he became very nervous.

In the evening his appetite was good. Later he became restless and manifested constant motor activity. Five grains of sodium rhodanate were given at 10:00 p.m. He slept for about seven hours thereafter. He cried out in his sleep once.

January 30, 1932.

Upon awakening in the morning the patient was very nervous. Five grains of sodium rhodanate were given at 7:00 a.m. He was restless during the morning. At 2:00 p.m. he was given ten grains of sodium rhodanate. While playing cards in the afternoon he did not bother to wait for the opponents to put their cards on the tricks.

In the evening at eight o'clock fifteen grains of sodium rhodanate were administered. Constant motor activity followed. He became more nervous and talked irrationally at times.

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[1] Bancroft and Rutzler: J. Phys. Chem., 35, 1185 (1931).

January 31, 1932.

He slept at intervals during the night, and cried out several times. During the early morning hours he was irrational most of the time. Ten grains of sodium rhodanate were administered at 7:00 a.m. In the forenoon he was nervous, irrational, and manifested constant motor activity. He complained that he was not being given any medication; he refused to eat dinner until sodium rhodanate was administered. He was given seven grains of the medicine at noon; after which he ate well. Ten grains of sodium rhodanate were given at 2:00 p.m.

In the evening the patient seemed quite confused at times; he was very nervous, talked incoherently, and forgot where his room was. At 8:00 p.m. fifteen grains of sodium rhodanate were given. Illusional episodes were observed, in that he heard low voices speaking in another room to someone else and thought that he was being addressed.

February 1, 1932.

The patient fell out of bed at 12:30 a.m. without being injured. The constant motor activity was in evidence at 1:00 a.m.; he was unable to answer questions coherently. Later in the norning he became noisy. He did not sleep much during the night. Throughout the morning the patient was irrational. He asked for sodium rhodanate frequently. Systematized delusions of persecution appeared. He talked about signing papers and about different people coming to see him. After becoming more irrational as the morning progressed, the patient jumped out of a window, despite a snow storm, clad only in his pajamas and a bathrobe. He ran into the entrance of the hospital, some eighty yards distant, calling for the police. He said that he came back into the hospital because he knew that he would be caught. The patient continued to be irrational.

It was realized then that the patient had been over-peptized and that a definite psychosis had developed therefrom. This was not the cause for very much concern because from previous work with functional psychoses[1] the use of an agglomerating agent was indicated. At 12:30 p.m. the patient was given six grains of sodium amytal in capsules by mouth to produce agglomeration. Shortly thereafter he began to scream and to talk constantly. At 3:00 p.m. he was still noisy and restless. At this time he refused sodium amytal claiming that he was being given poison.

Six grains more of sodium amytal were given at 5:00 p.m. This quieted him somewhat; he slept from seven until nine o'clock. The patient was restless and noisy in his sleep after eight o'clock. By 9:20 p.m. he was awake, irrational, and talking constantly. At eleven o'clock he was becoming uncontrollable. Six grains of sodium amytal were given at 11:30 p.m. He went to sleep at midnight.

February 2, 1932.

The patient slept until 2:30 a.m. He then became restless and very noisy. At 2:45 a.m. he was given six grains more of sodium amytal. It is

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[1] Lang and Paterson: J. Phys. Chem., 35, 3425; Bancroft and Rutzler: 3452 (1931).

well to point out here that despite the fact that the sodium amytal did not appear to be helping much, the firm conviction was held that agglomeration was indicated. With that in mind the sodium amytal was continued, and given to effect. At just such a juncture as this one could have fallen down completely by discontinuing the sodium amytal. The theory called for dosage to effect, and that procedure was followed.

The last of the sodium amytal kept the patient asleep until 6:50 a.m. When he began to become restless again, six grains more of the agglomerating agent were administered. Needless to say, fluids were kept up during this time. He was quiet until after 11:00 a.m.; he then became noisy. Three grains of sodium amytal were given at 11:50 a.m. He was restless again at 2:00 p.m.; so three grains more of the drug were administered. This kept him semi-conscious or asleep until midnight. He muttered a great deal during this time.

It took thirty-six grains of sodium amytal to keep the patient asleep for thirty-six hours. That being a rather large amount, would seem to give a quantitative measure of the over-dispersion that was produced by the sodium rhodanate.

February 3, 1932.

At 12:10 a.m. the patient was awake and screaming. Following that he was rational for a short time. He slept at intervals until 7:00 a.m.; another rational spell was observed at 3:10 a.m. The night was less stormy.

During the day the patient was restless at times and rational most of the time. He exhibited the definite delusion that the men attending him were police officers, and that there was a machine gun being aimed at him from the closet.

At noon a switch was made to another agglomerating agent, ipral; three grains were given by mouth. This was repeated at 11:00 p.m. It is interesting to note the paranoid coloring to this psychosis, which was characterized by over-dispersion. That agglomeration of certain centers, and also peptization, perhaps of other centers, gives rise to paranoid symptoms seems evident. Sodium rhodanate produces these symptoms by peptization. Also, morphine produces them by agglomeration. Finally, sodium rhodanate decreases the symptoms of dementia praecox paranoid, an agglomerated condition, but produces much the same symptoms when too much is used. This must mean that paranoid symptoms occur both in over-agglomeration and in over-dispersion. It is probable that cases will be found, which will be classified as dementia praecox paranoia, and which will respond favorably to treatment with sodium amytal.

February 4, 1932.

The patient slept well during the morning hours, and was much more rational at 8:00 a.m. Three grains of ipral were given at 7:45 a.m. and 10:15 p.m.; and one and one-half grains were given at 11:45 a.m.

During the afternoon the delusional field suddenly vanished completely, and the psychosis was at an end. The patient, curiously enough, was able to relate in detail all of his experiences since the last day that he had morphine.

From that point on, the patient improved very rapidly. The course was uneventful. His appetite became very good; his outlook was excellent and he was not nervous. There were no further signs of the psychosis. His irritability disappeared. At bed time on February 5, and 6, he was given one and one-half grains of ipral to ensure his sleeping. The drug was discontinued then. Iron, quinine, and strychnine was administered as a tonic. On February 15, the use of sodium rhodanate was recommenced. Five grains were given each night to help the patient sleep and to combat any nervousness that might arise.

As was usual with the cases reported in this paper, the patient complained of feeling weak. Exercise and food combined to eradicate that difficulty. The extreme jealousy of his own comfort seemed to disappear at least a week before the patient was discharged. All of the nervous tension disappeared from his face; and he was contented to stay in the hospital until told that it was advisable to go home. The patient was discharged on February 20 with instructions to report at times, and to combat any nervousness or sleeplessness by the use of small amounts of sodium rhodanate.

On March 20 the patient was interviewed and found to be in excellent condition physically, and mentally. On April 26 the patient was well, and in a happy frame of mind. There was apparently no need or desire for morphine. He even found that it was not necessary to use sodium rhodanate at that time. On June 18th the patient was well and not using morphine.

Table XII contains the blood pressure and weight variation data that were taken. As can be seen there was no significant change in the blood pressure. The patient lost only eight pounds during the treatment. That is not significant in view of the length of time that he was in a delirious state. The weight was regained fairly rapidly.

TABLE XII

Date	Blood Pressure	Weight in Pounds	Date	Blood Pressure	Weight in Pounds
1-19-32	115/80	141.5	1-30-32	—	133.5
1-20-32	115/70	141.0	2-18-32	—	147.0
1-21-32	105/80	140.0	3-20-32	—	160.0
1-22-32	105/70	140.0	4-26-32	—	167.0
1-27-32	125/78	—			

Data on the kidney function are given in Table XIII. Here as in Case 1 the function became very low after two days. That this is not an artefact of technique seems more certain, in view of finding it again.

TABLE XIII

Date	cc. Urine First Hour	cc. Urine Second Hour	% of Dye eliminated First Hour	% of Dye eliminated Second Hour	Total % of Dye eliminated
1-19-32	180	50	88	9	97
1-21-32	140	15	30	2.9	32.9
1-22-32	90	85	65	15	80

Urinalysis data are presented in Table XIV. Here again one finds a preliminary drop in the specific gravity, followed by a rise. Toward the end of the fall the urine became alkaline. There was then a rise in the specific gravity which was probably due to the same causes as were mentioned in the study of Case 1. When the sodium rhodanate was stopped the specific gravity fell again.

TABLE XIV

Date	Appearance	Reaction	Sp. Gravity	Albumin
1-19-32	straw-amber	acid	1.026	Negative
1-21-32	cloudy straw	acid	1.016	Negative
1-22-32	cloudy amber	alkaline	1.015	Negative
1-23-32	cloudy straw	alkaline	1.029	Negative
1-26-32	cloudy straw	acid	1.035	Negative
2-1-32	cloudy amber	acid	—	Negative
2-2-32	cloudy amber	acid	1.020	Faint trace
2-3-32	cloudy amber	alkaline	1.019	Faint trace
2-4-32	cloudy straw	alkaline	1.009	Negative
2-5-32	cloudy amber	acid	1.011	Negative
2-6-32	clear straw	acid	1.012	Faint trace
2-7-32	clear amber	acid	—	Negative
2-8-32	clear straw	acid	1.025	Faint trace
2-9-32	clear straw	acid	1.023	Negative
2-10-32	clear straw	acid	1.020	Negative
2-11-32	clear straw	acid	1.024	Negative
2-12-32	cloudy amber	acid	1.028	+
2-12-32	clear amber	acid	—	Faint trace
2-15-32	cloudy amber	acid	1.030	Faint trace
2-16-32	clear straw	acid	1.020	Trace

The data seem to show that when agglomerating agents were in the body with the peptizing agents the specific gravity fell. This may be because the peptizing agents were being utilized to a greater extent at that time.

In Table XV are found the hematological data. As in Case 1, the total white cell count was normal with a relative lymphocytosis at the start of the treatment; then a polymorphonuclear leucocytosis developed, and shifted to a lymphocytosis as the number of white blood cells decreased.

TABLE XV

Date	W.B.C.	Polys.	Lymps.	Monos.	Eosins.	Basos.
1-20-32	6,650	64%	35%	1%	—	—
1-21-32	7,900	60%	36%	4%	—	—
1-22-32	7,000	56%	43%	1%	—	—
1-25-32	15,000	80%	17%	3%	—	—
1-26-32	14,000	63%	34%	3%	—	—
1-29-32	10,800	59%	39%	2%	—	—

Psychological tests were given to the patient at various times. The data on the test of crossing out the letter "O" are given in Table XVI. As morphine was withdrawn the patient was slower at crossing out the letter "O" and more accurate. After rehabilitation he was much faster, and at the same time less accurate. On January 19th the test was given before a dose of morphine was due; and on the 20th just after a dose of morphine was given.

TABLE XVI

Date	Number of O's	Number missed	% Accuracy	Time in Seconds
1-19-32	50	2	96	130.8
1-20-32	50	0	100	140.0
1-22-32	50	1	98	143.4
3-20-32	50	3	94	98.8

The dictation test was given to the patient also. From Table XVII it can be seen that there was no severe disturbance, resulting from the withdrawal of three-quarters of the morphine under the influence of sodium rhodanate. Upon rehabilitation, the patient performed the test better in all respects.

TABLE XVII

Date	Space taken in lines	Number of words	Number of mistakes	Time in seconds	Remarks
1-19-32	30.5	84	1	176.2	Writing hardly legible
1-20-32	29.5	84	1	159.8	Writing more legible
1-22-32	31.25	84	4	180.0	Writing hardly legible
3-20-32	27.5	84	0	155.2	Writing legible

A word-association test was given to the patient. The test contained fifty words; an attempt was made to include about ten key words. It was often found that the patients reacted to words that were not meant to be key words. The reactions and time of response to each word were taken. The data are presented in Table XVIII. The words that were not associated well and those that took a longer time to associate are given in the table. It is interesting to note that as the treatment progressed, the patient performed the test more rapidly. The word morphine did not stir the patient up much after the treatment began. After rehabilitation it did not bother

TABLE XVIII

Date	Word	Response	Time in Seconds	Sum in Seconds of Times for 50 Words	Remarks
1–19–32	Woman	Table	3.0	103.3	No response to such words as: Knife Murder Suicide Syringe Home Prison Hospital
"	Morphine	Amytal	13.8		
"	Children	Woman	2.8		
"	Addict	Morphine	2.2		
"	Hotel	Langwell	5.0		
"	Doctor	Fakir	2.4		
"	Road	Rose	1.8		
"	Cuff	Leather	1.8		
1–20–32	Drawer	Box	2.0	83.	The word morphine elecited no special response, nor did the words Hotel and Woman
"	Addict	Morphine	2.0		
"	Water	Faucet	2.2		
"	Prison	Auburn	2.8		
"	Robe	Fur	2.0		
"	Intercourse	Yes	2.2		
"	Shield	Steel	2.0		
"	Tray	Platter	2.0		
"	Salesman	Bonds	2.2		
"	Hospital	Nurse	2.0		
"	Cocaine	Dope	1.8		These two words followed in order
"	Brace	Foot	2.3		
1–22–32	Line	String	2.2	84.6	Word after Woman
"	Morphine	Dope	2.4		
"	Bed	Pillow	4.8		
"	Intercourse	Up	2.6		
"	Doctor	Medicine	1.4		
"	Insane	Crazy	1.0		Very rapid
"	Cocaine	Dope	1.2		These three words followed in order
"	Brace	Get up	3.2		
"	Wire	Steel	1.0		
2–20–32	Morphine	Dope	1.2	77.8	
"	Woman	Man	1.2		
"	Faucet	Water	1.0		Very rapid
"	Drawer	Box	2.0		
"	Prison	Convict	2.0		
"	Hotel	Meals	2.4		
"	Doctor	Physician	1.4		These three words followed in order Again there is a mix-up caused by cocaine
"	Hospital	Sick	2.0		
"	Cocaine	Dope	1.5		
"	Brace	Iron	2.8		

him at all. On the other hand, the word cocaine gave rise to a delayed reaction every time that it was given. That brings up the question of his delirium, which was the longest one that any patient has had. Cocaine addicts often go into a delirium when they are withdrawn. When he was admitted, this patient was injecting a solution about which there was some mystery. He said at the time that it might have contained cocaine. The association test indicates that cocaine was on his mind. So, the delirium upon withdrawal (but not the psychosis which followed) may have been due to cocaine.

In summary, the only ordinary withdrawal symptoms that the patient exhibited were: vomiting, restlessness (hyper-motor activity and nervousness), loss of weight and appetite, twitches, and aching in the back and legs. The aching and vomiting were the only things that bothered him. After he had cleared from the psychosis he said that he did not suffer during withdrawal. He did not smoke much after the morphine was withdrawn. Everything considered, the prognosis seems good.

Case 3, C. B.

This patient was a physician, 48 years of age, who had been using morphine for about six years. When admitted to the hospital on January 24, he said that he was using four grains of morphine every twenty-four hours. He became addicted to morphine in an attempt to break an alcohol habit. He claimed to have withdrawn himself once, but was not able to refrain from using morphine for any length of time.

Upon admission to the hospital, the patient's belongings were taken from him, and a special nurse assigned to the case. It became evident in a short while that he was not a normal person in other ways than would be accounted for by morphinism. He was five feet eight inches high, and weighed 190 pounds. His countenance, while inclined to be jolly at times, more often was expressionless. The patient said that he was well-to-do. Later information showed that his financial status was not good, although it had been. Though he made no attempt to cover his identity, he said that he lived in one city, whereas actually he lived in another a hundred miles away. It was difficult to elicit information from him; and when it was forthcoming one often wondered whether or not it was accurate. Although he was a physician, and said that he was immediately upon arrival, he did not appear to be conversant with common medical terms and remedies. All efforts to make him talk on such subjects failed consistently; because he claimed generally that the things spoken of were not familiar to him.

A physical examination revealed several interesting things. His nutrition was adipose. There was considerable adipose tissue around the lower part of the face, neck, and limbs. The pupils of his eyes exhibited a sluggish response to light and accommodation. There was an ulcerated, necrotic sore on the right thigh measuring about two by three inches, and more than one-quarter of an inch deep. The origin of this could not be determined. At first the patient claimed that it came as a result of an automobile accident.

A month or so later, he said that it was the result of an injection of potassium cyanide. This gives something of a picture of the mental condition of the patient. The teeth were regular but a spacing between them was noticed. There was an extensive chronic gingivitis and expressed pus in various places. The nasal mucous membranes were somewhat congested. His tongue was heavily coated and extended in the mid-line with a very slight tremor. His fauces and pharnyx were slightly congested.

The patient was of the eunuchoid type, as shown by the hair distribution on his body, very small genitals, and the formation of breasts. When excited his voice reached a high pitch. The pubic hairs ended abruptly. The hair on his head was thin; but he had a normal beard. There were folds of fat on his wrists; and he was heavy jowled. About ten years previously he suddenly gained a good deal of weight which he did not lose.

The plan for this experiment was altered from that of the previous two. It was decided to reduce his dosage of morphine to about half of what it was upon admission to the hospital, and attempt to keep him comfortable for a few days with small amounts of sodium rhodanate. Table XIX shows how the morphine dosage was reduced, and the amounts of sodium rhodanate used.

TABLE XIX

Date	Grains Morphine	Grams NaCNS	Date	Grains Morphine	Grams NaCNS
1-25-32	1.50	0.00	1-29-32	0.25	2.33
1-26-32	2.25	0.67	1-30-32	0	3.33
1-27-32	2.00	2.33	1-31-32	0	2.00
1-28-32	1.50	2.67	2- 1-32	0	1.00

January 25, 1932.

In the morning the patient had a good appetite, and no complaints. He passed a fairly comfortable day. From 10:30 p.m. until midnight he was very restless. A headache bothered him during this time, also.

January 26, 1932.

The patient did not sleep until after 2:00 a.m., when one-half grain of morphine was given. He then slept for about four hours. From the restlessness on January 25, it was decided that a reduction in the morphine from four grains a day to one and one-half grains was too much. That is why the dosage was increased on this day. As a result of the increased dosage, the patient passed a more comfortable day. Ten grains of sodium rhodanate were given at 10:00 p.m. in an effort to help the patient sleep. Two Alophen tablets were given at 8:00 p.m.

January 27, 1932.

Five grains more of the sodium rhodanate were administered at 12:30 a.m. Despite the peptizing agent, the patient was very restless and unable to sleep. To one inexperienced in sodium rhodanate therapy the two nights of restlessness and little sleep would indicate that the method of treatment was falling down. There might be a strong tendency, in some quarters, to let the matter go at that. The successful use of sodium rhodanate requires both a thorough knowledge of the theory upon which it is based, in addition to a touch of "scientific backbone." With that in mind the case was carried on, giving sodium rhodanate to effect. While the restlessness was not very great, still it was not desirable to encounter it so early in the withdrawal. This indicates some of the difficulty that one might have upon attempting abrupt withdrawal with the help of sodium rhodanate. The peptizing agent is not so efficient in its function as morphine is as an agglomerating agent. It seems probable from these considerations that a high concentration of sodium rhodanate must be built up in the system before it becomes a useful aid in combatting withdrawal symptoms. Reference to the adsorption isotherm, pictured in any good book on colloid chemistry, will make this point clear. Therefore it would be inadvisable to attempt to commence medication and abrupt withdrawal coincidentally.

The patient was given one-half of a grain of morphine at 6:30 a.m.; that was followed by five grains of sodium rhodanate. He refused breakfast although he had no complaints other than being tired and sleepy. One-half of a grain of morphine was administered at 11:05 a.m.; following that five grains of sodium rhodanate were given. At 4:00 p.m. one-quarter of a grain of morphine was given, followed by five grains of sodium rhodanate.

He passed a quiet, comfortable day, except for the early morning, and an hour between 6:30 and 7:30 p.m., during which he was restless and nervous. He was fairly quiet at the latter hour. At 8:00 p.m. he complained of pain around the heart. He became nauseated, and vomited undigested food at nine o'clock. Following that, he was more comfortable. Ten grains of cascara were administered at 9:20 p.m. By ten o'clock the patient was very quiet and asked that his morphine hypodermic be delayed. Fifteen grains of sodium rhodanate were administered at this time. One-half of a grain of morphine was given at 10:45 p.m. At 11:30 p.m. he was quiet, but was not able to sleep.

It was found that the patient was exceptionally suggestible. The mental peculiarities that were noticed in the pre-treatment study were not changed at this time. He said that he did not feel the morphine "take hold" as it used to; but it quieted him, nevertheless.

January 28, 1932.

From 2:30 to 5:30 a.m. the patient slept lightly at intervals. He was somewhat restless after that. He slept very little; at the same time he was not nervous or restless until 5:30 a.m. At 6:30 o'clock one-half of a grain of morphine was given, followed by ten grains of sodium rhodanate. At nine o'clock in the morning he appeared to be very comfortable. He was given one-quarter of a grain of morphine, and five grains of sodium rhodanate at 1:00 p.m. Ten grains more of the peptizing agent were given at 4:00 p.m. The patient was comfortable and had no complaints throughout the day and evening except those that are indicated. At supper time his appetite was poor. He vomited at 5:30 p.m. One-quarter of a grain of morphine was administered at six o'clock. Near midnight the patient's face became slightly flushed. He did not feel sleepy at this time.

At 9:30 p.m. he was given two Alophen tablets. One-half of a grain of morphine was administered at ten o'clock; this was followed immediately by fifteen grains of sodium rhodanate.

January 29, 1932.

At times during the night, the patient was very restless. He was quiet the greater part of the night. Like many people using really large doses of sodium rhodanate, he complained of having bad dreams. From 5:45 to 7:00 a.m. he perspired moderately when awake. The patient took the regular hospital diet in the morning and at noon.

Despite a substratum of apprehension the patient was comfortable until 4:30 p.m. when he complained of nausea. He did not eat heartily at 5:00 p.m. The patient had no special complaints at 6:00 p.m.; after having spent most of the day in bed. He vomited once, shortly after six o'clock. During the early part of the evening he was very nervous. After 10:15 p.m. he quieted down, and was fairly comfortable. At no time did he thrash around in bed. He did not become nervous to the extent of exhibiting hyper-motor activity. After 11:30 p.m. he slept at long intervals.

The medication for the day was as follows: ten grains of sodium rhodanate at 11:00 a.m. and 4:00 p.m., and fifteen grains at 10:00 p.m., one-quarter of a grain of morphine at 6:30 p.m.

January 30, 1932.

At 3:30 a.m. the patient awoke suddenly, and was confused. He comcomplained that it was difficult to walk. He exhibited difficulty in holding a glass while drinking. He moaned in his sleep. Ten grains of sodium rhodanate were given at 3:30 a.m. He complained of abdominal cramps during the early morning. Upon awakening at six o'clock, he was confused and irritable, but not nervous. Ten grains of sodium rhodanate were given at 7:00 a.m.

The patient ate fairly heartily at 7:30 a.m., and then slept at intervals for about an hour. At nine o'clock hallucinations of sight were evidenced. He talked, in a quiet way, a good deal about women and millionaires. Definite delusions of grandeur were exhibited. The patient seemed confused until 10:00 a.m. He was given ten grains of sodium rhodanate at eleven o'clock. He refused the regular diet at noon.

The patient was not nervous or restless all day long. He stayed in bed, and had very little to say. There were no signs whatever of distress. Five grains of sodium rhodanate were given at 4:00 p.m., and fifteen grains at 10:00 p.m. The afternoon and evening were uneventful; the patient was rational and quite cheerful at 11:00 p.m.

January 31, 1932.

He slept from 12:30 until 3:00 a.m.; he moaned and talked a great deal during his sleep. At three o'clock he awoke dazed, irrational and irritable.

He was unable to stand when out of bed. An involuntary bowel movement occurred at this time; another occurred an hour later. Considerable mucous accompanied both movements. The patient slept quietly from 4:30 to 7:00 a.m., at which time there was another involuntary bowel movement. Five grains of sodium rhodanate were given, at this time. He refused nourishment until noon. The patient slept quietly off and on throughout the morning.

The delusions and hallucinations of sight persisted. When asked if he knew that he was having involuntary bowel movements, he replied that he did. He stated that he knew beforehand when they were coming; but he did not care enough to call the nurse. The patient was lethargic and had been more or less so for some time prior to this treatment. He talked very little during the day; he refused to swallow medication (sodium rhodanate, five grains) at 4:00 p.m.

The patient was quiet throughout the day. There were some muscular twitches about which he did not complain; but he was not nervous or restless. There was another "involuntary" bowel movement during the evening. The word involuntary is put in quotation marks because the act appeared to be due more to laziness and apathy than to loss of sphincter control. Fifteen grains of sodium rhodanate were given at 10:00 p.m. By 11:30 p.m. he was asleep.

February 1, 1932.

From 12:30 to 3:00 a.m. he talked constantly, and was very much confused. He did not sleep much during the night; but he was neither nervous nor restless. During the early morning the confusion seemed to come in waves. The patient was given five grains of sodium rhodanate at 7:00 a.m. He refused it during the rest of the day, along with other medication and food. The patient was quiet throughout the day. There were no complaints. He was not normal mentally. He only had one "involuntary" bowel movement. He did not want anyone to talk to him or disturb him in any way.

February 2, 1932.

Another "involuntary" bowel movement occurred at 2:40 a.m. He slept quietly at long intervals during the morning hours. Except that he seemed slightly more rational in the morning, his condition was unchanged. From the beginning of the psychotic condition, for several weeks the patient refused to feed himself. His appetite was better on this day.

At about 9:30 a.m., the patient had a ten-minute sinking spell. His pulse became slow and weak, and his lips cyanosed. The pupils of his eyes were dilated. This occurrence did not take place again.

It was noticed that the patient seemed frightened at times, about 4:00 p.m. Shortly thereafter he said that he was going to jump from an airplane. This was in the midst of confusion which continued unabated during the day. The patient was unquestionably suicidal, as he had been before treatment (the avowed injection of potassium cyanide). There was an "involuntary" bowel movement at 9:00 p.m. He said that he was going to die, for several days.

After a consultation with a psychiatrist concerning the condition of the patient, it was decided that there were three possibilities. Over-peptization with sodium rhodanate might have accounted for the mental symptoms. On the other hand, the patient might have had a brain tumor. The third possibility was that the psychotic condition might have been due to the misfunction of the endocrine glands. The first possibility had in its favor the fact that the patient had been given large amounts of the peptizing agent; and other patients had gone that way. Against that hypothesis was the fact that in the two days preceding this one, sodium rhodanate did not make the condition worse. Also, the psychotic condition was not typical of those that have been observed as the result of over-dispersion. Delusions of persecution were not a large part of this picture, while delusions of grandeur were. No motor excitement accompanied the condition. The possibility of a brain tumor was ruled out largely from the fact that an X-ray study revealed nothing; in this study an examination of the skull in both right and left lateral position revealed a normal sella turcica. A Wassermann test was negative. Table XX shows the result of a blood examination. The data reveal no abnormalities.

TABLE XX

Factor	Mg. per 100 cc. Blood	Normal Values Mg./100 cc. of Blood
Sugar	110	90–120
Urea Nitrogen	7.7	7–15
Calcium	9.8	9–11.5

The third of the above possibilities was suggested by the fact that the man was of the eunuchoid type. Several things were noticed in the physical examination (which see) that suggested hypopituitarism. In Table XXI are given the results of basal metabolic rate determinations. The data indicate a tendency to hypothyroidism. That left the possibilities of endocrine misfunction and over-dispersion to be investigated. The condition of the patient was considered to be due either to one or the other of these two things. It was easiest to test the over-dispersion hypothesis first. To that end, three grains of sodium amytal were given by the mouth at 10:35 p.m. He did not talk except to answer questions.

TABLE XXI

Date	Basal Metabolic Rate	Remarks
1–25–32	−19	Normal is ±10
1–28–32	+23	Patient nervous due to withdrawal
3–21–32	− 8	After attempting to raise rate.

February 3, 1932.

The patient had two "involuntary" bowel movements during the early morning hours, and another at 7:20 a.m. He slept well, however. No medication was given during this day. In the afternoon, the patient was rational at times. He would not talk except to answer questions and say irrational things. It was at about this time that he began to speak about the rays that were coming from the wall of the room. The rays carried messages to him. In addition, he stated that his abdomen was filled with helium.

There was no definite improvement in the condition of the patient.

A day by day report from this point on will not reveal enough to justify it. Therefore, a general description of the treatment and the patient's reaction will be given.

On February 4 and part of the 5th ipral and sodium amytal were given in order to make a final decision as to whether or not the patient would improve on agglomerating drugs. It should be mentioned that while the patient was able to be out of bed, he resisted efforts to induce him to do so. This was probably due to a general lethargy. Until the day that he was discharged he would always have preferred to remain inactive in bed. Later he did become more tractable and stay out of bed for longer intervals; but it always required an effort to keep him out of bed. Toward the end of his stay in the hospital, this appeared to be due more to plain laziness than anything else. No definite improvement was noticed as a result of the use of agglomerating agents.

Before making a final shift to a diagnosis of endocrinopathy, it was decided to be doubly certain that sodium rhodanate in fairly large quantities would not change the situation. Between 6:00 p.m. on February 5, and the same hour on February 8, one hundred forty grains of sodium rhodanate were administered. This had no effect other than to make the patient somewhat more irritable, and give him more sleep at night. The "involuntary" bowel movements, lethargy, and irrational condition, along with the delusions persisted, and became neither better nor worse. If the psychotic condition had been brought about by over-dispersion, or the use of sodium rhodanate, it seems fair to assume that sodium rhodanate would have made it worse. Since it did not change when fairly large quantities of the dispersing agent were given, the conclusion was drawn that it was not brought about by over-peptization. From what has been said of the case it seems apparent that the psychosis pre-dated the treatment. In all probability the starting point of the mental upset came prior to the chronic use of alcohol which latter led the patient to take morphine. In other words the drug largely covered up the mental imbalance.

It will be remembered that Lang and Paterson[1] found that it was not easy to produce changes by agglomeration and dispersion in the one endocrinopathy case that they studied. It was decided finally that this patient

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[1] J. Phys. Chem., 35, 3425 (1931).

was upset by hypothyroidism and hypopituitarism; and that it was not at the moment primarily a case to be treated by peptizing and agglomerating agents.

From the date of admission until February 4, the patient ran a fever which averaged 99° F. From the 4th to the 9th of February, his temperature averaged 98.4° F. The average was 100.2° F. from the 9th to the 16th. It went down slowly from the 16th to the 26th. The average from the 26th to the 7th of March was 99° F. From the 7th of March to the 25th the average was 98.4° F.

Treatment for the hypo-endocrine function was started on the 11th of February. Pituitary body (anterior lobe) emplets were used; four grains were administered daily until the patient was discharged. Thyroid gland emplets were administered; two grains per day were given. The patient was a little brighter by February 13; the "involuntary" bowel movements continued. The psychotic condition remained unimproved. The patient made somewhat more of an effort to help himself, however. Iron, quinine, and strychnine was given as a tonic. On the 14th of February, the patient began to perspire freely; a day later the reaction became profuse and then subsided.

By the 17th of February definite improvement was seen in the condition of the patient. No one of his symptoms had subsided a great deal, however. Some periods of restlessness were observed. The administration of thyroid gland emplets was reduced by half on February 19, and discontinued on February 20. This measure was taken because his pulse rate began to go above 100 consistently. After the 18th of February there were no more "involuntary" bowel movements. At the same time the patient became more cooperative. On the 23d and 24th of the month the patient complained of nervousness, and his mental condition was back-sliding slightly. From this time until he was discharged, one month later, three five-grain doses of sodium iodide were given daily. There were two reasons for this. In the first place stimulation of the thyroid gland was indicated; and secondly, by its peptizing action it was of use in allaying nervousness.

On February 26, the patient was somewhat brighter. He was taken for an automobile ride. The next day additional endocrine treatment was instituted. Nine "Testacoids" tablets[1] were given daily in three equally divided doses until the patient was discharged from the hospital. On the 29th he stated that he knew he was mentally upset. By March 2d the patient was decidedly more active and clearer mentally. The change was easily noticeable; and, as is evident, it came shortly after the start of the "Testacoids" medication. Daily improvement was the rule from that time on. He began to talk voluntarily; expression came into his face; he was less lethargic (although it was still difficult to keep him out of bed); and the psychosis was practically a thing of the past by the 7th of March. When asked what he was being treated for he said probably pituitary gland inefficiency. This

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[1] Reed and Carnrick Co. orchitic extract.

indicates that he knew that he had such a condition before withdrawal. When asked what he remembered after withdrawal, it was discovered that the experience was a blank in his mind. He claimed to have suffered no pain or distress during the treatment; and he was not observed to have any.

Were it not for the fact that there are people who are a bit too willing to condemn peptization therapy, no special effort would be made to establish the fact that this endocrine condition pre-existed the treatment for morphinism by quite a while.

By the 10th of March, the patient was taking a much greater interest in things. From March 8 to March 13, the patient was given Antuitrin hypodermically in place of the pituitary body emplets in order to obtain a greater efficiency from the drug. The patient began to complain bitterly that he did not care to have injections made because of his experience with morphine.

TABLE XXII

Date	Blood Pressure	Weight in Pounds	Date	Blood Pressure	Weight in Pounds
1-25-32	—	190	2-16-32	120/70	—
1-26-32	140/80	190	2-18-32	118/75	—
1-27-32	135/75	—	2-25-32	120/70	—
1-28-32	—	190	3-21-32	—	175
2-10-32	120/70	—	3-25-32	128/80	—

A shift was made to the emplets again. Despite the fifteen grains daily of sodium iodide the patient was not sleeping well at this time. From the 15th to the 20th of March the sodium iodide was augmented by ten grains of sodium rhodanate at bed-time. This allowed him to have longer and more sound sleep. Thereafter sodium rhodanate was given in ten-grain doses as needed.

The patient was discharged on March 25. At that time he was brighter and less lethargic than he was upon admission. His mind was definitely clearer than it was before morphine was withdrawn. There was a natural laziness that still had to be combatted. So far as could be determined there was no mental or physical need for morphine. He was instructed to continue the use of the pituitary extract and "Testacoids" for an indefinite period. Sodium iodide was to be taken for a few weeks, and then discontinued. Sodium rhodanate was to be used only as needed to combat sleeplessness and nervousness.

Table XXII shows the blood pressure and weight data that were taken. While these data are rather sketchy, they do illustrate several things. January 29 was the last day that the patient had morphine. On the 28th he had lost no weight. He exhibited practically no withdrawal symptoms, and his appetite did not fail until the psychotic symptoms appeared. The patient did not lose weight during the withdrawal period. Therefore, watching the patient, it was obvious that he lost most of his weight during the period when thyroid extract was being given. In fact it was planned to have him lose weight at that time. The drop in blood pressure during the treatment was probably due to the nervous relaxation afforded by the sodium rhodanate. That the blood pressure remained low indicates that there were no arteriosclerotic changes. It should be pointed out that the initial systolic pressure was the highest that has been observed in the eight cases of morphinism that have been studied.

TABLE XXIII

Date	Appearance	Reaction	Specific Gravity	Albumin
1-25-32	cloudy amber	alkaline	1.027	Very faint trace
1-26-32	cloudy straw	alkaline	1.016	Negative
1-27-32	cloudy straw	alkaline	1.017	Negative
2-1-32	clear amber	acid	—	Negative
2-3-32	clear amber	acid	—	+
2-4-32	clear amber	acid	1.029	+
2-5-32	clear amber	acid	1.030	+
2-6-32	clear amber	acid	1.030	+
2-9-32	clear amber	acid	1.030	+
2-10-32	clear amber	acid	1.026	++
2-11-32	cloudy straw	acid	1.030	Faint trace
2-13-32	cloudy amber	acid	—	Trace
2-17-32	cloudy amber	acid	1.020	+
2-20-32	cloudy straw	alkaline	1.016	Negative
3-18-32	cloudy straw	acid	—	Negative
3-19-32	amber	alkaline	1.019	Negative
3-21-32	cloudy straw	acid	—	Negative
3-23-32	straw	alkaline	1.020	Negative

TABLE XXIV

Date	cc. Urine First Hour	cc. Urine Second Hour	% Dye eliminated First Hour	% Dye eliminated Second Hour	Total % Dye eliminated
1-27-32	360	150	52	18	70
1-28-32	350	130	47	14	61

In Table XXIII the urinalysis data are presented. In these data there appears again a preliminary drop in the specific gravity followed by a rise after continued administration of sodium rhodanate. From the data, the alkalinizing effect of sodium rhodanate does not appear, as it did in Cases 1 and 2. The albuminuria indicated during the two weeks beginning March 3 was not so pronounced as the data appear to make it, for the readings of the Tompkins County Laboratory are on a high scale. Sugar was not found at any time.

Although only two kidney function tests were made, the data, in Table XXIV, suggest an early drop in the function like that found in the previous two cases. There was no reason to suspect that the renal function did not rise again.

The three hematological studies that were made showed only three things. The blood count was normal at the start of the treatment; there was not the usual relative lymphocytosis. On the last day that morphine was given a polymorphonuclear leucocytosis had developed with a total white cell count of 13,600.

The psychological tests on this patient gave very interesting results. The data for the test of crossing out the letters "O" are given in Table XXV. The results of this test show that during the first three days of the withdrawal, the patient was faster and more accurate. Shortly before he was discharged from the hospital, the patient was a great deal more accurate and somewhat faster. He had not reached normal accuracy however. He was more cooperative in securing the data also. It would seem, from the above data, that sodium rhodanate brought about better nervous function during withdrawal; and endocrine and sodium rhodanate therapy caused a great deal of improvement.

TABLE XXV

Date	Number of O's	Time taken in seconds	Number Missed	% Accuracy
1-25-32	52	74.0	29	44.4
1-27-32	53	68.8	17	67.9
3-21-32	53	63.2	10	81.1

The word-association test was performed with very interesting results. Table XXVI contains the data. After the first day the patient was much more rapid in his associations; also, there were not so many queer replies. The rate of association did not increase appreciably during convalescence. These tests seem to indicate that the mind of the patient became clearer after sodium rhodanate therapy was instituted.

In summary, this patient was withdrawn in five days from a daily dose of four grains of morphine, without any more than a transient appearance of withdrawal symptoms. There were no distressing withdrawal symptoms; had it not been that the patient was somewhat nervous at times upon a daily dosage of two and one-half grains of morphine, one would have suspected that he was not a drug addict at all, so far as withdrawal symptoms went. When morphine was cleared out of him a pre-existing psychosis developed which was traced to faulty endocrine function. The condition was treated by endocrine therapy. The patient improved and was discharged with neither a need nor a desire for morphine. The prognosis for continued abstinence from morphine seems to be good.

Case 4, C. W.

The patient was a male physician, 49 years of age, who had been addicted for about eighteen years. When admitted to the hospital he was using about six grains of morphine daily. Sciatica was the ostensible cause of the original addiction, along with nervousness and insomnia. The number of treatments that he had taken could not be ascertained. A few years ago, he attempted to blow his brains out with a revolver, but missed the mark entirely.

TABLE XXVI

Date	Word	Response	Time in Seconds	Total time for test in Seconds	Remarks
1-25-32	blotter	ink	4.4	181.6	
"	glass	plate	5.6		
"	morphine	getting over it	31.6		
"	addict	many	3.0		9 response words ending in "ing"
"	porch	winter	4.0		
"	leg	mutton	4.6		These 3 words followed in order
"	suck	calf	4.6		
"	eraser	blotter	9.8		
"	clip	hair	4.0		
"	murder	terrible	5.8		These words occurred together
"	trolley	passenger	5.0		
"	asylum	awful place	5.8		
"	spoon	celluloid	2.4		
"	anesthetic	ether	1.8		These words followed in order
"	fire	wood	7.0		
"	suicide	shooting	8.2		
1-27-32	morphine	addicts	1.8	79.9	
"	addict	morphine addicts	1.8		Not so many peculiarities in this test
"	eraser	rule out	2.0		
"	nurse	trained	2.4		
"	chart	memory	1.4		13 response words ending in in "ing"
"	murder	many	2.0		
"	asylum	insane	1.4		These words occurred together
"	wall	room	3.6		
"	suicide	murder	2.4		
3-21-32	morphine	addict	1.4	78.9	13 words ending in "ing"
"	leg	right leg	1.4		
"	suck	calf	3.0		
"	addict	morphine	1.2		
"	nurse	trained	1.6		
"	intercourse	relations	4.2		These words followed one another
"	ink	writing	1.0		
"	auto	car	2.8		
"	murder	killing	2.0		
"	asylum	insane	1.4		These words occurred together
"	wall	stone	2.8		
"	desk	writing desk	1.6		
"	suicide	murder	1.6		

Upon admission to the hospital the patient was very nervous; his speech particularly betrayed his nervousness. He was so nervous that he stammered. Psychomotor hyperactivity was a part of the general picture. He looked tired and had a cold. As with the other cases, the patient's clothes and all belongings which could serve to conceal morphine were taken from him, and locked up. The patient was then put to bed in a private room. As with the other patients no visitors were allowed except when a nurse was present.

Physical examination revealed very little that was abnormal. The patient was five feet ten inches tall, and weighed 160 pounds; there was a good moderate amount of subcutaneous fat over the entire body. His blood pressure was 115/80. His teeth were in poor condition, apparently as a result of neglect. The pharynx was congested mildly. The patellar reflexes were hyperactive and equal.

TABLE XXVII

Date	Grains Morphine	Grams NaCNS	Date	Grains Morphine	Grams NaCNS
1-29-32	5.00	0	2-3-32	2.00	1.33
1-30-32	3.75	0	2-4-32	1.23	2.00
1-31-32	5.25	0.67	2-5-32	0	3.67
2- 1-32	3.50	1.33	2-6-32	0	2.67
2- 2-32	3.00	2.33	2-7-32	0	0.67
			2-8-32	1.00	0

The patient was admitted to the hospital at noon on January 28. No attempt was made to study him on that day. Table XXVII shows the dosages of morphine and sodium rhodanate that were administered while the patient was in the hospital.

January 29, 1932.

From midnight on, the patient slept for six and one-half hours. He passed a comfortable night. He was not so nervous as he was during the previous half day. The day was spent attempting to arrest the cold with which the patient was afflicted. Ammonium chloride and magnesium citrate were used to that end. He was slightly nervous during most of the day. Morphine was given in five doses.

January 30, 1932.

The patient slept for about six hours during the early morning. He was very nervous and restless when he awoke in the morning at 7:00 a.m. Despite orders to stay in bed because of his cold, the patient became restless and walked about in a nervous manner at 9:00 a.m. The patient passed a restless and only fairly comfortable day. It was obvious that he had been used to more than 3.75 grains of morphine per day. Treatment for the cold was continued, though no cathartic was given. His appetite was only fair.

January 31, 1932.

The dosage of morphine was raised in an effort to keep the patient more comfortable. He slept for five hours after 1:30 a.m. His appetite was better in the morning. The patient was not so restless as he was during the previous day. The cold improved. Otherwise nothing unusual transpired.

Two Alophen tablets were given at night. Ten grains of sodium rhodanate were administered, by mouth as usual, at 11:00 p.m. The patient was given ammonium chloride at frequent intervals during the day.

February 1, 1932.

The patient awoke in a very nervous condition at 3:00 a.m., and complained of having had a horrible nightmare. He went to sleep again shortly. He passed a fairly comfortable night, and slept for about five hours. His appetite was better than it had been. At 3:15 p.m. the patient was very nervous. Again at 7:30 he had a nervous spell. If anything, the patient was less nervous and restless than on the previous day. No symptoms of withdrawal were seen. Sodium rhodanate was given at 8:00 a.m., and 7:00 and 10:00 p.m.

With this patient and others that followed, it was learned that it is most inadvisable to allow them to communicate with one another during withdrawal, for several reasons. They talk constantly of morphine, and their experiences with it. They all immediately exhibit any symptom that any one of them has. There is also a tendency to want to regulate their medication; though they know nothing about what doses are being administered.

February 2, 1932.

He slept well and passed a comfortable night. The patient was fairly comfortable throughout the day; although there were periods of restlessness and nervousness. Aside from that there were no complaints. The patient volunteered the information that the sodium rhodanate alone gave him a "kick," and then quieted him. The first part of his statement probably was a figment of the imagination. The second part was observed. His appetite was good at supper-time. Sodium rhodanate was administered at 5:00, 8:00, and 11:00 a.m., and at 2:00, 4:00, 8:00, and 11:00 p.m. The times of administration of the peptizing agent were arranged so that it was given one hour after each hypodermic of morphine.

February 3, 1932.

From midnight on the patient slept soundly, and almost continuously. About 10:00 a.m. he complained of abdominal cramps. This symptom disappeared in about an hour. There were periods during the day when the patient was nervous and restless; but the symptoms were not severe in any sense of the word. In the afternoon, he complained that the sodium rhodanate upset his stomach. That is not an unusual thing, even for normal people. Instead of discontinuing the drug, or reducing the dosage, ten grains of sodium bicarbonate were given with each dose. Had the sodium bicarbonate not ameliorated the condition it would have had to be tolerated; because the large doses of sodium rhodanate were necessary. The day was hardly different from the one preceding it. Sodium rhodanate was given only when it was needed.

February 4, 1932.

After 2:00 a.m., the patient slept soundly, and almost continuously, for nearly eight hours. The morning passed in an uneventful manner. At noon, the patient ate heartily. During the afternoon the patient was restless and nervous at times; beyond that no withdrawal symptoms were observed. The day was a fairly comfortable one *in toto*. The patient realized that his dosage of morphine was being reduced.

In the evening he was restless and walked around a good deal. Two mistakes were made at this time. In the first place, the patient was told that he had had only 0.73 grain of morphine during the last twenty-four hour period. From conversation with other addicts he learned that in some quarters it is usual to administer a final one-half grain "pick-up" dose of morphine at the end of the treatment. Shortly thereafter he demanded such a final dose. This was absolutely contraindicated because it made just so much more morphine to work against the sodium rhodanate, and to be cleaned out of the system. Since the man was a free agent, and cases were at a premium, and despite better judgment, the dose was given. In addition, that made the final reduction dosage a large one. The patient went to bed and slept from 11:30 until after midnight.

February 5, 1932.

At 12:30 the patient became nervous, and up and about feeling restless. To combat that fifteen grains of sodium rhodanate were given. The patient then slept soundly for almost seven hours. At 8:00 a.m. he did not care to eat breakfast because of nausea; he drank coffee and immediately vomited it. He was not so restless and nervous but that he was reading quietly at 9:30 a.m. He was dozing at 11:30 a.m. The regular noon diet was refused.

The patient complained of feeling chilly at 1:30 p.m.; he was put to bed and external heat applied. A half hour later he was more comfortable, except that he was quite restless and nervous. To quiet him, a grain and one-half of codeine was given hypodermically at 3:00 p.m. He was quiet and sleeping for about one-half hour thereafter. The day was rather an uncomfortable one. Fleeting signs of the symptoms of withdrawal were observed. The only thing that was a definite part of the picture was the restlessness and nervousness; those symptoms were more pronounced than on the previous day. He did not thrash around in bed, and was able to lie quietly therein. Morphine addicts are notoriously jealous of their own comfort, and this patient was no exception. Yet, very little attention was paid to him.

In the evening the patient was nervous and restless until ten o'clock; he slept for an hour after that. It does not seem extravagant to claim that no patient who is suffering greatly from withdrawal symptoms would sleep as much through the withdrawal period as this patient did. Upon awakening he had the fixed idea that the only way to be comfortable was for him to have chloral hydrate. Since this drug is an agglomerating agent, it was absolutely contraindicated at this stage of the treatment. However, the patient was obdurate, and absolutely satisfied that chloral hydrate was the only thing that would help him in any way, despite patient reasoning with him. He had ceased to "get a kick" out of the sodium rhodanate. The patient grew adamant and demanded chloral hydrate, the alternative being to leave the hospital. It is quite obvious now that the patient should have either followed the theoretical treatment or been discharged. He promised to take chloral hydrate on this date and then go along on a reduced dosage, finally stopping its use entirely. After being given twenty grains of the agglomerating agent he slept from 11:30 p.m. until 3:30 a.m.

Sterile hypodermics containing a little novocaine were given at intervals during the day.

February 6, 1932.

Giving sodium rhodanate and chloral hydrate at the same time was tantamount to giving nothing at all since one is a peptizing agent and the other an agglomerating agent. While the local concentration of either one is high, from the adsorption isotherm, the effect of that drug may predominate for a while, provided also that the two drugs are about as strongly adsorbed. That is about as far as it goes.

The patient read from 3:30 a.m. until four o'clock; he then slept until seven o'clock. He refused breakfast, although he said that he felt better. The statement that he felt better in combination with his appearance classified him immediately as one who would be very difficult to keep away from morphine. The facies appeared like that of a man who had been drinking whiskey all night long; it was gray and lined with nervous tension in contrast to the relaxed more healthy appearance that it had during withdrawal. He stammered consistently for the first time since the day that he was admitted to the hospital. There was psychomotor hyperactivity in addition, another symptom which had been under pretty good control during sodium rhodanate therapy. The man was what we choose to call a "pathological thrill-seeker."

As the morning wore on his appearance became better; the facies relaxed; the psychomotor hyperactivity subsided; and some color came into his face. Just as he finally threw off the effects of the chloral hydrate, he became very nervous and restless and demanded more of the drug, despite the fact that he said that he would only require it at night, and then in decreasing doses. The patient evidently had to feel euphoric. He became more nervous and restless and finally excited when the agglomerating agent was refused. Twelve grains had to be administered at 4:00 p.m.

During the day he complained of a feeling as though worms were crawling around in the epigastric region. This made him very nervous; but it quieted down completely when the upper abdomen was massaged in the region of the solar plexus. Despite all of this the patient passed a fairly comfortable day. He demanded twenty grains more of chloral hydrate at 9:15 p.m.; he was very nervous at the time. The patient slept from 9:30 p.m. to 12:30 a.m. He refused the regular diet throughout the day.

February 7, 1932.

He awoke at 12:30 a.m. and called for more chloral hydrate; he was very nervous. It was apparently taking more chloral hydrate to bring about euphoria which the patient desired, as the morphine was working out of his system. The patient slept well during the early morning. When visited during the morning, the patient was in the same condition as that described for February 6: ashen face, showing nervous tension, and psychomotor hyperactivity accompanied by stammering. When the condition wore off at around 2:30 p.m., he started his demands for chloral hydrate again. Six grains of the drug were given at 2:30 p.m. and again at midnight did not give him the "kick" that he sought. In addition he refused sodium rhodanate during the day.

TABLE XXVIII

Date	Appearance	Reaction	Specific Gravity	Albumin
1-29-32	cloudy amber	alkaline	1.019	negative
1-30-32	clear amber	acid	1.013	negative
2- 1-32	clear amber	acid	1.012	negative
2- 2-32	clear amber	acid	1.010	negative
2- 3-32	cloudy amber	acid	1.009	faint trace
2- 4-32	clear amber	acid	1.014	negative
2- 6-32	cloudy amber	acid	1.012	trace
2- 7-32	cloudy amber	acid	1.026	negative
2- 8-32	cloudy amber	acid	—	negative

February 8, 1932.

No medication was given on this day other than castor oil for the relief of constipation. In the early afternoon the patient requested that he be given one grain of morphine and discharged. Because he was a "pathological thrill-seeker" and apparently not very much interested in conquering morphinism his requests were granted. It is interesting to note that there was enough sodium rhodanate in the patient to cause the one grain of morphine to have greater than the normal amount of exciting action.

Table XXVIII gives the urinalysis data for this patient. Here again there is a preliminary decrease in the specific gravity, followed by a rise as the sodium rhodanate is eliminated along with increased amounts of sodium chloride. There was no sugar present at any time.

The one hematological study that was made upon admission showed a polymorphonuclear leucocytosis with a white blood cell count of 13,000. On the same date a test of the kidney function yielded a value of 69% of the dye eliminated in two hours.

That the laboratory studies on Cases 3 and 4 were not more complete was due to the failure of the Tompkins County Laboratory to cooperate in this work. Dr. Howe has commented on the situation recently.[1]

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[1] Ind. Eng. Chem., **24**, 479 (1932).

Discussion

In order to compare the withdrawal symptoms in these four cases with those seen when no drugs are used, it seems worthwhile to set down some of the findings of Lambert's Committee.[1]

"In order to compare different treatments it is important to know the characteristic symptomatology and reactions of drug addicts to the withdrawal of their narcotic drugs. These are varied, but surprisingly distinctive, and more or less uniform in the majority of cases.

"For the best picture of unaltered withdrawal symptoms we have used our observations of one hundred control patients who received injections of innocuous solutions at regular intervals after their morphine dosage was abruptly withdrawn, until all withdrawal symptoms were over. In these cases we see the characteristic symptoms in their full intensity over a shorter period of time.

"In general it is possible to subdivide the symptoms of the drug addict undergoing withdrawal of his accustomed narcotic into two groups: (1) Physical symptoms, (2) psychic symptoms. A great many of the physical withdrawal symptoms seen in human addicts are presented in experimentally addicted animals (dogs usually), but in human addicts a very important psychic factor is superimposed, making the problem of withdrawing a human addict considerably different from that of an animal.

"Withdrawal symptoms may be subjective or objective.

"In addition, the physical symptoms may be *real*—or they may be affected by the psychic factor so that they may be *simulated*. Still further they may be *exaggerated* or *minimized* deliberately.

"If simulated or exaggerated, the object is usually to obtain more morphine or sympathy.

"If minimized, i.e., if their suffering is wilfully suppressed, or concealed, the patient's object is usually to effect his discharge sooner. As far as dissembling is concerned, some drug addicts are consummate actors.

"Sometimes, as Light and Torrance mentioned in their article, patients who are in possession of smuggled narcotics will simulate suffering to allay suspicion.

"Symptoms of withdrawal or abstinence may be referred to almost any organ of the body. The psychic symptoms are usually first to appear. The patient becomes restless, uneasy, and fidgety, not remaining very long in one position, i.e., there is increased psychomotor activity of a disagreeable nature. He also shows fear, anxiety, and also some irritability.

"The method of treatment at this stage may either quiet him, or exaggerate his symptoms, or excite him.

"The fact that at this time mere assurance that he will be taken care of, or the giving of a sterile hypodermic will quiet him for quite a while, shows how important the mental factor is in the treatment of these cases.

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[1] Am. J. Psychiatry: 10, 488 (1930).

"Soon, within 12 to 24 hours, physical symptoms appear (the 'yen' as addicts call it), and these at times alternate with or are modified, or exaggerated by the psychic element.

"The patients complain of alternate hot or cold flashes, show vasomotor instability, may sweat profusely, or show blushing or erythema of the skin, or pallor and goose flesh. Sometimes the patients appear cyanosed. There may be slight rise of temperature for several days.

"Then a multitude of other symptoms may appear in any number of combinations or degrees of severity.

"There is an apparent increase of many of the bodily secretions; lachrymation, with dilated pupils; coryza, with sneezing and increased bronchial secretion with cough and expectoration, so that the patient complains that he has a 'cold in the head and chest.' There may be yawning, with sighing or dyspnoea, or, only increased rate of respiration.

"The pulse rate may remain unchanged or may show considerable fluctuation, becoming rapid or slow; small, weak, collapsible, thready, intermittent. The patient may complain of anginoid pains. The blood pressure in some conformity with the general vasomotor instability may show fluctuations, and there is often a fall in the systolic and diastolic readings. There may be a slight leucocytosis.

"There may be salivation, with nausea, retching and vomiting, which may become so marked as to be blood-streaked, with terrible, binding, colicky abdominal cramps, and more or less diarrhea. Sometimes the patients may vomit and have involuntary bowel movements simultaneously. The large amount of bile vomited in some cases may be significant. In some cases the patients put their fingers down their throats to induce vomiting when nauseated. Often also they complain of 'heart burn' (pyrosis) with acid eructation. The abdominal cramps, vomiting, etc., may simulate an acute surgical condition.

"With the anorexia, vomiting, inability to retain food or fluids, etc., there is a rapid loss of weight which may vary from a few pounds to twenty or more pounds in a few days. As a result the patients may show rapid emaciation; the change in their appearance may take place so quickly and be so marked as to make them appear to be entirely different individuals. As a result of emaciation and dehydration, etc., there may be marked prostration, sometimes collapse.

"In the genito-urinary system the patients may show a frequency of micturition, occasional albuminuria, or acetonuria; or increased sexual activity with numerous seminal emissions.

"There are very constant painful, spasmodic muscular aches, and twitchings, which, when very marked are called by the patient 'twisters.' There may be generalized fine tremors, simulating those of an alcoholic. Many patients complain of joint pains, and pains in the back (which they call 'kidney trouble').

"In the nervous system the symptoms may be very complex. First, there is a marked sleep disturbance, patients sleep fitfully, at irregular intervals;

often they remain awake all night, sleeping for short periods during the day time. Occasionally there is insomnia for several days.

"There may be headache, disturbance of vision with diplopia, or dimness; and the senses of hearing, smell, or taste may be either impaired, or rendered more acute (the keen sense of hearing of some drug addicts is well known). Occasionally they complain of ringing in the ears.

"There appears to be a generalized hyperesthesia to heat, cold, touch, and painful stimuli; and some scarred veterans of the hypodermic, who had jabbed themselves on innumerable occasions with eye-droppers, safety-pins, horse-shoe nails, and what not, will complain of the prick of a fine hypodermic needle. As they explain it their 'nerves are all on the outside.' Neuralgic pains may manifest themselves anywhere in the body, supra-orbital, facial, dental, intercostal, sciatic, etc. Some patients complain of testicular pain.

"The tendon reflexes are usually increased.

"Some patients may laugh or cry alternately, become hysterical, shout, curse, dash their heads or fists against the wall impulsively, or smash anything within reach. Sometimes they have a real or simulated convulsion or delirium, even a mild transitory psychosis, or mental confusion with impairment of memory. They become slovenly and untidy, expectorate in bed and on the floors. Some show exhibitionism.

"All their psychopathic or psychoneurotic traits become exaggerated and obvious during the withdrawal period. The emotional tone is one of extreme dissatisfaction, and the patients become very capricious in their wants, making all kinds of requests, and often they become very finicky about their food.

"Not every patient suffers all these symptoms. Some go through an abrupt withdrawal with little or no evidence of distress.

"Thus we see that every withdrawal is a test of the addict's resistance and endurance. The suffering and release of nervous energy suppressed for a long time, place a severe tax on all the vital organs and the period of unrest, suffering, and semi-starvation may result in death."

From this complete account it can readily be seen that the withdrawal symptoms suffered in the four cases presented here were not typical in extent, intensity, or duration. When patients were given a seven-day reduction treatment Lambert's Committee found that 8% of the patients suffered severe withdrawal symptoms and 64% had light withdrawal symptoms. There is nothing in the report to indicate that the number of withdrawal symptoms was decreased by the gradual reduction treatment. By comparison with that method of treatment, sodium rhodanate also reduces the suffering upon withdrawal of morphine. Many of the symptoms reported by Lambert have not been observed at all during this study.

From the graph presented on page 512 of Lambert's report, a relationship between the seven-day reduction treatment and the sodium rhodanate treatment can be obtained. The maximum intensity of withdrawal symptoms comes two days after the last dose of morphine, under the seven-day reduction treatment. Whereas, when sodium rhodanate is used, the maximum intensity, ruling out the delirious states that have been observed, comes on the last day that the patient is given morphine. This is shown in Fig. 1. This graph was made largely on the basis of Case 1. Nothing has arisen in the later cases to indicate that it does not represent the picture quite accurately. No attempt was made to evaluate the withdrawal symptoms numerically. Therefore, the ordinal values in Fig. 1 are purely arbitrary. The curves show three important things. In the first place, the withdrawal symptoms did not commence until the sodium rhodanate treatment was more than half through; whereas, in the seven-day withdrawal the symptoms were present throughout. Secondly, the shift in the maximum of the curve indicates very strongly that sodium rhodanate forces morphine out of the system more rapidly than it would go out normally. In other words, there is a forced period of irritability as a result of the peptizing effect of the rhodanate ion. The third deduction is that the withdrawal symptoms are less intense when sodium rhodanate is used.

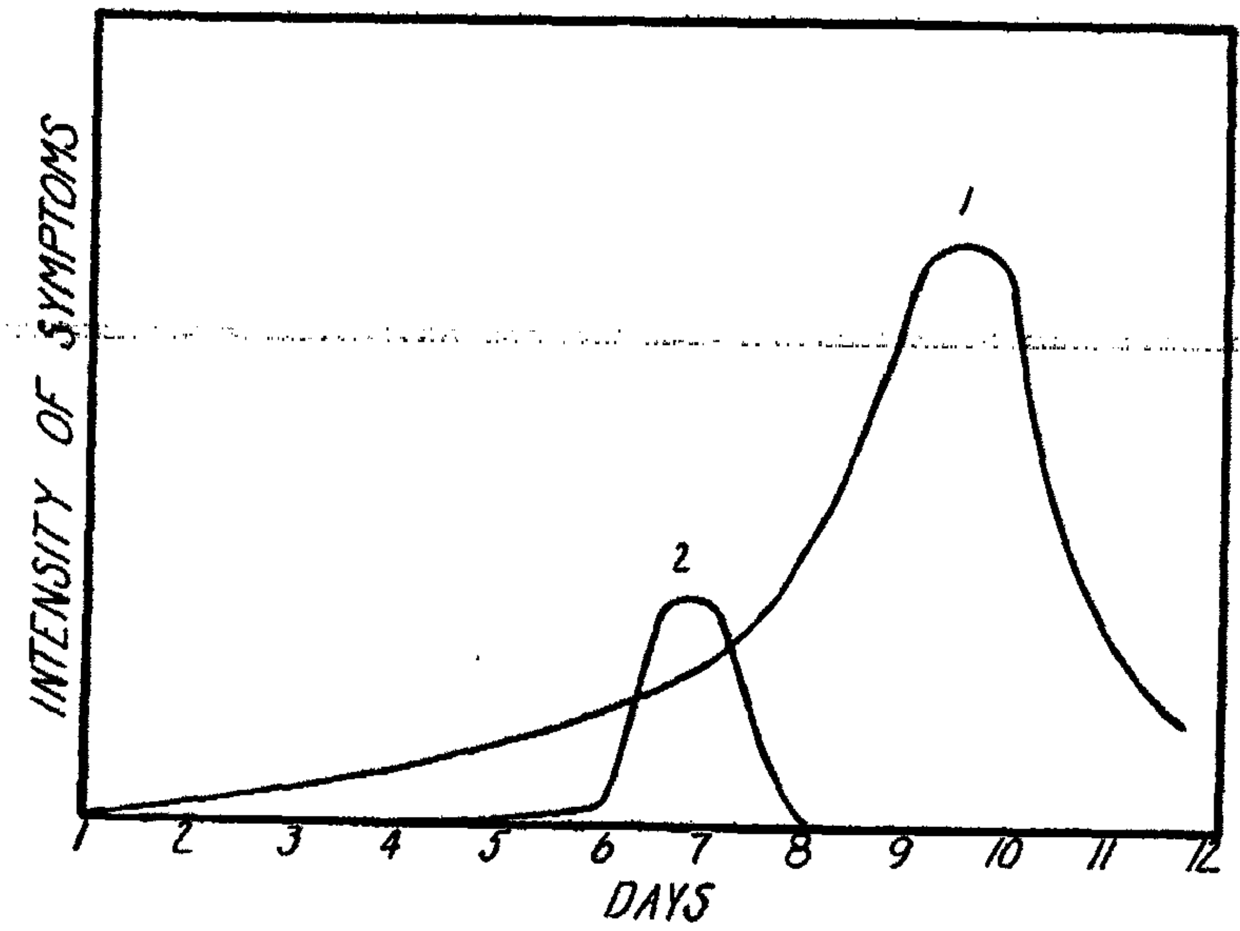

Fig. 1

Curve 1—Seven-day reduction treatment
Curve 2—Treatment with sodium rhodanate during six-day reduction

It is not amiss to re-state the proposition that the really important problem is not the reduction of discomfort during withdrawal, but rather the mental rehabilitation of the patient. As this report shows, a fair degree of success has been met with along the line of rehabilitation. It seems to be a peculiar twist of the medical mind[1] that it gets all tangled up with the word "specific." It is felt, in some quarters, that for a drug to be of use in drug addiction it must be a specific for that disease. The use of the word almost becomes anthropomorphic. On the other side of the question, there is no real reason why one should

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[1] Treadway: Science News Supplement, May 13, 1932.

have to use a drug which goes only to the centers affected by morphine, and acts as an antidote only to the alkaloid. If the nervous system, or part of it, is agglomerated there is no reason whatever why any effective peptizing agent should not be used to treat the condition, provided the drug used neither kills the patient nor causes permanent damage. Searching for a "specific" has been in the past and probably will continue to be rewarded only by the consumption of time. No claim of a miraculous cure has been made, Dr. Treadway's inference notwithstanding.

There are many stumbling blocks in the path to the successful use of sodium rhodanate in the treatment of drug addiction. The first difficulty that is likely to arise is with the purity of the sodium rhodanate. To be on the safe side the salt should be recrystallized from water solution at least once before use. The saturated solution of the drug should be filtered before crystallization is started. *Potassium and sodium rhodanates are not interchangeable, and only the sodium salt should be used.* When administering the peptizing agent *it should be given to effect,* barring only very serious complications. Using very large doses of the drug in many cases in the course of this and other studies in reversible agglomeration and peptization in living tissue, no permanent damage has been done in any case by the sodium rhodanate. Discontinuing the drug can generally be relied upon to remedy any side effects. Because a patient becomes dizzy, nauseated, weak, or exhibits any one of a number of other symptoms is generally no excuse for discontinuing the use of the peptizing agent. Because one does not see an effect is no reason to presume that sufficient dosage will not produce it. That may be poor medical practice; but it is sound scientific procedure. It has been pointed out how psychoses can be handled. There is some danger in using too much sodium rhodanate after withdrawal; and care must be exercised that a condition of over-peptization, such as that which makes some addicts begin the use of morphine, is not produced. If such a state is brought about, agglomerating agents should be employed immediately in order that the patient shall not revert to the use of drugs. Such a case has been observed experimentally, and will be presented in a later paper. Sodium rhodanate should not be used to control weakness. If a great deal of the drug is used, and sleeplessness results, the sleep center is probably over-dispersed; a decrease in the dosage is then indicated. Extreme care, and careful study, in the light of the theory, must be taken in deciding whether to use agglomerating or peptizing agents during the rehabilitation. If the patient was originally over-peptized before taking morphine, sodium amytal will be useful. If the reverse is true, sodium rhodanate or bromide is indicated. There is nothing to be gained at the present time by attempting to apply colloid therapy to anyone who does not desire sincerely to be cured; such is almost surely the case with many prisoners.

Sodium rhodanate should not be used in cases of active or arrested tuberculosis, because it is probable that it will aggravate the condition. Patients suffering from kidney disorders, heart disease, functional or organic, and painful organic diseases should not be given more than five grains of sodium rhodanate a day. Such a small amount is totally useless in the treatment of drug addiction. In cases of severe hypotension, sodium rhodanate and ephedrine can be used to advantage almost surely. It should be pointed out that sodium rhodanate does not act rapidly and that its maximum peptizing action comes at a high concentration in the body. Therefore, one can not expect good results by starting to give this drug simultaneously with abrupt withdrawal. It is probably inadvisable to use abrupt withdrawal and sodium rhodanate therapy.

The deliria and psychoses that have been observed did not cause particular concern at the time because after a short study it became obvious how to treat them. Naturally it is felt that it is not necessary or desirable to have these two factors as part of the picture. Further study is needed in order to determine how to avoid them.

Despite all of this, the treatment of drug addiction with sodium rhodanate is not yet standardized by any means. It requires a thorough understanding of the theory and principles underlying the treatment and the action of the drug, combined with the determination and courage to go ahead. Skill and practice in the use of sodium rhodanate for various conditions is a necessity. Dr. Treadway[1] reports that his experiences with the use of sodium rhodanate do not parallel those reported in this paper. Despite a request, he has not released information as to exactly what he found, or the procedure followed in making his experiments. It is certain that he was dealing with a different type of case than those reported here. From the very nature of the thing, he could not have duplicated the treatment as used here. Every addict presents a slightly different problem, and the treatment is not yet standardized. There was no sufficiently pure sodium rhodanate on the market, so far as we are aware, at the time that his experiments were made. Until such time as further and more specific information is forthcoming, Dr. Treadway's conclusions will have to be considered as based on bad experimentation. Just where he slipped up can not be stated at the moment.

So far as is known, no two agglomerating drugs, working on the same set of nerves, will produce the same intensity of symptoms in equal doses. In other words, different drugs agglomerate to different degrees. Heroin is approximately three times as strong as morphine; that is, about one-third of the dose produces the same results. The theory of the action of heroin, and the method of treatment of heroin addiction, is the same as for morphine. Yet, it is theoretically possible, and indeed even probable, that sodium rhodanate is not strong enough as a peptizing agent to overcome the withdrawal symptoms when heroin is taken from an addict, either abruptly or gradually. Large doses of sodium rhodanate are necessary to alleviate the abstinence symptoms in morphine withdrawal. Heroin, being stronger than morphine, is a better agglomerating agent. It probably will require correspondingly more sodium rhodanate to relieve the abstinence symptoms of heroin withdrawal.

It seems probable that the safest procedure in the treatment of heroin addicts is to withdraw the heroin and substitute morphine. In carrying this

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[1] Science News Supplement, May 13, 1932.

out enough morphine should be used to prevent the appearance of any withdrawal symptoms. Then, after one or two weeks, when the addict has become thoroughly accustomed to the morphine, the usual sodium rhodanate treatment should be instituted. Even then, larger amounts of sodium rhodanate may be necessary.

Were sodium rhodanate clinically of practically no use at all in the treatment of heroin addicts, it would not affect the theory in the slightest. A case that is entirely analogous has been reported.[1] Sodium amytal and nembutal are both anesthetics of the barbituric acid series. Less nembutal is required to produce anesthesia. Sodium rhodanate exhibits a marked antagonistic action against sodium amytal; but it was a long time before it could be shown that it antagonizes nembutal; and a marked antagonistic action has never been observed. Along the same line veronal is not such a good coagulating agent as morphine; and veronal addiction is easier to treat than morphinism.

Eighty cases of drug addiction were treated with sodium rhodanate in another place. The source of the sodium rhodanate is not known. Because they felt that there was danger connected with the use of large doses of sodium rhodanate, these people did not use much more than five grains of the drug per day during withdrawal. They combined it with ammonium bromide, thus introducing a much weaker peptizing anion and a toxic cation. Five grains of sodium rhodanate daily is not to be expected to produce any visible ameliorating effect on the abstinence symptoms. It is clear where this experiment went wrong.

A doctor reported that upon giving a veronal addict, who was using fifteen grains of the drug a day, five grains of sodium rhodanate daily he became very excited and nervous. The theory is the same as that underlying the treatment of morphinism. It is clear that the doctor only gave enough of the dispersing agent to peptize the agglomerated colloids to the stage of irritability. He should have given about six times as much sodium rhodanate rather than shifting to sodium amytal, another agglomerating agent.

There is one fact that remains to be explained, if the assumption is made that this work is wrong; that fact is that we can treat morphinism successfully.

Four more cases of morphinism that have been treated by this method will be reported shortly.

The general conclusions to be drawn from this paper are:

1. A review of the theories of drug addiction reveals that they do not account for the facts met with; and do not give a rationale for the action of habit forming drugs upon which to base a proper treatment.

2. A review of the various methods for the treatment of drug addiction shows that, aside from the methods used by Poppe and by MacLeod, there is no satisfactory drug to combat withdrawal symptoms.

3. The problem of rehabilitation is the only important one that has to be faced. The literature shows that the surface has only barely been scratched.

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[1] Bancroft and Rutzler: J. Phys. Chem., 35, 1185, 3036 (1931).

4. Combining Abe's ideas with the theory of reversible agglomeration in living tissue, a useful theory of drug addiction and its treatment has been evolved.

5. The new theory accounts for the facts of drug addiction, withdrawal, tolerance, and rehabilitation.

6. Since by the theory morphine causes agglomeration of certain of the protein colloids of the nervous systems, peptization with sodium rhodanate should be a useful method for treating drug addicts.

7. Four cases of morphinism were treated using large amounts of sodium rhodanate. Laboratory, clinical, and psychological data are presented which show the various reactions of the patients.

8. Sodium rhodanate, when used properly, alleviates withdrawal symptoms.

9. Delirium resulted in 75% of the cases at the end of the withdrawal period.

10. Transient psychoses developed in two cases. Colloid therapy straightened one case out, and endocrine therapy the other.

11. Mental rehabilitation was accomplished, on the basis of the theory, in 75% of the cases. One case was a "pathological thrill-seeker" and was discharged using morphine.

12. The new treatment of drug addiction has not been standardized.

13. Some morphine addicts exhibit paranoid symptoms which are due to agglomeration.

14. There are many pitfalls in the reduction of the theory to practice. These are discussed. Illustrations of how some of them are surmounted from the point of view of the theory are given.

15. Intelligent application of the theory makes it possible to use large amounts of sodium rhodanate and accomplish the successful treatment of morphinism. Despite the statements of some medical men, pure sodium rhodanate is not toxic in doses up to 90 grains in a day.

16. Morphinism is a disease.

17. Sodium rhodanate forces morphine out of the body more rapidly than if no medication were used.

18. Much progress has been made; but much work remains to be done.

19. The conclusions drawn by the United States Public Health Service are undoubtedly based on bad experimentation, though the actual mistakes cannot be pointed out until the details of those experiments have been released.

20. The treatment of heroin addicts can probably be accomplished best by substituting morphine for the heroin, and then withdrawing the morphine with the aid of sodium rhodanate.

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18.29

SULPHATES OF MERCURY AND STANDARD CELLS

BY R. B. ELLIOTT AND G. A. HULETT

A most important stage in the development of our standards of electromotive force was the introduction of mercurous sulphate as a depolarizer. The unique properties of this salt have made our standard cells possible. It is a mercurous salt with a rather small solubility (about a gram in a liter) so that diffusion from the cathode system is not excessive, while the solubility is sufficient to give a rather large potential at a mercury electrode. Some 90% of the E.M.F. of the cadmium cell is at the cathode.[1] Now this cathode potential depends upon the ability of the mercurous sulphate depolarizer to establish and maintain a very precise concentration of mercury ions at the mercury electrode, so that the reproducibility and constancy of standard cells depends on this property of mercurous sulphate, and obviously the chemical and physical properties of mercurous sulphate are the important factors. Any factor that has a bearing on the mercury concentration resulting from a given preparation of mercurous sulphate is important from the standard cell standpoint. Any impurities are to be feared, especially any other mercury salts present as a result of adsorption or isomorphism. Also it is well known that solubility varies with the size of the particles of the solid.[2] When the electrolytic method of preparing mercurous sulphate was developed it was found that when the product was stirred with electrolyte to become sufficiently coarse-grained so that it settled rapidly, that this product showed no measurable effect due to surface tension. Later von Steinwehr[3] attempted to explain the variations of standard cells as due to size of particle of the depolarizer.

Now, a product that is obtained as well-formed crystals with reflecting surfaces is less subject to these chemical and physical defects. Consequently, considerable attention has been given to obtaining a well crystallized preparation of mercurous sulphate. Both the chemical and electrochemical method of preparing mercurous sulphate give products of good particle size which appear to be crystalline, but a microscopic examination reveals no reflecting crystalline surface but a rather rough crust-like aspect that by no means excludes adsorption or surface tension effects.

Gardiner and Summers[4] took advantage of the difference in solubility of mercurous sulphate in 1.5 molar sulphuric at 100° and 20° and by a hot-cold circulation method, succeeded in obtaining some sizable water-clear crystals with perfectly reflecting surfaces. The yield was not satisfactory so we have pursued the problem further. Mercuric sulphate is readily reduced by SO_2

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[1] Int. Electrical Congress, St. Louis, 2, 113 (1904).

[2] Surface tension effect, Hulett: Z. physik. Chem., 37, 385 (1901).

[3] Z. Instrumentenkunde, 20, 205 (1905).

[4] Trans. Am. Electrochem. Soc., 56, 143 (1929).

or mercury and the products give perfectly normal values to cells in which they are used as depolarizers. It was thought that by bubbling air-diluted SO_2 through an acid solution of mercuric sulphate that it might be slowly reduced and give a crystalline product but no matter how much the SO_2 was diluted the mercurous sulphate appeared as a fine-grained precipitate.

Now experience shows that most satisfactory crystals appear in quiet solutions where slow diffusion brings the reagents together, so it seemed possible that by allowing SO_2 to slowly diffuse into an acid solution of mercuric sulphate our objective might be attained. A solution of mercuric sulphate was placed in a deep crystallizing dish and in this was placed a bottle partly filled with dilute SO_2 solution and all covered with a glass plate with the idea that the SO_2 would diffuse out of the bottle slowly and reduce the mercuric sulphate. The diffusion was too rapid and the undesired precipitate appeared. Therefore, the bottle was removed from the crystallizing dish and connected to the upper part of the dish through a long tube with a stopcock. By this means it was possible to so restrict the flow of SO_2 that definite crystals appeared and grew on the bottom of the dish. The solution was about 1 cm. deep. Now it was desirable to use the SO_2 direct from a cylinder of the liquid with a pressure of some 4 to 5 atms. By using a very fine capillary, the flow was sufficiently retarded. A piece of 6 mm. thermometer tubing was softened in the flame and drawn down to a capillary about .3 mm. in diameter with a calculated internal diameter of only .013 mm. Some 1/2 meter lengths of this capillary joined to the liquid SO_2 cylinder restricted the flow of the SO_2 satisfactorily so that brilliant crystals formed on the bottom of the crystallizing dish. By adjusting the length of the capillary a desirable variation in the rate was attained and by leading the SO_2 into 0.1 normal iodine solution the rate of flow was determined. With a 30 cm. crystallizing dish satisfactory crystals were obtained when the capillary delivered SO_2 into the upper part of the dish at a rate of 200 cu. mm. (0.2 $cm.^3$) a second, while with a rate of .77 $cm.^3$ per second, a precipitate was formed in the mercuric sulphate solution.

Clear crystals with dimensions of 1/2 to 1 mm. were readily grown. These were very brilliant crystals indicating a high refractive index. Some of this product turned slightly yellowish in contact with a neutral cadmium sulphate solution. On carefully examining the crystals they were seen to be made up of two types, little plates and cubes. On separating them it was found that the plates were pure mercurous sulphate, while the cubes turned yellow in neutral electrolyte and proved to be mercuric sulphate.

The product had been obtained from a 1 to 6 sulphuric acid saturated with mercuric sulphate and it seemed that some mercuric salt crystallized from this solution as the mercuric was reduced to the less soluble mercurous sulphate and crystallized. With a solution only 75% saturated with mercuric in the crystallizing dish, diffusion of SO_2 yielded only plates and it appears that a 50% saturated solution is quite satisfactory. 150 grams of mercuric sulphate in a liter of 1 to 6 sulphuric acid is quite safe, as only plates of pure mercurous sulphate crystallize from such a solution and these plates may be thoroughly washed with dilute sulphuric acid to remove every trace of the electrolyte and crystallized mercuric sulphate. These crystals may be washed with alcohol and ether and dried and may then be used directly in cells.

Some of these crystals have been analyzed by a method developed in this laboratory.[1] A platinum crucible was amalgamated internally and the crystals weighed in, then covered with distilled water and with a platinum spiral anode above the crystal. A current of .01 amperes deposited the mercury as fast as the crystals dissolved, liberating the acid. When the mercury was all deposited the acid was syphoned off, water being added simultaneously, so that when milliammeter showed zero reading the deposit was completely washed. The last wash water was removed and the crucible and deposit dried in a vacuum desiccator, and the mercury weighed directly, while the acid was titrated with 0.1 N NaOH solution.

The sum of the weights of mercury and mass of SO_4 titrated gave a check on the weight of crystals used.

Two analyses gave as the ratio of mercury to SO_4, 2.009 to 1 and 2.010 to 1, so that the plates are Hg_2SO_4 and an exceptionally pure product and the behavior of this product as a depolarizer in cells is of interest. A typical cadmium and zinc cell gave the following record at 25.00:—

Time after construction	Saturated cadmium cell	Saturated zinc cell
1 day	1.018419 V.	1.420244 V.
1 week	1.018281 V.	1.420200 V.
2 weeks	1.018261 V.	1.420197 V.
7 weeks	1.018234 V.	1.420201 V.

Gardiner and Summers[2] were successful in preparing some water-clear sizable crystals of mercurous sulphate by crystallization from 1.5 molar sulphuric acid, by a hot-cold circulation method. These were exceptionally well formed crystals with reflecting surfaces, but since these crystals gave a higher value to the cadmium cell than did the gray electrolytic mercurous sulphate, this gray electrolytic has been taken as the standard on account of its reproducibility and excellent record in standard cells. There is certainly some difference between the electromotive properties of the two products, and one would be inclined to regard the well crystallized product as giving the "normal value." Certain it is that the crystals are quite free of surface tension effects on the solubility. If this were a factor we would find the electrolytic giving the greater concentration of mercury in the electrolyte and so the greater E.M.F. to the cell but just the opposite is observed. Therefore such an explanation is untenable.

Aside from crystalline differences there is much finely divided mercury on the surfaces of the electrolytic product and this may well be a factor.

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[1] Perdue and Hulett: J. Phys. Chem., 15, 147 (1911).

[2] Trans. Am. Electrochem. Soc., 56, 143 (1929).

Now if the crystals are brought into a dilute sulphuric acid solution of SO_2 they are at once covered with a grey coat of finely divided mercury globules, so it is a simple matter to add this factor of finely divided mercury to crystals of mercurous sulphate. It is only necessary to wash the crystals on the filter with a dilute acid solution of SO_2. They turn grey and with continued washing the product may be made to appear quite black. Crystals of mercurous sulphate treated as just indicated have been used for the depolarizer of standard cells with the following results:

Time after construction	Saturated cadmium cell	Saturated zinc cell
1 day	1.016840	1.41975
1 week	1.017924	1.420108
2 weeks	—	1.420174
7 weeks	1.018105	1.420203

Obviously finely divided mercury plays an important rôle in the depolarizer of standard cells and calls for a careful study from the practical and theoretical standpoints.

THE HYDROGEN ION CONCENTRATION OF FERRIC HYDROXIDE SOLS

BY WINIFRED L. McCLATCHIE

Although a number of the more common sols of the suspensoid type have been extensively studied, the problem of accurately deducing their constitution is far from completely solved. A critical examination of the literature reveals many serious discrepancies, not the least of which is in the hydrogen ion concentrations determined by different methods with otherwise similar sols. For example, Browne,[1] using a hydrogen electrode directly in a ferric hydroxide sol, found a hydrogen ion concentration of 3×10^{-7} N for a sol comparable in the concentration of iron and chlorine and in electrical conductivity to one for which Wintgen and Biltz[2] report a concentration of 3.8×10^{-4} N on the basis of hydrogen electrode measurements with the ultrafiltrate.

Reliable values for the hydrogen ion concentrations of sols of metallic oxides and hydroxides are especially important in deducing the constitutions of these sols, for hydrogen ion is both the principal electrolytic cation and a part of the hydrolytic equilibrium, hydroxide + acid $\rightleftarrows$ basic salt + water, that is presumably responsible for the stabilizing agent of many of these sols.

Many methods have been used for evaluating these hydrogen ion concentrations, but no one has subjected the methods to a critical comparison, so that there is no reliable basis for evaluating the existing data, or of accounting for the discrepancies therein. The object of this investigation with ferric hydroxide sols was twofold. It was desired to compare the results obtained by several of the more common methods, in hopes that this might help to explain some of the present discrepancies. The principal object, however, was to establish a reliable method for such determinations, and to use the hydrogen ion concentrations thus obtained in conjunction with other physical and chemical data to deduce the constitution of these sols.

Ferric hydroxide sols were considered to be most suitable for the investigation, for they have been the subject of extensive study, their chemical constitution is well established, they have been found to remain stable over a long period of time,[3] and their electrical properties are fairly constant with time.[4]

Experimental

Preparation of Sols. Sols for this work were prepared by neutralizing ferric chloride solutions with aqueous ammonia. The required amount of ferric chloride was dissolved in distilled water, the solution was cooled to

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[1] F. L. Browne: J. Am. Chem. Soc., **45**, 297 (1923).

[2] R. Wintgen and M. Biltz: Z. physik. Chem., **107**, 403 (1923).

[3] J. Böhm: Z. anorg. Chem., **149**, 203 (1925).

[4] R. Wintgen and M. Biltz: Z. physik. Chem., **107**, 403 (1923).

about 10°, and an approximately 12 per cent solution of ammonia was added dropwise, with mechanical stirring, until the amount added was equivalent to 60 to 70 per cent of the iron. The ammonia solution was prepared by redistilling the stock reagent. Three sols were prepared by this method, ferric chloride solutions of the following concentrations being used: for sol 3, 600 g. of Sterling's C. P. $FeCl_3.6H_2O$ in 4.5 liters of water; for sol 13, 500 g. of Kahlbaum's $FeCl_3.6H_2O$ "for analysis" in 2 liters of water; and for sol 20, 800 g. of Merck's $FeCl_3.6H_2O$ "free from phosphorus" in 3.5 liters of water.

These sols were purified by dialysis for several weeks against continuously changing boiled-out distilled water with a specific conductivity of 1.5 to 2.5×10^{-6}. The water was boiled in interconnected flasks, from which it passed into a large flask in which cellophane tubes containing the sol were suspended. All glass was Pyrex. Air entered the system only through wash bottles of 50 per cent sodium hydroxide and boiled-out distilled water.

The removal of carbon dioxide was considered important in view of the work of Freundlich and Wosnessensky[1] who showed that carbonate ion can serve as the stabilizing agent for ferric hydroxide sols, and it was thought possible that it might tend to replace chloride ion.

Soft glass was used in the apparatus for the dialysis of sol 3, and the water showed a pH of 8.5 and a specific conductivity of about 1.5×10^{-5}. Experiments with this sol are therefore of only secondary value.

All sols were stored in Pyrex containers equipped with inlet and outlet tubes, which were kept closed except for the removal of samples.

Chemical Analysis of Sols. The sols were analyzed for iron and chlorine, both determinations being made on the same sample. The ferric hydroxide was dissolved by warming with concentrated sulfuric acid, and a double precipitation of iron was made. Iron was determined as ferric oxide, and the combined filtrates from each sample were used for the determination of chlorine as silver chloride. Each value in the second, third, and fourth columns of Table I represents the average of at least two determinations.

TABLE I

Iron and Chlorine Concentrations of the Sols and the Specific Electrical Conductivities at 25° ± 0.02°C

Sol	Gram atoms of Fe per 1000 g. H_2O	Gram atoms of Cl per 1000 g. H_2O	$\frac{\text{Gram atoms Fe}}{\text{Gram atoms Cl}}$	$K \times 10^4$
3	0.1797	0.02242	8.02	3.287
13	0.3073	0.04450	6.91	5.695
20	0.274	0.0379	7.7	4.190

Electrical Conductivity. The electrical conductivities of these sols were measured by a simple Wheatstone bridge method. The sols were allowed to stand for at least two months before final measurements were made, for it has been shown that their conductivity becomes practically constant within this time.[2] The electrical conductivities obtained are given in column 5 of Table I.

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[1] H. Freundlich and S. Wosnessensky: Kolloid-Z., 33, 222 (1923).

[2] R. Wintgen and M. Biltz: Z. physik. Chem., 107, 403 (1923).

Hydrogen Ion Concentrations

The hydrogen ion concentrations of the sols were determined directly by means of the hydrogen, quinhydrone, and glass electrodes; and in the ultrafiltrate by means of the glass electrode.

A. Measurements with the hydrogen electrode. Hydrogen electrode measurements were made by a method similar to that of Browne,[1] and of Pauli and Matula.[2] Sol 3, with which the measurements were made, had a ratio of gram atoms of iron to gram atoms of chlorine of 8, and, according to Browne, a stable equilibrium can be obtained with all sols for which the ratio is greater than 5.

A cell of Pyrex with lightly platinized platinum wire electrodes was used. The electrodes were replatinized after each measurement with the sol. Hydrogen was supplied from a cylinder and was passed through solutions of mercuric chloride, silver nitrate, alkaline pyrogallol, alkaline permanganate, and distilled water. A dilute bridge solution containing simultaneously approximately 0.0039 N potassium chloride and 10^{-4} N hydrochloric acid was used.

The cells measured may be written as follows, the arrow indicating the direction of positive current within the cell:

Pt	H_2, sol	0.004 N KCl	Sat.	N/10, Hg_2Cl_2	Hg
platinized	1 atmos.	+ 10^{-4} N HCl	KCl	KCl solid	

$$\longrightarrow$$

The difference in potential was measured by means of a type K Leeds and Northrup potentiometer with a high resistance, high sensitivity galvanometer.

Electrodes were used with the sol only when they had given stable potentials with potassium acid phthalate solution. In a number of cases erratic results were obtained, or there was no approach to equilibrium in 60 to 90 minutes. The determinations in which equilibrium appeared to have been attained are summarized in Table II, where E is the observed electromotive force of the cell and C_{H^+} is the corresponding activity of hydrogen ion.

TABLE II

Hydrogen Electrode Measurements

Time in minutes to attain equilibrium	E	pH	$C_{H+} \times 10^5$
30	0.628	5.03	0.93
40	0.620	4.92	1.20
40	0.639	5.22	0.60
10	0.623	4.95	1.12
60	0.655	5.53	0.29

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[1] F. L. Browne: J. Am. Chem. Soc., 45, 297 (1923).

[2] W. Pauli and J. Matula: Kolloid-Z., 21, 49 (1917).

These results lead to the same conclusions that have been drawn by other experimenters;[1] namely, that equilibrium is difficult to attain, and that the results are not reliable. This is not surprising, for a system containing even traces of ferric ion would show an oxidation reduction potential that would vary with the degree of reduction. There is also the possibility of flocculation of the colloid by the gas bubbles.[2]

B. Measurements with the glass electrode. Of all of the methods that have been used with ferric hydroxide sols, the glass electrode was considered to be the most promising for reliable results. It eliminates most of the difficulties associated with the hydrogen electrode, such as oxidation reduction potentials and flocculation by gas bubbles. The only serious uncertainty is the liquid junction potential between the sol and bridge solution, which is necessarily present in any electrometric determination of a single ion activity.

Two methods for measuring the electromotive force of the cells were used. The first was that described by Kerridge,[3] a Lindemann electrometer being used as null point instrument in conjunction with a type K potentiometer. The second method was that of Robertson,[4] for which a high resistance, high sensitivity galvanometer was substituted for the electrometer of the previous method. It was sensitive to less than one millivolt with electrode resistances under ten megohms.

Each electrode was standarized against M/20 potassium acid phthalate buffer, with an approximately neutral reference buffer, and a saturated potassium chloride bridge. The cells measured may be written as follows:

Hg	Hg_2Cl_2, KCl solid sat.	Bridge sol'n.	M/20 KHP or sol	Glass	Ref. buffer	KCl sat.	Hg_2Cl_2 solid	Hg

$\longrightarrow$

The results obtained are summarized in Table III. E_{sol} is the total electromotive force of the cell with the sol, and E_{KHP} is that with M/20 potassium acid phthalate. The KCl, HCl bridge was the same as that used with the hydrogen electrode.

Glass electrode measurements were also made with several samples of ultrafiltrate. The sol was filtered through a cellophane membrane by means of a high pressure apparatus, the details of which will be described in a subsequent communication. The hydrogen ion concentrations depend upon the conditions of ultrafiltration, as will be explained in discussing the significance of the results of ultrafiltration. This method is therefore an uncertain means of finding such values for the sols. The range of results is given in Table V.

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[1] R. Wintgen and M. Biltz: Z. physik. Chem., **107**, 403 (1923); A. W. Thomas and A. Frieden: J. Am. Chem. Soc., **45**, 2522 (1923).

[2] H. M. Stark: J. Am. Chem. Soc., **52**, 2730 (1930).

[3] P. T. Kerridge: Biochem. J., **19**, 611 (1925).

[4] G. R. Robertson: Ind. Eng. Chem., Anal. Ed., **3**, 5 (1931).

TABLE III

Glass Electrode Measurements

Sol	Bridge	E_{sol}	E_{KHP}	T°	pH	$C_{H^+} \times 10^5$
3	N/10 KCl	0.154	0.171	21	4.26	5.5
3		0.151	0.171	21	4.31	4.9
3		0.146	0.163	18	4.26	5.5
3		0.146	0.163	18	4.26	5.5
3	KCl–HCl	0.1407	0.1310	21	4.14	7.2
3		0.1402	0.1310	21	4.14	7.2
13	N/10 KCl	0.145	0.164	20	4.30	5.0
13		0.146	0.164	20	4.28	5.2
13		0.144	0.163	17	4.30	5.0
13		0.140	0.163	17	4.37	4.3
13		0.142	0.163	17	4.33	4.7
13	KCl–HCl	0.1327	0.1310	21	4.00	10.0
13		0.1325	0.1310	21	4.00	10.0
20	KCl–HCl	0.1550	0.1310	21	4.38	4.2
20		0.1520	0.1300	20	4.35	4.5

TABLE IV

Quinhydrone Electrode Measurements

Sol	Bridge	E	T	pH	$C_{H^+} \times 10^5$
3	KCl, HCl	0.1270*	20	4.16	6.9
		0.1271	20	4.16	6.9
3	Sat. KCl	0.1145	23	4.18	6.6
3	N/100 KCl	0.1182	23	4.12	7.6
		0.1170	23	4.13	7.4
3	N/500 KCl	0.1220	23	4.05	8.9
13	KCl, HCl	0.1329*	20	4.06	8.7
		0.1335	20	4.05	8.9
20	Sat. KCl	0.0980	24	4.43	3.7
		0.0975	24	4.44	3.6
20	N/100 KCl	0.1061	24	4.30	5.0
		0.1062	24	4.30	5.0
		0.1064	24	4.29	5.1
20	N/500 KCl	0.1193	24	4.07	8.5
		0.1173	24	4.19	8.0

* This calomel half cell showed an E.M.F. of 0.3345 V. In all others it was 0.3410 V.

C. Measurements with the quinhydrone electrode. The quinhydrone electrode, in conjunction with various bridge solutions, was used with the same potentiometric set up as was the hydrogen electrode. With saturated potassium chloride, which was more dense than the sol, the siphon leading from the electrode compartment was filled with sol, which prevented mechanical mixing, and also coagulation in the region of the electrode, the latter occurrence having been found radically to alter the readings. The calomel half cell was checked against an M/20 potassium acid phthalate buffer. The cells measured may be written as follows:

$$\begin{array}{c|c|c|c|c} \text{Hg} & \text{Hg}_2\text{Cl}_2\text{, N/10 KCl} & \text{Bridge} & \text{Sol, quinhydrone} & \text{Pt} \\ & \text{solid} & \text{sol'n.} & \text{solid} & \end{array}$$

$$\longrightarrow$$

Discussion of Results

The following is a comparison of the values that were considered to be the most reliable by the various methods used.

TABLE V

Summary of Results of Hydrogen Ion Determinations

Electrode	Bridge	Age in weeks	pH	$C_{H^+} \times 10^5$
		Sol 3		
Glass	N/10 KCl	28	4.26	5.5
"	KCl, HCl	42	4.14	7.2
Quinhydrone	Sat. KCl	61	4.18	6.6
"	N/100 KCl	61	4.12	7.5
"	N/500 KCl	61	4.05	8.9
"	KCl, HCl	33	4.16	6.9
Hydrogen	KCl, HCl	30	5.66 to 4.92	0.22 to 1.20
		Sol 13		
Glass	N/10 KCl	21	4.30	5.0
"	KCl, HCl	35	4.00	10.0
Quinhydrone	KCl, HCl	26	4.05	8.9
		Sol 20		
Glass	KCl, HCl	7	4.37	4.3
Quinhydrone	Sat. KCl	28	4.43	3.7
"	N/100 KCl	28	4.30	5.0
"	N/500 KCl	28	4.08	8.2
		Ultrafiltrate from Sol 13		
Glass	N/10 KCl			2.8 to 8.4

An examination of these results shows that the glass and quinhydrone electrodes agree fairly well when used with the same bridge solution and with sols of the same age. The hydrogen electrode, however, although used with the same bridge solution, indicated a concentration of only from one-fifth to one-thirtieth of that shown by the other methods. It may, therefore, be concluded that the glass and quinhydrone electrodes give a true measure of the hydrogen ion concentration of ferric hydroxide sols, and that the hydrogen electrode gives values that are erroneous and much too low.

The effect of different concentrations of bridge solution is shown by the quinhydrone electrode determinations. The differences in hydrogen ion concentration may be seen from Table V and in terms of electromotive forces are shown by the following values:

Sol	$E_{\text{sat. KCl}} - E_{N/100\ \text{KCl}}$	$E_{\text{sat. KCl}} - E_{N/500\ \text{KCl}}$
3	0.0030	0.0075
20	0.0085	0.0205

In general, an increase in the concentration of the potassium chloride bridge solution decreases the apparent concentration of hydrogen ion; and there is no discontinuity in this effect when flocculation of the sol occurs so long as the sol in the region of the electrode is unaffected. It, therefore, seems probable that concentrated potassium chloride bridge solutions give the more nearly correct results, as is the case with simple electrolytes, for they more nearly eliminate diffusion potential, and there is no evidence of a membrane potential due to flocculated colloid.

It has already been pointed out that the hydrogen ion concentrations previously recorded for ferric hydroxide sols, determined by various methods, show wide and inconsistent differences. Several investigators have used these values as a basis for deducing the constitution of the sols studied, and a critical examination of their methods and results is essential in evaluating their conclusions. This is especially true of much of the work of Pauli and his associates, who use such determinations as part of their evidence for classing ferric hydroxide sols as polyvalent strong electrolytes. Pauli and Matula,[1] by use of the hydrogen electrode in the sol, obtained about 8×10^{-6} N; Pauli and Walter,[2] by means of the hydrogen electrode in the flocculation filtrate, found it to be 3×10^{-6} N; and Kühnl and Pauli[3] used a microtitration method to obtain 3.6×10^{-4} N.

It has already been shown that the first method gives low results, and there is no reason to assume that the flocculation filtrate would be identical with the dispersion medium of a sol, and results in this paper show that trustworthy measurements could not be made if coagulation occurred near the electrodes. It is also to be expected that titration would alter the hydrolytic equilibrium of a sol, and results by this method were higher than would

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[1] W. Pauli and J. Matula: Kolloid-Z., **21**, 49 (1917).

[2] W. Pauli and G. Walter: Kolloidchem. Beihefte, **17**, 256 (1923).

[3] N. Kühnl and W. Pauli: Kolloidchem. Beihefte, **20**, 319 (1925).

be predicted by comparison with sols 13 and 20 of this paper. It must, therefore, be concluded that the hydrogen ion determinations used by Pauli and his collaborators are not to be depended upon, but must be replaced by the much higher acidities here shown to be found with glass and quinhydrone electrodes.

Summary

Apparent hydrogen ion concentrations as given by hydrogen, glass, and quinhydrone electrodes have been compared, using sols of ferric hydroxide prepared with special precautions to avoid impurities and of known chemical composition and electrical conductivity. Results with glass and quinhydrone electrodes agree, but hydrogen electrodes give very low and erroneous results.

From experiments with various concentrations and acidities of the bridge solutions it was concluded that concentrated solutions of potassium chloride give the most nearly correct results, especially since flocculation of the sol has no effect so long as it does not occur in the neighborhood of the electrode.

My cordial thanks are due to Professor James W. McBain at whose suggestion this work was carried out.

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THE HYDROLYSIS OF MERCUROUS SULPHATE

BY O. B. HAGER AND G. A. HULETT

The unique properties of mercurous sulphate have made our standards of electromotive force possible, since one may employ mercury and a liquid amalgam for electrodes and a saturated salt solution for the electrolyte, in which mercurous sulphate is sufficiently soluble to give good depolarization.

The only defect so far encountered is the tendency of mercurous sulphate to hydrolyze in aqueous solution. The salt is a combination of a weak base and a strong acid with a pronounced tendency to hydrolyze but this tendency is counteracted by sulphuric acid and by some sulphates in solution. There appears to be no hydrolysis of mercurous sulphate in a saturated zinc sulphate solution, but it does measurably hydrolyze in a neutral cadmium sulphate solution. This fact leads to some important differences between the zinc cell, and cadmium cell and the Weston (unsaturated cell).

The first important information on the hydrolysis of mercurous sulphate was obtained by Gouy.[1] Gouy agitated 10 grams of normal mercurous sulphate with 500 cc. of water at room temperature (± 20°) until saturation was attained when the solution was removed and a fresh 500 cc. portion of water added, etc. The successive solutions were alike. Gouy analyzed them by removing the mercury electrolytically and then titrating the sulphuric acid. He found a liter of the solution to contain 400 mg. of mercury and the solution from which the mercury had been removed showed, on titration, 160 mg. of SO_3 to the liter. The eleventh 500 cc. portion showed a lower concentration of Hg and SO_3. Subsequent portions decreased in concentrations until the fourteenth portion, showing only small concentrations. Subsequent portions showed this same small concentration.

Gouy's experiments give a quite clear picture of the hydrolysis of mercurous sulphate by water. The first eleven portions were saturated with respect to mercurous sulphate with an increasing amount of basic sulphate present, and after the fourteenth treatment only the basic salt was present. Gouy observed this residue to be yellow-green and on analysis he arrived at the formula $Hg_2(OH)_2.Hg_2SO_4$. The next important contribution was by Cox[2] from Abegg's laboratory. Cox used Gouy's data in a phase rule diagram and was able to show that between the normal mercurous sulphate and mercurous oxide there is evidence of only one basic salt. Of the composition described by Gouy, Cox also concluded that .002 molar sulphuric acid inhibits the hydrolysis of mercurous sulphate. On page 18 (loc. cit.) Cox gives .0041 normal equivalent as the acidity which inhibits hydrolysis but there appears to be an error due to a misinterpretation of Gouy's data. Cox con-

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[1] Compt. rend., **130**, 1400 (1900).

[2] Z. anorg. Chem., **28**, 361 (1901); **40**, 180 (1904).

cluded that the first eleven solutions obtained by Gouy had an acidity of .002 molar sulphuric acid. Gouy analyzed these solutions by removing the mercury electrolytically and then titrating the exhausted electrolyte and found .002 moles of sulphuric acid in a liter. But part of this acid was associated with the mercury which had been removed electrolytically so that the acidity of the original solution, the "equilibrium water" was not that finally titrated but only half that or .001 molar sulphuric acid.

We have obtained a check on this value. On bringing the system mercurous sulphate-water and mercury to equilibrium at 25° it was found that the equilibrium water contained .002 moles of $HgHSO_4$ in a liter which is an acidity of .001 molar sulphuric acid or .002 normal equivalent. Writers who have followed Cox and assumed that .002 moles of sulphuric acid inhibit the hydrolysis of mercurous sulphate should now defend the proposition that .001 molar sulphuric acid inhibits the hydrolysis of mercurous sulphate. The equilibrium water .002 molar $HgHSO_4$ will neither dissolve nor hydrolyse mercurous sulphate, but it does not follow that water with .001 moles of H_2SO_4 to the liter will also inhibit this hydrolysis. We have evidence to show that a very much greater acidity is needed.[1]

By determining the solubility of mercurous sulphate in sulphuric acid of varying concentrations one finds a break in this solubility curve, at the acidity at which the basic salt appears as a phase. Starting with a strong acid, e.g., 4 × molecular H_2SO_4 where there is no suggestion of hydrolysis, the solubility of mercurous sulphate is quite small, .00087 moles Hg_2SO_4 in a liter. On diluting the acid the solubility increases quite rapidly to .002208 moles in a liter at molecular acidity. Here the curve takes a sharp downward trend uniformly to an acidity of 0.27 moles H_2SO_4 in a liter. At this point there is a slight inflection in the curve as it decreases less rapidly from here on to a minimum value at about .025 molar acidity. Henceforth there is a slow increase in the solubility of mercurous sulphate in distilled water where the hydrolysis furnishes an acidity of .001 molar sulphuric acid and here the experimental curve necessarily ends. The slight inflections in the curve at 0.27 and .025 molar acidities may be connected with a change in the heats of solution at these points. There is no evidence of the appearance or disappearance of a phase at either of these points, while at the sharp break at molecular acidity there is a marked change in the solid phase. Above molecular acidity analysis of the solid phase has shown normal mercurous sulphate while below molecular acidity analysis of the solid phase shows the presence of basic sulphate. Furthermore, the behavior of these products as depolarizers in standard cells confirms these conclusions.

These facts have led to the conclusion that in order to prepare normal mercurous sulphate one must have present at least molecular acidity of sulphuric acid. The curve (loc. cit.) clearly leads to the conclusion that mercurous sulphate may hydrolyse in sulphuric acids of less than molar concentrations.

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[1] Int. Electrical Congress, St. Louis, 2, 115 (1904).

We have attempted to test this conclusion by treating normal mercurous sulphate with a large excess of 0.1 molar sulphuric acid, which is 100 times greater acidity than is claimed to inhibit the hydrolysis of mercurous sulphate. Ten grams of chemically prepared normal mercurous sulphate[1] were washed with 0.1 molar sulphuric acid and brought together with 500 grams of mercury and some 1000 cc. of 0.1002 molar acid into a large rotating tube and brought to equilibrium at 25°. 800 cc. of the clear solution was now removed and replaced with an equal volume of the 0.1 molar acid. Successive portions showed the same concentration of mercury but after thirty changes of the electrolyte an accident interrupted the experiment, but the contents of the tube were intact and satisfactorily recovered and enough of the residue obtained for analysis and for filling a cadmium cell.

We have developed a very precise method for determining metals electrolytically[2] and this method is particularly satisfactory for determining mercury in the rather insoluble sulphate and basic salts. A platinum crucible was amalgamated internally, vacuum desiccated, weighed, and the salt weighed into the crucible. 10 cc. of water was added and a small platinum anode placed just above the salt permitted the mercury to be deposited on the amalgamated platinum as fast as the salt dissolved, leaving the acid in solution. About .010 amp. current served for this purpose. When the salt had disappeared and the mercury had all been deposited with the current left on, the sulphuric acid was syphoned into a little flask, water being simultaneously added until the milliammeter showed zero reading, indicating the complete washing of the deposit.. The last of the wash water was removed by a pipette and added to the acid which was titrated by a carefully standardized 0.1 normal NaOH solution, thus giving the SO_4 of the salt taken. The crucible was placed in a vacuum desiccator where it soon dried and was ready to weigh, giving directly the mercury of the sample of salt taken.

Experiments have shown that the weights of these amalgamated and vacuum-dried crucibles are very precise and reliable. The solubility of platinum in mercury is so small that no damage to a crucible results. The process is direct and most satisfactory for these mercury salts. The residue from the above rotation experiment was washed with alcohol and ether, dried in a vacuum desiccator, and 0.4011 grams weighed into the amalgamated crucible on electrolysis this salt was found to yield .3259 g. of mercury, while the acid syphoned off was titrated and required 14.27 cc. of 0.1096 normal NaOH. This gave a calculated .0751 grams of SO_4. Now .4011 g. of normal mercurous sulphate should give .3226 g. of mercury and .07856 g. of SO_4 so that the residue had lost relatively more acid than base by the action of the 0.1 molar sulphuric acid, that is, the salt had been partly hydrolyzed. Some of the residue from the rotation tube was now used for the depolarizer of a cadmium cell which was filled on September 7, 1931 according to the procedure in this

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[1] Int. Electrical Congress, St. Louis, 2, 126 (1904).

[2] Perdue and Hulett: J. Phys. Chem., 15, 147 (1911).

laboratory.[1] But it was not possible to get a reading at 25° until October 26, when it was 1.01685. The following observations have been made by Mr. R. B. Elliott:

September	7	1.01878 (extrapolated)	February	9	1.01501
October	26	1.01685	February	15	1.01482
November	18	1.01601	March	8	1.01458
December	16	1.01563	April	2	1.01443
January	18	1.01544	May	2	1.01408
February	3	1.01502	June	4	1.01374

The initial value is an extrapolated value but the first part of the decrease is nearly linear, so this must be a quite reliable value. At present the rate of decrease is diminishing and probably will continue to do so. But the initial high value and subsequent decrease are quite characteristic of depolarizers that carry basic salt. There appears to be no doubt that normal mercurous sulphate may be so altered by 0.1 molecular sulphuric acid that it gives a high and inconstant value to the cadmium cell when used as a depolarizer. This is quite in line with previous experience. It was found[2] that mixtures of normal and basic salt always gave a high initial value to cells followed by a decrease and it also developed that a mercurous sulphate which had been partially hydrolyzed by agitating together definite amounts of salt and water give greater effects on the E.M.F.'s than was the case when the depolarizer was made by mechanically mixing the basic salt with the normal salt. It is quite logical to conclude that the basic salt coats or becomes an intimate constituent of the surface of the particles or crystals of the normal salt, when it was first realized[3] that the basic mercurous sulphate was the main disturbing factor in the constancy of standard cells, it was thought that any commercial sample of mercuric sulphate might be satisfactory if treated with sulphuric acid so as to change the basic salt to normal and then properly preparing the paste so as to avoid forming the basic salt. A good grade of commercial mercurous sulphate was digested over night with a 12 times molecular sulphuric acid. The product was improved, but the cells in which it was used still clearly indicated the presence of basic salt. Whenever mercurous sulphate forms under conditions such that the basic mercurous sulphate may form, this basic salt appears to build into the crystal structure of the normal salt, so that treatment with sulphuric acid does not correct the difficulty. The basic salt does not appear where the sulphuric acid acidity is molecular or greater. This principle has permitted the preparation of normal mercuric sulphate both chemically and electrolytically.[4]

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[1] Hulett: Phys. Rev., 32, 257 (1911).

[2] Phys. Rev., 22, 328 (1906).

[3] Trans. Am. Electrochem. Soc., 5, 59 (1904).

[4] Carhart and Hulett: Trans. Am. Electrochem. Soc., 5, 59 (1904).

KINETICS OF THE DISSOLUTION OF DILUTE SODIUM AMALGAM*

BY ROBERT LIVINGSTON

Brönsted and Kane[1] have recently demonstrated that the rate of dissolution of sodium from a dilute amalgam into a solution of a weak acid is given by the following equation

$$-\frac{d(\Sigma Na)}{dt} = k(\Sigma Na)^{\frac{1}{2}}(A) \qquad 1$$

where (ΣNa) is the stoichiometric concentration of sodium in the amalgam and (A) is the concentration of the acid in the aqueous (or benzene) layer. In interpretation of these results, they advance the following mechanism.

$$A + \ominus \rightarrow B + H \text{ (slow)}^{2} \qquad 4B\text{-}K$$

$$2H \rightarrow H_2 \text{ (relatively rapid)} \qquad 6B\text{-}K$$

$$\underset{\text{(metal)}}{Na^+} \rightarrow \underset{\text{(dissolved)}}{Na^+} \text{ (relatively rapid)} \qquad 3B\text{-}K$$

While this mechanism affords an explanation of the proportionality of the rate to the concentration of the acid, it does not offer a direct explanation of the dependence of the rate upon the square root of the sodium concentration.

It is well known that sodium and mercury form the compound $NaHg_2$. Evidence for the stability of this compound may be obtained (1) from the sharpness of the corresponding maximum in the melting-point curve,[3] (2) from the high heat of solution of sodium in mercury,[4] and (3) from the large difference of electrical potential between sodium and sodium amalgam.[5]

It seems probable therefore that the following equilibrium (which may take place in steps) is an important factor in determining the rate of dissolution.

$$NaHg_2 \rightleftarrows Na^+ + \ominus + Hg_2 \text{ (rapid reversible)} \qquad 2$$

The rate of reaction 4B-K is

$$V_{4B-K} = k_{4B-K}\,(A)\,(\ominus) \qquad 3$$

But applying the mass action law to reaction 2

$$(\ominus) = K\left[\frac{(NaHg_2)}{(Hg_2)}\right]^{\frac{1}{2}} \qquad 4$$

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* Contribution from the School of Chemistry, University of Minnesota.

[1] Brönsted and Kane: J. Am. Chem. Soc., 53, 3624 (1931).

[2] A and B represent a conjugate acid and base respectively. See Brönsted: Rec. Trav. chim., 42, 718 (1923).

[3] Inter. Crit. Tables, 2, 436.

[4] Inter. Crit. Tables, 5, 202.

[5] Inter. Crit. Tables, 6, 332.

Since the greater part of the sodium exists as the compound, equation 4 may be written approximately as—

$$(\ominus) = K^{1}\,(\Sigma \mathrm{Na})^{\frac{1}{2}} \qquad 4a$$

The combination of equations 3 and 4a leads directly to the empirical equation 1. It should be mentioned that no mechanism which postulates the existence of appreciable concentrations of the ion $NaHg^{+}{}_{2}$ need be considered, since such a compound, between the mercury molecule and the sodium ion (with its rare gas structure) would undoubtedly be relatively unstable.

In other amalgams where there is less tendency toward compound formation, the rapid reversible step may be

$$\mathrm{Me} \rightleftarrows \mathrm{Me}^{+} + \ominus \qquad 5$$

This reversible step would be consistent with an empirical equation similar to equation 1, if the metal were largely non-ionized; but if it existed chiefly as ions and electrons, the rate of dissolution would be directly proportional to the stoichiometric concentration of the metal. This suggests a possible explanation of the results of Fraenkel and Heinz[6] on the rate of dissolution of alkaline earth amalgams.

Summary

A mechanism is presented for the dissolution of sodium from dilute amalgams.

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[6] Fraenkel and Heinz: Z. anorg. Chem., **137**, 39 (1924).

While this paper was in proof two articles have appeared which discuss the results of Brönsted and Kane (1). C.V. King and M.M. Braverman (J. Am. Chem. Soc. 54, 1744 (1932)) have studied the rate of dissolution of solid metals in acid solutions containing depolarizers, and have concluded that the rates are entirely determined by diffusion speed. L.P. Hammett and A.E. Lorch (J. Am. Chem. Soc. 54, 2128 (1932)) advance the theory that the square root law is to be attributed to a phenomenon related to over voltage. Needless to say, the mechanism discussed here is a significant explanation only if the measured rates were not influenced by the speed of diffusion. (cf. Ref. 1, pp. 3634-5).

NEW BOOKS

A Text-Book of Experimental Cytology. *By James Gray. 23 × 16 cm; pp. x + 516. New York: The Macmillan Company, 1931 Price: $7.50.* The chapters are entitled: the cell as a unit of life; the cell as a physical unit; cell dynamics; the cell as a colloidal system; the physical state of protoplasm; cell membranes and intercellular matrices; the nucleus; mitosis; cell division; the shape of cells; the growth of cells; cell variability; the equilibrium between a living cell and water; the permeability of the cell surface; the nature of the cell surface; contractile cells; phagocytosis.

"Until recently the central theme in zoological thought has been Evolution and whatever be the mechanism whereby one species has given rise to others we may be quite sure that the processes involved are essentially of a dynamic nature; the potentialities of the organism and the nature of the environment have operated together to produce new and varied forms of life. Any real insight into the causes of Evolution involves a knowledge of function, and any conception of the organism as a dynamic unit is incomplete without a knowledge of its evolutionary history. It is just as illogical to restrict the study of animal life to morphological observations as it is to study an aeroplane as though it were a static and inert machine. Precise knowledge of the reactions between an organism and its environment is, however, very rare in those cases where the sequence of evolutionary forms is best known, and students of Evolution must either be content with relatively vague and indefinite speculation or must set to work to analyse environmental responses for themselves," p. vii.

"Cytology may rightly claim to be the frontier state in the biological commonwealth, for within its borders biologists and chemists find common ground. The chemist is interested in the activities of living matter and the biologist is impressed by the orderly analysis to which the chemist can submit his facts. A biologist who attempts to give a generalised conception of the living cell inevitably invites active criticism, for the attempt to co-ordinate the relevant facts is fast becoming a task beyond the competence of any one individual. Sir William Hardy has recently described the ideal biological college: 'It should have three floors—a ground floor for molecular physics, a first floor for biophysics, and a top floor for cell mechanics.' The present book represents an honest, if pathetic, attempt to creep downstairs. It represents the impressions which the author, as a biologist, has gained by contact with such physical facts as appear to him to bear on the structure of living matter, and which can be imparted to others like himself, whose knowledge of inanimate matter is limited," p. viii.

"As a physiological unit the rôle of the individual cell is not quite so clear. In the first place the cell is not a fundamental unit in the sense that any process of subdivision leads to a complete disorganisation of its properties. An enucleated fragment of an amoeba or of a sea urchin's egg is by no means dead, but retains for a considerable time typical properties of living matter; bacteria are alive, yet their structure is by no means similar to that of a typical cell; fungi are also alive, and yet they exhibit no cell structure in the strict sense of the word. Difficulties of this kind have perplexed cytologists for many years and are still real objections to the time-honoured Cell Theory," p.1.

"Even within inanimate colloidal systems the statistical laws break down when we deal with units which are no larger than typical living cells. Using a suspension of gold particles, whose average radius was 19 $\mu\mu$, Smoluchowski (see Svedberg, 1928) found that within a volume of the suspension equal to 1064 μ^3 (i.e. the approximate volume of many living cells) there was an *average* number of particles equal to 1.545. When this small volume of suspension was examined from time to time, however, the actual number of particles visible varied very considerably—sometimes no particles were visible, at other times as many as seven could be seen. This variation is, of course, due to random Brownian movement," p.7.

"Quite clearly the degree of statistical variation which will occur in molecular systems depends largely on the magnitude of the system examined. If we examined 1 cc. of the gold suspension the amount of variation would be relatively small: if we use a volume of 10 μ^3 it will be very large indeed. As long as we are dealing with large systems, any significant variation in the distribution of matter or energy occurs for such short periods of time or on so very few occasions, that we are justified in ignoring any state other than the one which is the most probable. In other words, in large systems the statistical possibilities postulated by the kinetic theory of matter are arbitrarily eliminated by assuming the truth of the Second Law of Thermodynamics," p.8.

"A more adequate picture of intracellular oxidase systems is available from the work of Keilin (1925, 1926, 1929). Keilin showed that nearly all cells contain an oxidisable pigment, *cytochrome*, which, in the reduced form, exhibits a definite series of spectral bands. If a suspension of cells in an oxygenated medium is examined spectroscopically no spectral bands of cytochrome are visible; if, however, the oxygen be removed, four distinct bands of reduced cytochrome become visible, which again disappear on admitting oxygen. We may conclude, therefore, that oxidised cytochrome is rapidly reduced by the cell and that reduced cytochrome is rapidly oxidised by atmospheric oxygen. In other words cytochrome can act as carrier of oxygen.

"Keilin has shown that cell narcotics, e.g. urethane, can prevent the reduction of cytochrome but they do not inhibit its oxidation. For instance, if ethyl urethane is added to a yeast suspension, the cytochrome is immediately oxidised and is not reduced on the removal of oxygen. On the other hand, a trace of cyanide will immediately reduce oxidised cytochrome, and will prevent its oxidation by free oxygen. There are, therefore, two distinct processes at work—those concerned with the oxidation of reduced cytochrome and those concerned with the reduction of oxidised cytochrome; the cytochrome is acting normally as an intermediate carrier of oxygen between these two processes. Keilin (1929) has recently shown that the systems responsible for the reduction of oxidised cytochrome are the dehydrase system of enzymes, whereas the catalyst responsible for the oxidation of reduced cytochrome is none other than the indophenol oxidase system so universal in animal tissues. All factors which influence the activity of dehydrase enzymes inhibit the reduction of cytochrome and all factors inhibiting indophenol oxidase inhibit the oxidation of cytochrome. It looks as though the 'respiratory ferment' of Warburg is really the indophenol oxidase system, and that it is only a part of the whole respiratory mechanism," p. 20.

"The conception of the cell as a colloidal system is probably one of the most important landmarks in the history of cytology. For nearly a century our knowledge of cell structure was based, not on observations of living units but upon cells which had been stabilised by fixation and artificially differentiated by staining reactions. Almost simultaneously, Fischer (1899) and Hardy (1899) demonstrated, without any element of doubt, that these standardised but arbitrary processes were of the same fundamental nature as those which effect the precipitation of inanimate protein systems and which control the uptake of dyes by the coagulated particles. This fundamental discovery showed that the only reliable guide to protoplasmic structure must lie in a study of uncoagulated colloidal systems and not in a meticulous observation of coagulated cells. For more than thirty years every student of cell structure has had, of necessity, to follow the rapid march of colloidal chemistry. To some extent the position is satisfactory: the colloidal properties of cell constituents are now realised and we are not likely to make very gross errors in the interpretation of cell structure. At the same time, we must constantly bear in mind that the living system is incomparably more complex than any which has, so far, attracted the undivided attention of the chemist," p.33.

A priori, one would suspect the phenomena of *antagonistic ion action* to be concerned with the equilibrium between metallic ions and protein systems, and to a significant extent this view is supported by experimental facts. There always remains, however, one outstanding difficulty. From a chemical point of view the equilibrium between proteins and potassium ions is very similar to the equilibrium between proteins and sodium ions, and yet the biological properties of the two ions are profoundly different," p. 47.

"Except in the particular case of the Feulgen reaction it is not very easy to assess the cytological value of microchemistry. When we state that protoplasm invariably contains proteins and derivatives of the fats, the contribution to cytology is comparable, in aeronautics, to a statement that an aeroplane invariably contains iron and copper. Either the essential constituents of the living machine are composed of protein and lipoids or they are orientated in a matrix of these compounds. Both for a study of the cell and of an aeroplane we require to know not only the shape and function of the various chemical constituents, but we want to know how they are oriented in respect to one another to form a working and useful unit," p. 84.

"It has been long known that the hyaline surface of a cell is instable in the absence of divalent cations (e.g. calcium, magnesium) from the external medium. In the absence of calcium no hyaline surface forms on an echinoderm egg, and in 1900 Herbst showed that in calcium-free sea-water the intercellular matrix of an echinoderm larva is dissolved and the cells separate freely from each other. In the case of *Mytilus* tissues the matrix is disorganised if magnesium is absent (Gray, 1926), whilst Galtsoff (1925) found that calcium and magnesium are both required for the reunion of artificially separated sponge cells. We thus reach the conclusion that the normal elastic surface of the cell is a gel whose cohesive properties depend upon the presence of divalent metallic ions. The only compounds which appear to have the property of forming cohesive membranes in the presence of calcium appear to be the proteins and possibly some of the polysaccharides. If substances such as gluten, casein, or mucin are powdered and rubbed with a little water they readily yield a tough coherent mass which is practically insoluble in water, and which can be pressed out into a more or less transparent membrane. The factors influencing the stability of such protein gels are strikingly similar to those which influence the stability of the hyaline gel which binds together the cells on the gills of *Mytilus edulis*," p. 107.

"The universal presence of nucleic acid in animal nuclei leaves little doubt that this compound is essentially the same as the 'chromatin' of histologists. Free nucleic acid has just those affinities for basic stains as are characteristic of chromatin, and the variation in the staining properties of the kinetic nucleus are paralleled by the staining properties of nucleic acid when saturated to varying degrees by combination with basic proteins. The evidence supporting an identity of chromatin and nucleic acid is greatly strengthened by the recent work of Feulgen and others. If a tissue be exposed for a suitable time and at a suitable temperature to a solution of mineral acids the distribution of chromatin can be detected by subsequent staining with acid fuchsin," p. 128.

"The most direct proof that the asters form an active part of the cleavage mechanism is provided by the fact that any irregularity in the size or position of these structures is invariably accompanied by an irregularity in the form and position of the cleavage furrow," p. 201.

"In 1919 Hartridge suggested that the characteristic discoidal form of mammalian erythrocytes is an adaptation to the physiological functions of the cell. In order that oxygen should reach the centre simultaneously from all points of the surface, the cell must be either a sphere or an infinitely thin disc. If the red blood cell were spherical, however, it would present a minimum surface per unit volume, and consequently the rate at which oxygen would enter would be reduced to a minimum. In a flat disc, however, oxygen would reach the centre more readily at the periphery than elsewhere. The peculiar form of the mammalia erythrocyte compensates for this by its greater thickness at the periphery—so that oxygen will reach the centre of the cell simultaneously from all part of its surface," p. 263.

H. V. Wilson found that "if the tissues of the sponge *Microciona* are cut up into small fragments and squeezed through bolting silk, the resultant pulp of cells is capable of reorganising itself into compact tissues or even into new sponge individuals," p. 297.

"There is so much evidence to show that the cell surface is not equally freely permeable to both anions and cations, that one tends to overlook the fact that nevertheless a growing cell must be in a position to absorb both types. How far the recent work of Mond (1927) throws light on this difficulty remains to be seen. Mond has shown that if red blood-corpuscles are on the acid side of their iso-electric point their chlorine content goes up and their potassium content goes down, whilst on the alkaline side the relative concentrations are reversed," p. 370.

"Ruhland (1908-13) showed that there are a number of dyes (e.g. methylene green and thionin) which enter cells readily but which will not dissolve in cholesterol: similarly there are a number of 'fat-soluble' dyes (cyanosin, Bengal rose) which will not enter the living cell," p. 371.

"He points out that the ability of dyes to enter a plant cell is often less than its ability to enter an animal cell, and that this is particularly obvious when the fat-soluble dye is in the colloidal state: it is therefore possible that the failure to enter the plant cell may be due to the inability of a molecular aggregate to penetrate the cellulose wall. If this conclusion is justified, one grave objection to Overton's hypothesis disappears, but it is still necessary to account for the fact that methylene green and thionin (both insoluble in lipoids) will enter both animal and plant cells. Hertz (1922) showed that the entrance of these dyes into *Opalina* is unaffected by the presence of anaesthetics, whereas the entrance of fat-soluble dyes was inhibited. Höber, therefore, suggests that lipoid-soluble and non-lipoid-soluble dyes enter by a different mechanism. Similarly Nierenstein (1920) found that an adequate correlation between the ability of basic and acid dyes to enter *Paramecium* and their partition coefficients between a fat-soluble substance and water only exists when the fat solvent (e.g. olive oil) contains both a base and an acid (e.g. diamylamine and oleic acid). So far as these facts can be summarised, they seem to suggest that most cell surfaces are permeable to those dyes which can either (i) dissolve in fats, or (ii) react with some constituent of the membrane, provided that in all cases the molecular aggregates of the dyes are not beyond a certain maximum size (Höber and Kempner, 1908; Höber and Chassin, 1908)," p. 372.

"The relationship which exists between a contracting muscle and diffusible ions has also been investigated by Mitchell and Wilson (1921), who found that when frog's muscles are stimulated to contract under conditions which do not involve irreversible stages of fatigue, the cells lose no more potassium than is attributable to a potassium-free medium; on the other hand, it is only during contraction that a muscle will absorb rubidium or caesium. The interpretation of these facts is not easy, but they indicate that the act of contraction alters in some way the diffusibility of electrolytic ions. Parallel to McClendon's results with excited muscle fibres are the observations of Blackman and Paine (1928) on the exosmosis from the pulvinus of *Mimosa* during stimulation," p. 401.

Wilder D. Bancroft.

The Adsorption of Gases by Solids. *A General Discussion held by the Faraday Society, Jan. 1932. 25 × 16 cm.; pp. iii + 318, London, Gurney and Jackson, 1932, Price: 15 shillings.* It is important now and again, for scientists in any particular field to get together and thrash out the various problems, experimental and theoretical, which may have arisen during a period of years. The frequent discussions organised by the Faraday Society bring together workers in many branches of physical chemistry and perform a valuable service. All such discussions tend to centre on the more recent developments and the volume under review is no exception. In the nature of things, however, the substance of a number of the papers is to be found in many journals and proceedings published during the last few years.

The papers are collected under three main heads; Experimental Methods, Kinetics and Energetics of Adsorption, and, finally, Theories of Adsorption. The adsorptive properties of glass vessels are well known and the necessity of using clean de-sorbed glass has made most chemists and physicists familiar with the elementary principles of adsorption. The growth of experimental evidence during recent years has led to the recognition of more than one type of adsorption.

At very low temperatures gases are strongly adsorbed by solids. At moderately low temperatures the adsorption passes through a minimum and at high temperatures strong adsorption sets in again, followed by a decrease at still higher temperatures. Adsorption at low temperatures is associated with small binding energy and is generally ascribed to forces of the van der Waals type. The term "dispersion forces" is also used by some continental writers to describe the same phenomena. The heats of adsorption at these low temperatures are generally of the order of one or two thousand calories per gm. molecule of gas adsorbed. Adsorption at liquid air temperature is usually instantaneous, but high temperature adsorption proceeds with a measurable velocity, which increases rapidly with temperature, and because of this analogy with chemical reactions has been termed "activated" adsorption by some writers, "chemisorption" by others. An activation energy is required for this type of adsorption and evidence is brought forward in the introductory paper to show that this energy is acquired after contact with the solid has been attained. If the necessary energy were possessed by the impinging gas molecules, the quantity of gas adsorbed in a given time should be much greater than is actually observed. The heats of adsorption associated with the high temperature phenomena are roughly ten times those associated with the van der Waals or low temperature adsorption. Further distinctions between the two types of adsorption can be made. In low temperature adsorption the sorbate is recoverable by pumping. With "activated" or "chemisorption" the gas is sometimes recoverable, but frequently the process is irreversible. The well known case of oxygen and charcoal is an example of the latter type, where the oxygen is usually given off as oxides of carbon. Apparently the C-O binding is stronger than the C-C binding of the solid at high temperatures.

Of special interest in the first section one may note the discussion on the determination of the specific surface in the introductory paper, the use of thermionics in adsorption problems, and the question of the mobility of adsorbed atoms which is discussed, *inter alia*, by many of the contributors. One may venture the opinion that the work of Langmuir, Becker and others on the effect of adsorbed layers on the thermionic properties of metal wires, and the work of Volmer and his school on the mobility of adsorbed molecules are the most elegant experimental methods of recent years, which are likely to have a fundamental bearing on the theoretical development of the subject. The unique properties of electron beams in discovering the arrangement of adsorbed gas molecules are likely to be much used in the near future, although the applications may be somewhat limited. The method may be restricted to low-velocity electrons in high vacua. It is possible that a study of the melting properties of two-dimensional adsorbed films may be of the utmost importance in the theory of the liquid state. Another paper in this section deals with the sorption of gases by glass, and although the pressures are too high to be of practical interest to those who use high vacua, one notes with interest the effect of various treatments, such as washing and annealing the glass surface. This raises the vexed question of the preparation of adsorbents which is also discussed by other contributors.

The second part of the discussions on the kinetics and energetics of adsorption processes contains many interesting papers. The use of the *ortho-para* hydrogen conversion in adsorption problems is specifically discussed in several papers and appears to have aroused a good deal of interest. The mechanism of the catalysis of ammonia on tungsten is also very thoroughly dealt with, and the occlusion of hydrogen by palladium is considered in a series of papers from Oxford. Interest in this section will perhaps, however, centre on the discussion of discontinuities in adsorption processes, to which several groups of workers have now testified. It appears that the adsorption isotherm is not really a continuous curve but a succession of sharply defined loops concave to the pressure axis. Discontinuities have been observed with charcoal, silica gel and copper and iron catalysts as adsorbents. It is too early to give adequate reasons for the discontinuities and the general impression derived from these discussions is that much more data are required before a solution of the problem can be reached.

One of the outstanding difficulties of all work on adsorption is connected with the adequate preparation of the adsorbent for the experiments. It is an unfortunate fact that most of the substances suitable from the point of view of porosity and large specific surface area are almost complete unknown from the structural point of view. In order to free any surface of gas it has been necessary, until recently, to degas the material to a comparatively high temperature, and this procedure has automatically produced sintering of the adsorbent and alteration of surface area, etc. Considerable doubt may, in fact, be expressed as to whether adsorbents treated in this manner *are* gas-free. Consequently, one is led to the conclusion that many of the values for λ, the heat of adsorption, whilst no doubt reliable for the particular complex examined, should be taken as the heat of adsorption of gas A on the gas-solid complex B-C rather than the true value of λ for the complex A-C. The discussions under review emphasized, to one reader at least, the importance of a new method of producing a clean adsorbent. This method consists essentially in passing a stream of vapour, such as CCl_4 or CS_2, over the adsorbent. It is even suggested that a connection exists between "activated" adsorption and gas displacement effects. The process which requires energy of activation may be that of displacement of residual gas from the adsorbent by the adsorbed gas.

The final section contains many papers of great interest. Before passing on to these, one may note an interesting paper on accommodation coefficients where the interchange of energy between gas atoms and solid surfaces is shown to depend on the cleanliness of the adsorbed surface. As an example one may compare the older value of 0.3 for helium and tungsten with the recent value of 0.057. The introductory paper to section 3 consists in a general theoretical survey in which the influence of electrostatic forces, valence forces (of the Heitler-London type) and van der Waals forces on adsorption are considered. The paper on accommodation coefficients already referred to presages the fact that the interactions of gas and solid can only be fully worked out by the applications of the methods of wave mechanics. At the risk, therefore, of presenting the gist of this part of the discussion in an unbalanced manner, one would like to attempt a summary of the theory of Lennard-Jones which has already explained a number of adsorption phenomena in more than a qualitative manner.

The low temperature, or van der Waals type of adsorption is first discussed. All of the ultimate reactions between atoms and molecules, whether they be in the same phase or not, must be explicable in terms of the interactions of the systems of electrical charges of which they are constituted. It is now known that atoms attract each other at large distances according to an inverse seventh power law and this "seems to be due to a sympathetic fluctuation of the electron space clouds of the two atoms which produces in the atoms effective dipoles tending to move more in phase than out of phase." The case of the interaction of gas atoms and a metallic conductor is considered, modern theories allowing the latter to be regarded as a perfectly polarizable system. The interaction of the gas atom and the metal can then be treated according to the classical method of electrical images and the potential energy of the atom due to its image is given by $mc.^2\chi R^{-3}$ where m is the mass of the electron, c the velocity of light, χ the magnetic susceptibility of the gas atom, and R its distance from the metal surface. From this it has been possible to estimate the heats of adsorption of argon, hydrogen and nitrogen on copper. The figures obtained are of the same order as the observed values. The potential fields of argon and neon outside crystals of KCl and NaF are considered, and it is pointed out that these fluctuate according as the gas atom is above the centre or corner of a unit cell. The surface of a crystal from the point of view of a gas atom outside it is a regular series of mountains and valleys. The theory is then developed qualitatively to include the phenomenon of "activated" adsorption to include the phenomenon of "activated" adsorption of, for example, hydrogen on a metal. The cohesion between the metal and a hydrogen atom is supposed to be greater than half the dissociation energy of H_2 and the height of the point of intersection of the potential energy curves of the two systems metal and molecule, and metal and atom A + atom B gives the activation energy for a transition from metal + molecule to metal + atoms. The conceptions of the metallic state which have had so much success in explaining the phenomena of thermionics and electrolysis are seen to throw considerable light on the current problems of adsorption. The theory is further applied to the slow sorption of hydrogen on copper to which experimental observations had also attributed an energy of activation and a simple interpretation of this quantity is given. It may be added that the conception of two-dimensional melting involves the penetration of the potential barriers of the crystal surface already referred to. The mathematical difficulties confronting the worker in this field, are, to say the least, very considerable, and one feels that the way to a better understanding of the fundamental processes of adsorption phenomena has been pointed out. The volume should be of considerable value and inspiration to all workers on the subject. The introductory papers alone form an admirable synopsis of the present stages of development and are worth study by those to whom the subject is only of general and not particular interest.

J. T. Randall

Repertorium der physikalischen Chemie. *By H. Zeise. 21 × 13 cm; pp. vi + 215. Leipzig and Berlin: B. G. Teubner, 1931. Price: 8 marks.* Dr. Zeise has skilfully compressed into about 200 pages of well printed and illustrated text a surprising amount of clear and accurate information. The size of the strongly bound book enables it to be carried in the pocket and makes it suitable for reading at odd moments as well as for sustained study. All the important branches of the subject are covered and the treatment, whilst thoroughly modern, is not out of balance. The sections on quantum mechanics, wave mechanics, spectra (including band and Raman spectra), atomic and molecular structure, types of linking and strong electrolytes are clear and intelligible and really convey information, yet the sections on the properties of gases, solutions, thermodynamics, phase rule and electrochemistry are equally good and as carefully developed. The book is one which can be warmly recommended and its low price is a welcome feature in these days of expensive books. The student who reads German will find it most useful in revising a large amount of material, and the chemist who is not a specialist in physical chemistry will get from its pages a good understanding of modern developments in that science. There are several misprints and quite minor errors besides those listed on p. vi; for example in the discussion of isotopes on p.5, and in the values of the potential of the decinormal calomel electrode on p.201, which have not been corrected for the arithmetical error in Randall and Young's paper. It is unusual to apply Pauli's principle to five quantum numbers (p. 24). A reference to Sutherland's formulae might have been given on p.107 (it is given on p.111), and something said about recent investigations as to its validity. The statement on p.123 that the different specific heat curves of the solid elements in Fig. 36 are due to different expansions does not seem correct, since the abscissae are not reduced temperatures. *J. R. Partington*

Gmelins Handbuch der anorganischen Chemie. *Edited by R. J. Meyer. Eighth edition. System-Number 7. Brom. 25 × 16 cm; pp. xxxvi + 342. Berlin: Verlag Chemie, 1931. Price: 56 marks (Subscription price 49 marks).* With the publication of this section the great treatise on inorganic chemistry moves a step further towards the goal of completeness which, in some past works of this type, has proved a limit reached asymptotically. The rate of progress seems to promise that the whole work will be achieved within a reasonable time, and that the earlier sections will not be completely out of date by the time the later ones are issued. The present volume on bromine sustains the excellent standard of previous ones, the element and its compounds with water, hydrogen, oxygen (including oxyacids), nitrogen, fluorine and chlorine, being considered from all points of view, physical, physico-chemical and purely chemical, with great completeness. The information is up to date: there is a long section, for example, on bromine oxide, and the optical proof of the existence of bromine chloride is also described in detail. A great amount of numerical information is incorporated into the text, and there are useful curves and figures. The information on technical processes is quite detailed, and includes the aniline precipitation method tried out by the Ethyl Gasoline Corporation. The section on technical purification of bromine is fuller than usual, and there is a long section on production data. In view of the strong contradictory experimental evidence, the long section on the Budde effect and the effect of moisture on it, might have been shortened with advantage. *J. R. Partington*

Physikalisches Handwörterbuch. *Edited by A. Berliner* and *K. Scheel. Second edition. 28 × 20 cm; pp. vi + 1428. Berlin: Julius Springer, 1932. Price: 96 marks, bound in cloth 99.60 marks.* The book under review is the second edition of a work which, inscribed to Nernst on the occasion of his sixtieth birthday, first appeared in 1924. The new version has been brought up to date in a comprehensive manner, which has involved increasing the number of pages by well over one-half. But, printed as it is, on thin but good paper, in adequate type and with two columns per page, it remains a volume of reasonable size, convenient to handle and to read.

For the contents, there can be little but praise. Designed by the editors, not so much for the physicist who wishes to obtain a first broad impression of subjects outside his own special field, as for those who use the science of Physics "als Hilfsfach," it appears to the reviewer that it is a volume which will be of emphatic service to any physical chemist who has access to it. For, whilst there are paragraphs or articles on all the usual topics hitherto comprised under physical chemistry in its narrower sense, these are generally very brief, much more attention being paid to aspects of theory and of technique, with which most of us have had a rather perfunctory acquaintance in the past, but with which it is increasingly important that we be familiar. And, as far as the reviewer can judge, the contributions maintain throughout a high level in respect of accuracy, conciseness and clarity.

At the risk of appearing invidious, a few of the topics treated will be selected for specific mention. The *Atom* and the *Atomic Properties* are dealt with in a series of articles covering ten pages, written by Hahn, Gerlach, Kohlrausch, Scheel and others. Here, as elsewhere, a number of contributions are unsigned. The whole forms a compact and authoritative summary. *Explosions* are treated in seven pages, chiefly by Wendlandt, and the very informative article on *Glass* (by R. Schaller, of Jena), is of the same length. Eight pages are devoted to *Colour* and to related subjects which, between them, cover a very wide field. *Photometry* is dealt with from many points of view by Liebenthal (17 pp.). Eleven pages cover various aspects of the older and newer *quantum theory*. The articles are unsigned. The subject of *crystals* is treated in considerable detail by Schiebold (32 pp.). *Heat* and related subjects occupy 14 pp., written by such authorities as Henning, Scheel and Gröber. Henning is responsible for most of the articles on *thermodynamics*, good representative contributions being those on *Entropy*, *Gas Degeneration*, and *Equations of State*. W. Jaeger writes, inter alia, on *Galvanometers*, and deals authoritatively with *electrical units* and their dimensions. The articles on *Dark-Field Illumination and Ultramicroscopy* by M. Berck and on *Diffraction* by Boegehold, on *Hardness* (Schleicher) and on *Plasticity* (Nádai), are typical of the useful and competent material with which the book is packed. *Radioactivity* is accorded full treatment—thus the contribution by Kohlrausch on *Actinium* occupies three pages.

Good typical articles on physico-chemical themes are those by Wohl on *Reaction Velocity* and on *Gas Equilibria*, but frequently, though chemists need not complain, the treatment of such subjects is so very brief as to make it doubtful whether it retains any value. Schwab writes in an interesting way on *Activation*. A note of a different kind is struck in the contributions by Reichenbach entitled *Wahrscheinlichkeit* and *Wahrheit*.

Beyond the matter just touched on, it is difficult to criticise. The short article on *Drying* is without value; reference is made to a laboratory manual of organic chemistry as the authority on the subject. The relative lengths of the contributions vary somewhat curiously in certain cases. Three pages on *Isomerism* hardly compensate for the fact that only about half this length, in all, is devoted to the subjects of *Alloys*, *Solubility* and *Solution*. But emphasis on such minor points would be ungracious; the editors, in face of the familiar difficulties which they describe in their preface, have achieved a very considerable success, and one which will be really appreciated by all who use the book. *A. J. Allmand*

Rechenverfahren und Rechenhülfsmittel mit Anwendungen auf die analytische Chemie. *By Otto Liesche (Die chemische Analyse. Band XXX.) 25 × 16 cm; pp. viii + 201. Stuttgart: Ferdinand Enke, 1932. Price: 20 marks, bound 22 marks.* In this monograph Professor Liesche deals entirely with arithmetical processes as applied to chemical science. The object is to instruct the student how to shorten his computations and to make him familiar with the theory underlying each method. The author holds that axiomatic truths are neglected or are not properly mastered either at school or university. Hence the detailed explanatory statement accompanying each method he describes, which should prove most useful not only to teachers in secondary schools and institutes but also to workers in chemical laboratories. The author revises Seneca's view of school and after life and writes "Non vitae sed scholae discimus" and we agree with him when the phrase is applied to mathematics, the basis of all physical science. Many school problems are rather artificially set, as the boy finds when he becomes a laboratory worker. Thinking on inductive lines should be more prevalent than it is in schools. The processes of deduction are more appropriate in later life. Every schoolboy with average brains should leave school well grounded by practice in arithmetical processes. The author strongly recommends the methods of exposition devised by Dr. Ferrol and holds that formidable looking problems yield simple and spontaneous solutions if Ferrol's technique is used. We agree that a careful study of Ferrol's processes would be a great advantage to the scholar. He would be trained in algebraic thinking of a character most useful in after life in the laboratory. We fear however it will take some time for Ferrol's method to penetrate in schools.

The first chapter of Dr. Liesche's book is devoted to an exposition of the four rules of arithmetic, using Ferrol's processes. Logarithms, the slide rule and calculating machines are discussed in a wholly elementary manner in the second chapter. We think the slide rule should give place to the calculating machine in all laboratory calculations where multiplication and division are necessary. Time is lost in logarithmic computations and there is a loss of accuracy in using the slide rule. In describing the Brunsviga the author mentions Leibnitz as the first inventor of a calculating machine but omits to notice the pioneer work of Babbage in this country. The calculating machine is merely a time-saving device but this is what is wanted in a laboratory. The worker is saved mere mechanical mental activity and is free to apply his mind fully to the theoretical side of his problem.

. The author shows in the third chapter how algebra can be used effectively in computations as a time-saving device, particularly in problems of physical chemistry such as mass action problems. The fourth chapter is devoted to an elementary exposition of nomography, the name given by d'Ocagne in 1884 to describe the graphical method of solving all equations of a given type by means of one diagram. A simple example is a quadratic equation of the type $x^2 + ax + b = 0$. A diagram constructed to solve an equation of this type is called a nomogram. A number x is determined by means of a nomogram when two numbers a and b are given. Two straight lines for a and b are graduated and the x curve is so graduated that if a straight line is drawn joining the graduation a on the a scale to the graduation b on the b scale the line cuts the x curve at the graduation x where x is the desired result. Nomography is a new branch of applied geometry and a nomogram if the scales are fine enough dispenses with the solution of the equation. In general the worker gets at once a result approximately correct. Nomograms can be prepared for simple addition, subtraction, multiplication and division, for logarithmic and trigometrical functions and also for empirical data. The reader is shown how to prepare nomograms applicable to chemical problems.

The list of nomographic literature given is incomplete. All the German publications are mentioned but the author appears to be unaware of Brodetsky's "First Course in Nomography" published in 1925 by Messrs. G. Bell & Sons. We recommend Dr. Liesche's monograph to teachers of elementary chemistry and to all laboratory workers.

J. F. Tocher

Photochemical Processes. *A General Discussion held by the Faraday Society, April 1931. 25 × 15 cm.; pp. 218. Aberdeen: The University Press, 1931. Price: 10 shillings, 6 pence.* This volume is an account of the fifty-fifth general discussion organised by the Faraday Society, and is mainly a review of the progress made in photochemistry since the last discussion in the subject which took place at Oxford in 1925 (Photochemical Reactions in Liquids and Solids, Trans. Faraday Soc., **21**, 437 (1925)). The meeting was held at the University of Liverpool under the chairmanship of the President (Dr. Robert L. Mond). It was attended by eleven overseas guests who as authorities in the subject brought important contributions. There were in all four sessions. The first of these comprised a discussion and contributions of new researches on molecular spectra in relation to photochemical change. The introductory paper by Professor R. Mecke included an interesting historical account of this comparatively recent branch of photochemistry, which has helped so much to elucidate the early stages of photochemical changes. The second and third sessions were devoted to the consideration of photochemical changes in (1) gaseous, and (2) liquid and solid, systems. The sessions were opened by suggestive addresses delivered respectively by Professors Max Bodenstein and A. Berthoud and were followed by a considerable number of contributions on special aspects of the subject. The fourth session on photosynthesis was introduced by Professor E. C. C. Baly and was also followed by an illuminating general discussion.

A comparison of the volume with that issued after the meeting at Oxford in 1925 shows that considerable success in the meantime has been attained in interpreting the results obtained with the spectroscope, whereas the theories advanced to account for most of the complete photochemical changes are still uncertain. Nevertheless it is an uncertainty which has provided entrancing problems for solution. The survey of the position of the subject presented is so comprehensive, and the references given so complete that the volume will be an invaluable aid to students and a necessary reference book for research workers in the subject. *D. L. Chapman*

Atomtheorie und Naturbeschreibung. *By Niels Bohr. 24 × 16 cm; pp. iv + 77. Berlin: Julius Springer, 1931. Price: 5.60 marks.* This book consists essentially of four articles previously published separately in *Die Naturwissenschaften* and originating mainly from addresses delivered by Professor Bohr to various Scientific Meetings and Congresses. They are preceded by a valuable Introductory Survey (written in 1929, with an addendum dated 1931), which serves as a useful guide to the origin, nature, and development of the facts and theories discussed in the four sections of the book.

Many thousands of readers in all parts of the world will welcome the appearance of this volume. Practically without the use of mathematical symbolism, the whole history of the origin and development of modern atomic and quantum theory is given to the reader by the man who has played the leading rôle in this immense advance of science. It would be a great mistake to imagine that we have here simply a historical account, however, admirable and lucid, of the subject. What is most significant and most important to the reader is the profoundly philosophical and—let it be added—profoundly sane character of all Bohr's thought and reasoning. This is particularly true of the great events of 1925 and afterwards. Every physicist knows the fundamental part that the great pioneer of 1913 has played in the most recent advances of quantum mechanics. What Heisenberg has most aptly named the *Kopenhagener Geist der Quantentheorie* is evident in every page of this book. Bohr is not only a great and original discoverer in theoretical physics, but also and *always* the profound philosophical thinker, who, rising above symbolism, perceives the inner meaning of the facts and the conceptual relationships employed in the interpretation and representation of these facts. Nothing could be finer than the exposition given here by Bohr of the limitation placed by the observer (or observing instrument) on the reality of the thing observed, and the consequent *complementarity* (to use Bohr's own expression) of the space-time description on the one hand and the principle of causality on the other. As the reader progresses in the careful study of this book he finds, even though he be not a theoretical physicist, that he is gradually acquiring a very precious possession, namely a real insight into the revolutionary change of thought which modern quantum mechanics has brought about. Great indeed as was the change of thought caused by the work of Einstein and Minkowski and those who have followed them, it is probably no overstatement to say that quantum mechanics has led to an even greater change in the scientific outlook, and that Bohr has been the leader in this tremendous *mutation* of thought, which has brought a disciplined and restrictive sanity into the effort of the human mind to find an adequate *Naturbeschreibung.*

In the latter part of the book (addresses of date 1929), Bohr introduces ideas which may be destined to exert a great influence on the development of biological and psychological science. He raises the question, for example, whether the peculiar characteristic of the phenomena of the living organism may perhaps reside in the impossibility of a deep analysis of the physical conditions of such phenomena. An atomic analysis of a living organism would, in fact, require for its adequate specification a manifold of measurements and observations which would be incompatible with the stable existence of the organism. It must be confessed that this statement may be a very inadequate, or indeed possibly an erroneous, expression of Bohr's train of thought. He is such a profound thinker that it is not easy to follow him into an entirely new field of ideas. But one gains the impression that he regards a living organism as a system which may not be susceptible to experimental definition in terms of the measurements and concepts which are applicable to inanimate physical systems. It is to be hoped that Bohr will develop this train of ideas. Quantum mechanics can deal statistically with an inanimate system of atoms. A living cell or a living organism is an organised market of exchange (of energy and atoms) with its external environment. The world of science has long been waiting for some new fructifying and *precise* concept, or a series of concepts, which will make a fundamental advance in the understanding and investigation of the phenomena presented by the process of life. So far, thermodynamics alone has given help. Is there some unitary or indivisible x which, incorporated into a higher thermodynamics (in the sense that quantum mechanics is a higher mechanics) will yield the desired result?

F. G. Donnan

L'Atome de Bohr. *By Léon Brillouin. 24 × 16 cm.; pp. 363. Paris: Les Presses Universitaires de France, 1931. Price: 100 Francs.* The subject matter of this volume was first presented in a course of lectures given in 1928 at the University of Wisconsin, and later at Sorbonne. It concerns the older now classical view of the theory of spectra which owed its being to the speculations of Bohr.

The author devotes the first third of the book to an examination of the laws of physics of twenty years ago which were capable of being represented by a set of logically inter-related differential equations. It is shown how these equations cease to be valid when applied to the interior of the atom.

The theories of quanta, the Stark effect, the Zeeman effect, optical spectra, structure of multiplets, the spinning electron, X-ray spectra, and the laws governing the intensity of spectral rays are dealt with in separate chapters in such a manner as to prepare the reader for the next step in the line of historical development, that is, the more recent advances of wave mechanics.

This is a very clear exposition of the Bohr atom, and will prove to be of great value to students of molecular physics for many years yet.

W. E. Garner

Recent Advances in Organic Chemistry. *By A. W. Stewart. Sixth edition. 22 × 15 cm; Vol. I, pp. xii + 429, Vol. II, xii + 432. London: Longmans, Green & Co., 1931. Price: 2 shillings each volume.* This Edition of an already well known book contains new chapters on the Polymethylenes, Isomerism in cyclic compounds of the Decalin type, the Diphenyl problem and Di- and Tri-terpenes. A survey of the general methods for the preparation of polymethylenes and an account of the synthetical methods of Ruzicka for the production of large carbon rings are given. The constitution of Civetone and the nature of Muscone are discussed. Baeyer's Strain theory is outlined and the theory of strainless rings indicated; this subject is further developed in the later chapter dealing with the isomerism of the decalin type. The diphenyl problem is treated chronologically and the work which culminated in the collapse of the Kaufler hypothesis is described. The significance of the resolution of 3:3'-diaminodimesityl and of a *peri*.naphthalene derivative by Mills is pointed out. An extension of this chapter to include other examples of molecular dissymmetry such as the spiran type would be of value. The methods employed in the study of Di- and Tri-terpenes are outlined by reference to work on the Camphorenes and Squalenes.

A considerable extension of existing chapters has been made. The skeletal relationships of the terpenes are now emphasised with advantage. The synthesis of Norpinic acid and industrial methods for the production of camphor are new features. A brief account of Eudesmol is also included. Reference to the formation of "sugar carbonates" and "acetone compounds" and a fuller account of the oxidation of methylated sugars are welcome additions to the chapter on the carbohydrates. The use of O-monobenzoylphloroglucinaldehyde in the synthesis of anthocyanidins is a valuable extension of the chapter on this group. Other new features are an outline of Staudinger's views on the structure of ozonides and the introduction of a short account of the Parachor.

The oxidation of N-methylnicotine to hygric acid might have been included with advantage in the proof of the constitution of nicotine. The author retains the open-chair formulae for the aliphatic diazo compounds.

A number of misprints in the earlier edition have been corrected. The author writes with his accustomed clarity and presents the matter in a form which can be easily assimilated. In a book of this size, intended for honours students, and ranging over a wide field, the treatment of each subject is necessarily only an outline but the numerous references to original papers and monographs should encourage the student in the author's words "to go further."

E. W. McClelland

Colloid Aspects of Food Chemistry and Technology. *By William Clayton. 25 × 15 cm; pp. vii + 563. London: J. and A. Churchill, 1932. Price: 36 shillings.* Although practically every process employed in the preparation and treatment of foods presents problems in colloid chemistry, it is a surprising fact that this volume is the first attempt, so far as the reviewer is aware, to bring together the knowledge in this important field of applied science. The author is to be congratulated on having brilliantly achieved his aim to fill this gap in textbook literature. A very wide range of subjects is covered and in every case the exposition is lucid and the treatment commendably balanced.

The value of the work is much enhanced by a comprehensive list of selected references drawn both from the scientific and technical literature.

The book will be indispensable for all chemists and technologists who are concerned with the preparation or control of food products. The scope of its utility might be even wider, for I am inclined to think that the ordinary undergraduate science student would find that this work presented the essentials of colloid chemistry quite as clearly and far more entertainingly than most of the volumes on which he usually depends.

A wholly admirable production. *J. C. Drummond*

Matière et Atomes. *By A. Berthoud. Second Edition. 18 × 11; pp. 324. Paris: G. Doin & Cie. Price: 26 francs.* This is a second edition of Professor Berthoud's "Nouvelles Conceptions de la Matière et des Atomes" first published in 1922. The earlier volume has been completely remodelled and a new chapter added dealing with wave mechanics. The result is an excellent descriptive account of the development of modern ideas about atoms and quanta. The style is clear and concise, and only the simplest mathematical knowledge is assumed. Nevertheless the more difficult topics are not avoided and the reader is enabled to apprehend the physical principles which underlie such subjects as wave mechanics and relativity.

Professor Berthoud is to be congratulated on this very readable volume; it should appeal not only to chemists but also to the general reader who wishes to learn something of the trend of scientific ideas. *S. Sugden*

Messungen elektromotorischer Kräfte galvanischer Ketten mit wässerigen Elektrolyten. *By Carl Drucker. 24 + 17 cm; pp. xx × 234. Berlin: Verlag Chemie, 1929. Price: 24 marks.* This is No. 10 of the *Abhandlungen der deutschen Bunsengesellschaft* and is a supplementary volume to No. 5. It contains chiefly data which appeared from 1914 to 1927 both inclusive. Cells in which non-electrolytes have been added are also included. The book is invaluable for reference purposes. *Wilder D. Bancroft*

Errata

Make the following changes in the article by Reed and Theriault: J. Phys. Chem., 35, 673 (1931).

p. 677. Insert "t" as an exponent after 0.01 in the first equation;

p. 693. Insert equality sign between σ_h and the radical in equation 20;

p. 964. In Equation 15 read $(5)^3$ instead of (5).

Make the following change in the article by Cullinane, Embrey and Davies: J. Phys. Chem., 36, 1434 (1932).

p. 1441. In the fifteenth line, after "hole' 'insert "over which filter paper was attached. The weighing bottle was fitted with a hollow ground-glass stopper containing at the side a small hole."

Make the following change in the article by Davis: J. Phys. Chem., 36, 1449 (1932).

p. 1452. In the third line from the bottom read "alkali" instead of "alumina."

THE ADSORPTION OF CATIONS FROM AMMONIACAL SOLUTION BY SILICA GEL*

BY I. M. KOLTHOFF AND V. A. STENGER

Preliminary Communication

In a note on the preparation of metallized gels, Grant W. Smith and L. H. Reyerson[1] called attention to the strong adsorption of complex ammonium ions of copper and nickel by silica gel. It seemed to us that the significance of the ammonia in the complex is of secondary order only, in so far as various cations are kept in solution by the formation of complex bases and ions. This assumption appeared to be true, as will be shown later on in this paper. A more detailed study of the adsorption of cations by silica gel from alkaline medium was of interest, also with regard to the problem of coprecipitation in analytical chemistry. Preliminary experiments showed that the adsorption of cations by hydrous oxides from alkaline medium was qualitatively determined by the same factors as the adsorption by silica gel. Since the former undergo, after their precipitation, rapid changes on aging, the use of silica gel seemed very promising for a systematic study of the factors governing this adsorption.

The exact interpretation of the results of the adsorption experiments is made very complicated owing to the highly porous structure of the silica gel. Active silica gel appeared to be fairly soluble, even in relatively weakly alkaline solutions; the solubility increasing with time of shaking. Furthermore, the adsorption equilibrium is attained very slowly due to the slow penetration of the ions into the interior of the gel, and consequently the adsorption is not reversible. During the course of the investigation various factors were found to influence the adsorption process, making a quantitative interpretation impossible. A report of the results so far obtained—although of preliminary character—is of interest, since it is possible to derive some general conclusions concerning the factors affecting the adsorption of cations from alkaline medium by silica gel.

Materials used: Silica gel: The silica gel was purchased from the Silica Gel Corporation. The particles ranged from about 1 to 2 millimeters in diameter, the shapes being irregular. The product was purified by[2] heating with concentrated nitric acid until the particles were clear and colorless; the gel washed with water until no acid could be detected in the wash-water, and thereafter electrodialyzed for four weeks. During the last week the water added to the dialyzer did not show a change in conductivity. The product

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* Contribution from the School of Chemistry of the University of Minnesota.

[1] G. W. Smith and L. H. Reyerson: J. Am. Chem. Soc., 52, 2584 (1930).

[2] The authors wish to thank Mr. W. J. Mitchell for his assistance in the preparation of the pure gel.

was dried first at 200° and then at 600° and kept in well-closed bottles, After heating a long time over the blast lamp a loss in weight of 3% was noticed. No acid could be detected in the gel after the electrodialysis.

Ammonia: The ammonium hydroxide used was obtained carbonate free by distillation from barium hydroxide, and kept in paraffined bottles with protection from carbon dioxide from the air. Its strength was about 4N. The other products used were C. P., and if necessary purified by repeated crystallizations.

General procedure: The solutions were made up in a 100 c.c. volumetric flask, previously freed from carbon dioxide, and transferred to a 200 c.c. Erlenmeyer flask of Pyrex glass containing a weighed amount of silica gel. The flask was stoppered and rotated for the indicated time at room temperature, usually around 25°. At the same time a blank without gel was run under the same conditions and the amount of adsorption calculated from the difference in concentrations. In many cases the gel was quickly washed with conductivity water (usually four times), and then extracted with an excess of acid. By back titration with standardized sodium hydroxide the total amount of base adsorbed was found, and the cation, whose adsorption was studied, determined in the neutralized solution. The direct determination of the amount of ammonia and cation present in the gel was of distinct advantage in cases where relatively strong ammoniacal solutions had been used.

Experimental

Adsorption of sodium hydroxide by silica gel.

TABLE I

0.5 g. of gel was left in contact with 100 c.c. sodium hydroxide solution for 40 minutes with occasional shaking by hand. (Room temperature 25°).

The amount of base adsorbed was determined by back titration of the supernatant liquid, and also by extraction of the gel with hydrochloric acid.

Original normality sodium hydroxide	Final normality	Milli eq. NaOH adsorbed per 1 g. silica gel (titration solution)	Milli eq. NaOH adsorbed per 1 g. silica gel (extract gel)
0.01	0.0079	0.424	0.37
.025	.0216	.68	.60
.05	.0458	.84	.71
.075	.0704	.90	.84
.10	.0942	1.16	1.02
.15	.144	1.20	1.11

In agreement with Patrick and Barclay[3] and F. E. Bartell and Y. Fu[4] it was found that the adsorption of sodium hydroxide takes place according to the ordinary adsorption isotherm. However, it should be mentioned that

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[3] Patrick and Barclay: J. Phys. Chem., **29**, 1400 (1925).

[4] Bartell and Fu: J. Phys. Chem., **33**, 676 (1929).

the figures in Table I are more or less arbitrary; the adsorption increases with the time of standing; after 12 hours standing with occasional shaking about double the amount of base was adsorbed from the first four solutions. It seems impossible to reach the equilibrium conditions; on standing more of the gel is going into the solution, and the figures given in Table I have not been corrected for the dissolved part. After one to two days of standing all the gel went into solution in 0.1 to 0.2 N sodium hydroxide.

Adsorption of barium hydroxide by silica gel.

TABLE II

0.5 to 1 g. of gel was left in contact with 100 c.c. barium hydroxide solution for 13 to 17.5 hours, with occasional shaking by hand. Further conditions as in Table I.

Original normality barium hydroxide	Contact 13 hours 0.5 g. silica gel		Contact 17.5 hours 1 g. silica gel	
	Final norm. $Ba(OH)_2$	m. eq. $Ba(OH)_2$ ads. per 1 g. gel (titration solution)	Final norm. $Ba(OH)_2$	m. eq. $Ba(OH)_2$ ads. per 1 g. gel (titration solution)
0.002	0.00066	0.268		
.005	.00157	.686		
.010	.00416	1.168		
.020	.0106	1.88		
.050	.0315	3.70	0.0168	3.32
.070	.0544	3.12		
.100	.0863	2.74	.0708	2.92
.150	.1365	2.70		
.200	.1884	2.32	.176	2.40

A maximum in the adsorption is noticed in about 0.05 N barium hydroxide solution. It seems that the appearance of this maximum has to be attributed to an obstruction of the pores of the gel by the adsorbed barium hydroxide.

Adsorption of calcium hydroxide by silica gel.

TABLE III

0.5 g. of gel was left in contact with 100 c.c. calcium hydroxide solution for 17 hours with occasional shaking by hand.

Original normality of $Ca(OH)_2$	Final normality of $Ca(OH)_2$	m. eq. $Ca(OH)_2$ ads. per 1 g. gel (titration solution)	m. eq. $Ca(OH)_2$ ads. per 1 g. gel (extract gel)
0.0037	0.00097	0.562	0.56
.0093	.00252	1.354	1.42
.0187	.00442	2.86	2.48
.0281	.00995	3.58	3.70
.0375	.0155	4.40	4.26

In the last three experiments a precipitate of calcium silicate was formed.

Comparison of the results in Tables I, II, and III shows that the alkaline earth hydroxides are stronger adsorbed than sodium hydroxide. This result was to be expected considering the slight solubility of the alkaline earth silicates. Calcium hydroxide is somewhat more strongly adsorbed than barium hydroxide. The adsorption is not reversible, and the reported figures have no exact significance. It seems that the internal structure of the gel is changed during the adsorption of the hydroxides.

In the following experiments the adsorption of calcium hydroxide was determined in the presence of various concentrations of ammonia, ammonium salts, and alkali salts. Later the results will be compared with those obtained in the adsorption of copper ions in similar solutions.

The results given in Table IV show that the amount of calcium adsorbed from ammoniacal solution increases with the time of contact between the gel and the solution.

TABLE IV

0.5 g. of gel was left in contact (occasional shaking) with 100 c.c. of a solution containing 0.05 N calcium chloride and 0.5 N ammonium hydroxide. After the indicated time of standing the calcium was determined in 50 c.c. of the supernatant solution according to the oxalate method.

Time of Contact in hours	Final normality Ca^{++}	M. eq. Ca^{++} adsorbed per 1 g. silica gel (titration solution)	Time of contact in hours	Final normality Ca^{++}	M. eq. Ca^{++} adsorbed per 1 g. silica gel (titration solution)
4	0.0372	2.56	30	.0288	4.25
8	.0346	3.09	40	.0278	4.44
12	.0334	3.33	70	0252	4.97
20	.0305	3.91	100	.0262	4.75

Table IV shows that the adsorption increases regularly with the time of contact between solution and gel. Only in the last case (100 hours standing) was there apparently less adsorbed than after 70 hours. Special experiments showed that this deviation is to be attributed to the increasing solubility of the gel with the time of standing. After the longer time of standing it was impossible to extract the calcium quantitatively from the gel with an excess of acid. The pores of the gel were obstructed by the calcium silicate formed and the diffusion of the acid into the interior of the gel was strongly inhibited.

In order to get reproducible results it is necessary to treat solutions and gel under exactly the same conditions.

In the study of the influence of the concentration of ammonia upon the adsorption of the calcium hydroxide, 0.5 to 1 g. of the gel was *shaken* at uniform speed with a calcium chloride solution, containing various concentrations of ammonia.

The adsorption of the calcium reaches a maximum in about 1 N ammonium hydroxide solution. A special study was made of the complex cation formation between calcium ions and ammonia; no indication was obtained of the existence of that type of complex ions. The results of this study will be re-

TABLE V

0.5 to 1 g. gel shaken for 21 hours with 100 c.c. solution containing 0.05 N calcium chloride and various concentrations of ammonia. Amount of calcium adsorbed determined in 50 cc.. supernatant liquid by the oxalate method.

Grams silica gel used	Concentration ammonia added	Final normality Ca^{++}	M. eq. Ca adsorbed per 1 g. gel (titration solution)
1	0	0.0498	0.02
1	0.001	.0450	.50
1	.01	.0416	.84
0.5	.05	.0372	2.55
1	.10	.0241	2.59
1	.50	.0130	3.70
1	1.00	.0129	3.71
0.5	1.00	.0292	4.15
0.5	2.00	.03395	3.21
1	5.00	.0301	1.99

ported in a later paper; they show that the effect of the concentration of the ammonia upon the calcium adsorption cannot be explained in terms of the formation of an ammonio complex. The ammonia has a replacing effect upon the adsorbed calcium ions; with increasing ammonia concentration the ratio NH_4OH to $Ca(OH)_2$ adsorbed increases regularly as is shown by experiments reported in Table VI.

The amount of calcium adsorbed was determined by analysis of the solution. It was impossible to extract all calcium from the gel with dilute acid, and the figures given in the table are considerably in error and placed between parentheses. However, it was possible to extract practically all ammonia from the gel, and from the total basicity of the extract and its calcium content the amount of ammonia adsorbed could be calculated. These figures are more reliable than those found in the titration of the supernantant liquid of the gel, especially in the more concentrated ammonia solutions; therefore the latter are given between parenthesis. In the calculation of the ratio *moles* NH_4OH: $Ca(OH)_2$ adsorbed the figures in the eight and fifth columns have been used.

The figures in Table VI are not strictly comparable with those in Table V. because in Table VI a mixture of the two hydroxides was used and the hydroxyl ion concentration was much larger than in the mixtures used in Table V. The replacing effect of the ammonium hydroxide in the experiments of Table VI is quite evident, in spite of the fact that the adsorption of calcium hydroxide was made more favorable.

In Table VII the effect of the presence of ammonium, sodium and potassium salts on the adsorption of calcium at various ammonia concentrations is given. Alkali salts decrease the adsorption of calcium, owing to their partial replacement of this ion at the surfaces of the silica gel. Ammonium salts exert a similar influence, but in addition decrease the hydroxyl ion concentration of the solution, and therefore their effect upon the calcium adsorption is larger than that of sodium or potassium salts.

TABLE VI

0.5 g. of silica gel in contact with a mixture of calcium and ammonium hydroxide for 2 hours with occasional shaking.

Original normality $Ca(OH)_2$	Original normality NH_4OH	Final normality $Ca(OH)_2$ (oxalate method)	Final normality NH_4OH	M. eq. Ca^{++} adsorbed per 1 g. gel (titration solution)	M. eq. Ca adsorbed per 1 g. gel (extract gel)	M. eq. NH_4OH adsorbed (solution)	M. eq. NH_4OH adsorbed extract (gel)	Molar ratio $NH_4OH:Ca(OH)_2$ adsorbed
0.0033	0	0.00219	0	0.022	(0.220)	—	—	—
.0083	0	.00547	0	.566	(.576)	—	—	—
.0165	0	.0102	0	1.26	(1.10)	—	—	—
.0165	0.05	.0069	0.0488	1.92	(1.37)	(0.24)	.294	.306
.0165	.10	.00715	.097	1.87	(1.17)	(.60)	.614	.656
.0165	.50	.00703	.4897	1.90	(0.98)	(1.06)	1.37	1.44
.0165	1.00	.00619	.9788	2.06	(0.86)	(2.24)	1.99	1.93
.0165	2.00	.00721	1.968	1.86	(0.69)	(2.4)	2.27	2.44
.0165	3.00	.00603	2.946	2.10	(0.64)	(4.0)	2.98	2.84

TABLE VII

0.5 to 1 g. of silica gel was shaken for 21 hours with solutions containing 0.05 N calcium chloride and the indicated amounts of other constituents

Grams gel taken	Original normality ammonia	Kind and concentration salt added	Final normality calcium	M. equivalents Ca^{++} adsorbed per 1 g. gel
1.0	0.01	0	0.04165	0.835
1.0	.01	0.01 N NH_4Cl	.04235	.775
0.5	.05	0	.03725	2.55
.5	.05	0.1 N NH_4Cl	.04478	1.044
.5	.05	1 N NH_4Cl	.0500	0.0
.5	.05	0.1 N KCl	.0393	2.14
.5	.05	1 N KCl	.04335	1.33
.5	.05	1 N NaCl	.04375	1.27
.5	.5	0	.03255	3.49
.5	.5	0.1 N NH_4Cl	.0364	2.72
.5	.5	1 N NH_4Cl	.0473	0.54
.5	1.0	0	.02925	4.15
.5	1.0	0.1 N NH_4Cl	.0326	3.48
.5	1.0	1 N NH_4Cl	.0462	0.76
.5	1.0	1 N KCl	.0442	1.16
.5	1.07	1 N NH_4Cl	.04478	1.04
.5	1.07	1 N NH_4NO_3	.04483	1.03
.5	4.0	0	.0416	1.68
.5	4.0	1 N NH_4Cl	.042	1.60

Adsorption of copper from ammoniacal solution.

Silica gel shaken with an ammoniacal copper solution assumes immediately an intense dark blue color, indicating the adsorption of the ammonio copper ion. As in all other cases the amount of copper adsorbed increases with the time of shaking of the solution with the gel.

In the following experiments two types of copper solutions have been used.

Solution A: Hydrous copper oxide was precipitated by adding a recrystallized copper sulfate solution to a slight excess of ammonia. The precipitate was washed with distilled water until the washings were no longer basic to phenolphthalein and then treated with a solution containing 1.5 N ammonia. Part of the precipitate dissolved with the formation of the dark blue solution, (the undissolved part was shown to be free of sulfate) containing 0.05 molar copper, 0.03 molar sulfate and 1.313 N ammonia. It was considered to be equivalent to a mixture of 0.05 molar $Cu(NH_3)_4(OH)_2$; 0.030 molar ammonium sulfate and 1.052 N ammonia in excess. This solution and some of its dilutions have been used in the experiments.

Solution B: The undissolved part of the hydrous copper oxide from the previous treatment was shaken with 1.5 N ammonia, the solution becoming only a faint blue. In order to increase the solubility of the ammonio copper hydroxide it was necessary to add some ammonium salt. The final solution obtained contained 0.0261 molar copper as $Cu(NH_3)_4(OH)_2$; 0.02 molar ammonium chloride and 1.064 N ammonia in excess.

It may be mentioned here that all copper solutions used contained some ammonium salts; since the latter decrease the hydroxyl ion concentration markedly, the adsorption experiments are not strictly comparable with those obtained in a mixture of calcium chloride and ammonia, to which no ammonium salt had been added.

In Table VIII it is shown that the adsorption of copper from ammoniacal solution increases with the time of shaking. In the first six and the last six experiments the copper content was determined in 25 cc. of the supernatant liquid after 2, 6, and 24 hours shaking respectively and after 24, 49 and 90 hours shaking respectively. From the difference in concentration the amount of copper adsorbed was calculated. The figures so obtained have no exact significance, since part of the gel went into solution. In some cases the gel after extraction of the copper was collected and weighed after ignition over the blast lamp. In this way the actual amount of copper adsorbed per 1 g. of gel was found; the figures are given in the last column of Table VIII. These corrected figures are markedly higher than those calculated with the assumption that the silica gel remained unchanged. The relative change in the adsorption is approximately the same in both columns.

TABLE VIII

0.25 g. silica gel was shaken with a copper solution prepared by diluting various amounts of solution B to 100 c.c., with or without addition of more NH_4OH. 0.5 g. silica gel was shaken with solution B undiluted. After various times the solutions were analyzed for copper iodometrically.

Grams of gel	Time of shaking in hours	Original molarity Cu^{++}	Original normality NH_4Cl	Excess of NH_4OH (normality)	Milli-eq. Cu^{++} adsorbed per 1 g. gel	Milli-eq. Cu^{++} adsorbed (Corrected for solubility of gel.)
0.25	2	0.0130	0.01	0.532	2.44	
0.25	6	0.0130	0.01	0.532	3.64	
0.25	24	0.0130	0.01	0.532	4.44	
0.25	24	0.0130	0.01	0.532	4.04	
0.25	49	0.0130	0.01	0.532	5.42	
0.25	90	0.0130	0.01	0.532	5.64	7.67
0.25	24	0.0147	0.01	1.12	3.61	5.29
0.25	24	0.0147	0.01	1.73	3.25	5.41
0.25	24	0.0147	0.01	2.34	2.43	4.55
0.25	24	0.0147	0.02	1.12	3.47	4.78
0.5	2	0.0261	0.02	1.064	2.74	
0.5	6	0.0261	0.02	1.064	3.22	
0.5	24	0.0261	0.02	1.064	3.88	
0.5	24	0.0261	0.02	1.064	3.90	
0.5	49	0.0261	0.02	1.064	4.45	
0.5	90	0.0261	0.02	1.064	4.61	6.19

Similar experiments as described in Table VIII have been made with copper solution A. Some of the results are given in Table IX.

TABLE IX

0.5 g. silica gel was shaken with 100 c.c. of diluted copper solution A, pipetting out 25 cc. after 2, 6, and 24 hours shaking, respectively.

Time of shaking in hours	Original molarity Cu^{++}	Original normality $(NH_4)_2SO_4$	Excess of NH_2 (normality)	Milli eq. Cu^{++} per 1 g. gel (uncorrected for solubility gel.)
2	0.0251	0.03	0.526	2.14
6 ⅔	.0251	.03	.526	3.22
24 ⅔	.0251	.03	.526	4.08
2	.0250	.05	.500	2.34
6	.0250	.05	.500	2.82
24	.0250	.05	.500	3.59
2	.050	.06	1.052	1.82
6	.050	.06	1.052	2.26
24	.050	.06	1.052	3.67

The results of Tables VIII and IX show that even after a few days of shaking the adsorption equilibrium is not yet established. In order to get comparable results in the study of the influence of various factors upon the adsorption of copper from ammoniacal solution, it is necessary to work under the same experimental conditions.

The results in the following table show that the adsorption of copper first increases with increasing ammonia concentration, reaches a maximum and decreases thereafter with increasing ammonia concentrations. In order to be able to work at low ammonia concentrations, copper solutions with a higher ammonium salt content were used. 10 c.c. 0.5 molar copper sulfate were mixed with various amounts of 0.5 N ammonia and diluted in a volumetric flask to 100 c.c. The solutions were analyzed for copper and total ammonia content. In the expression of the concentration of the excess of ammonia it was assumed that the copper was present in the form of $Cu(NH_3)_4(OH)_2$ or of $Cu(NH_3)_4^{++}$.

TABLE X

0.5 g. silica gel with 100 c.c. copper solution, containing 0.025 molar copper and 0.025 molar ammonium sulfate; occasionally shaken for 12 hours and thereupon mechanically shaken for 3 hours.

Normality of NH_3 in excess	Final molarity Cu	Milli eq. Cu adsorbed per 1 g. gel	Normality of NH_3 in excess	Final molarity Cu	Milli eq. Cu adsorbed per 1 g. gel
0.05	0.0173	3.08	.40	.0165	3.38
.10	.0163	3.45	.90	.0180	2.80
.15	.0150	4.01	1.00	.0181	2.76
.20	.0141	4.36	4.00	.0196	2.15

The location of the maximum also depends upon the concentration of ammonium salt present; for this reason the results are not directly comparable with those in Table V on the adsorption of calcium.

Table XI shows that potassium chloride and ammonium salts have a similar effect upon the adsorption of copper from ammoniacal solution as upon that of calcium (compare Table VII).

TABLE XI

0.5 g. silica gel with 100 c.c. copper solution containing 0.025 molar copper and 0.025 molar ammonium sulfate; occasionally shaken for 12 hours and thereupon mechanically shaken for 3 hours.

Normality excess NH_3	Kind and normality of salt added	Final molarity copper	Milli eq. Cu adsorbed per 1 g. gel
0.05	—	0.0173	3.08
.05	.05 N NH_4Cl	.0172	3.12
.05	.5 N NH_4Cl	.0210	1.62
.10	—	.0163	3.45
.10	.05 N NH_4Cl	.0164	3.41
.10	.5 N NH_4Cl	.0215	1.38
.10	.5 N KCl	.0178	2.88
.20	—	.0141	4.36
.20	.5 N NH_4Cl	.0210	1.58
.20	.5 N NH_4NO_3	.0211	1.54
1.0	—	.0181	2.76
1.0	1 N NH_4Cl	.0240	0.38
4.0	—	.0196	2.15
4.0	1 N NH_4Cl	.0249	0.04

It was of interest to determine the molecular ratio of adsorbed ammonia and copper. If the copper cation would be adsorbed as the ammonio complex $Cu(NH_3)_4^{++}$, this ratio should be higher than 4:1, since some ammonia is adsorbed simultaneously with the copper. As Table XII shows, the ratio is decidedly lower than 4, indicating that part of the copper is adsorbed as aquo ion and part as ammonio ion, or that originally the ammonio complex is adsorbed, splitting off ammonia after the adsorption. The decrease in the ratio of adsorbed ammonia and copper with the time of shaking is in harmony with the latter assumption. More experiments will be made before definite conclusions can be drawn.

Reversibility of the adsorption:

Several experiments showed that neither the adsorption of the calcium nor that of copper is reversible. If a gel having copper and ammonia adsorbed is washed with water for long periods of time, part of the ammonia goes into solution; the copper remains in the gel and even with the sensitive ferrocyanide reagent its presence cannot be detected in the solution. A gel, which had been

TABLE XII

0.25 to 0.5 g. silica gel was shaken for 24 hours with 100 c.c. copper solution A or B. The residue was quickly washed four times with water, and treated with an excess of standardized sulfuric acid, until the gel was colorless. The solution was back titrated with sodium hydroxide, thus giving the total amount of base adsorbed. The copper content of the original filtrate was determined in an iodometric way.

Normality excess NH_3	Normality ammonium salt	Original molarity copper solution	Milli eq. NH_3 adsorbed	Milli eq. Cu adsorbed	Molar ratio $(NH_3):(Cu)$ adsorbed
0.532	0.01 N NH_4Cl	0.013	5.29	3.83	2.76
1.064	0.02 N NH_4Cl	0.0261	5.65	3.43	3.29
0.782	0.01 N NH_4Cl	0.013	5.02	3.28	3.06
0.500	0.05 N $(NH_4)_2SO_4$	0.025	5.13	3.01	3.40
0.526	0.03 N $(NH_4)_2SO_4$	0.025	5.14	4.06	2.53
1.052	0.06 N $(NH_4)_2SO_4$	0.050	6.15	3.72	3.30

shaken for 90 hours with an ammoniacal copper solution, was treated with 10 c.c. 5.0 N ammonium chloride for three days. Although the ammonium salt decreases the adsorption of copper very much (compare Table XI), it only replaced 25% of the copper from the gel after the metal ion had been adsorbed. Under similar conditions potassium chloride did not replace any copper from the gel. The ammonia content of the gel, however, decreased very much, thus decreasing the ratio of NH_3 to Cu present in the gel. This again may indicate that the copper originally is adsorbed as ammonio ion, which can split off the ammonia held in complex form. Such experiments, however, do not yield a definite proof that originally the complex copper ion is adsorbed, as the speed of adsorption and desorption of ammonia may be much larger than that of the copper ion.

It may be mentioned that it is very hard to remove all the copper from a gel, after it has been shaken for a longer time (90 hours) with an ammoniacal copper solution. Even after continuous extraction for 6 months with cold and hot mixtures of sulfuric and nitric acid some copper was present in the interior of the gel.

Discussion: The experiments described in this paper revealed various difficulties making an exact interpretation of the results impossible. Various factors hereunder mentioned, affecting the adsorption, will be made the subject of a more detailed investigation:

1. Silica gel dissolves in alkaline solution.

2. By the aggressive action of the solvent, the outside and internal surface of the gel may change during the experiment.

3. The adsorption equilibrium is reached very slowly; even after shaking for a few days the maximum in the adsorption-time curve is not reached in many cases.

4. After shaking the gel for a long time with the solution, it seems impossible to extract divalent cations entirely from the gel, even upon treatment with strong acids.

5. The pores of the gel may be obstructed by the adsorbed ions, owing to a formation of insoluble silicates in the capillaries. (Ca;Cu).

6. The adsorption process is not reversible.

7. The speed of adsorption (diffusion into the interior of the gel) and desorption may be different for different ions and molecules. Thus it seems that ammonia is much faster adsorbed and desorbed than calcium and copper.

In the literature on the adsorption of ions and molecules by silica gel, these various factors have not been considered, and it is possible that the conclusions inferred need some correction.

In spite of the difficulties mentioned, the following conclusions may be drawn from the present study:

The adsorption of cations from alkaline solution by silica gel is a secondary adsorption; the hydroxyl ions being primarily adsorbed, dragging an equivalent amount of cations to the surface. Therefore, the adsorption will increase with increasing hydroxyl ion concentration. The adsorption of a cation salt in ammoniacal medium first will increase with the ammonia concentration as a consequence of the increase of the hydroxyl ion concentration. However, the ammonia being a base itself, is also adsorbed by the gel and has a replacing effect upon the adsorbed cation. Therefore, quite generally a maximum in the adsorption of any cation will be observed at a certain ammonia concentration, and the cation adsorption will decrease at higher ammonia concentrations. It seems that this behavior is not specific for adsorptions by silica gel; hydrous oxides like those of aluminum and ferric iron behave in a similar way. In the literature this maximum in the adsorption of cations by hydrous oxides at a certain ammonia concentration is always connected with complex formations between the cation and ammonia; this, however, is only a circumstantial coincidence and does not explain the experimental facts. The adsorption of cations by hydrous oxides resembles that by silica gel very closely, as will be shown in future papers.

The addition of ammonium salts to the ammoniacal solutions decreases the adsorption of calcium and copper for two reasons. In the first place, the ammonium ions decrease the hydroxyl ion concentration, and, in the second place, they have a replacing effect upon the adsorbed calcium and copper. This last effect is also exerted by sodium and potassium salts, which decrease the adsorption of calcium and copper from ammoniacal solution.

It has been mentioned in this paper that calcium does not form an ammonio ion, and therefore is adsorbed as aquo calcium ion. The adsorption of copper from ammoniacal solution is quite similar to that of calcium; the main function of the ammonia being the prevention of the precipitation of the copper cations from the solution. An ammoniacal copper solution contains few aquo copper ions; if the latter were soluble in alkaline medium, they would be adsorbed as well as the ammonio copper ions. This was proved by the following experiments:

Silica gel was treated with an alkaline copper salicylate solution. In such a solution most of the copper is firmly bound as a complex copper salicylate anion, which will not be adsorbed. Only few aquo copper cations can be present in the solution. On shaking of the silica gel with the alkaline copper salicylate, the gel assumed a light bluish color by the adsorption of copper. The gel was washed with water for a long time in order to remove any salicylate which had diffused into the interior of the gel; the latter did not give off any copper during the washing process. The washed gel was extracted with sulfuric acid, thus bringing all the copper into the solution. The latter and the gel were shaken out with ether, and the ethereal extract evaporated at room temperature. No salicylic acid could be detected in the residue, showing that the copper had been adsorbed as aquo cation. The copper content in the acid extract was determined iodometrically. Since the aquo copper ion concentration in the alkaline salicylate solution is extremely small, the amount of copper adsorbed by the gel is also very small. This is shown by the figures in Table XIII.

TABLE XIII

Adsorption of copper from alkaline copper salicylate solution. Copper salicylate was prepared by mixing equivalent amounts of pure copper sulfate and sodium salicylate. The crystals formed were collected, washed, and dried in the air. 20 grams of the crystals were treated with 19 grams of sodium salicylate (roughly the quantity needed to form $Na_2Cu(Sal)_4$), 20 grams anhydrous sodium carbonate and diluted with water to 500 c.c. The copper content of the solution was 0.1155 molar, 25 c.c. of this solution was diluted with water to 100 c.c. and shaken with 0.5 g. silica gel for 2 hours.

Addition to copper salicylate solution	M. equivalents Cu adsorbed per 1 g. gel (titration solution)	M. equivalents Cu adsorbed per 1 g. gel (extract gel)
—	0.172	0.186
1.05 g. $NaHCO_3$	.075	.090
5 g. Na_2CO_3	.264	.264
0.5 g. salicylic acid	.108	.100

If the washed bluish gel, containing the copper as aquo cation was shaken with a dilute ammonia solution, it immediately assumed a dark blue appearance as a result of the formation of the ammonio copper ion. It is quite possible that the latter is more strongly adsorbed than the aquo copper ion. The last experiment, however, does not prove this point. The conclusion seems warranted that the strong adsorption of copper from ammoniacal solution takes place by virtue of the fact that the metal can exist as cation in this alkaline medium, and not because the ammonio ion is so much more strongly adsorbed than the aquo ion. The fact that the adsorption of calcium, which does not form ammonio ions, is similar to that of copper from ammoniacal solution justifies the above conclusion.

Summary

1. The study of the adsorption of cations from alkaline solutions is complicated by the facts, that the gel dissolves even in dilute alkali, changing its structure during the experiment, that the adsorption equilibrium is reached very slowly, the adsorption process is not reversible, that the pores of the gel may be obstructed by formation of insoluble silicates, and that the speed of adsorption and desorption of various ions and molecules may be different.

2. The adsorption of calcium and copper from ammoniacal solutions shows a similar character in spite of the fact that the calcium is adsorbed as aquo ion, the copper as ammonio ion. In the latter case the ratio of NH_3 to Cu present in the gel, however, is always smaller than 4:1.

3. The adsorption of calcium and copper from ammoniacal solution first increases with the ammonia concentration until a maximum is reached. At larger ammonia concentrations the adsorption decreases, owing to the fact that the replacing action of the ammonia upon the adsorption of the cations has a larger effect than the increase of the hydroxyl ion concentration.

4. Ammonium salts decrease the adsorption of calcium and copper by silica gel, because they decrease the hydroxyl ion concentration and the ammonium ions have a replacing effect upon the adsorption of the cations mentioned. Potassium and sodium salts have a similar replacing effect.

Minneapolis, Minnesota,
May 16, 1932.

THE HEAT CAPACITY AND FREE ENERGY OF FORMATION OF ETHYLENE GAS*

BY MATTHIAS E. HAAS WITH GEBHARD STEGEMAN

Thermal data of the required accuracy are frequently lacking when it is desired to calculate the free energy of a given chemical reaction that is carried out under isothermal conditions. The minimum data required for such a calculation are: (1) the heat capacities of all the substances involved in the reaction for the particular range of temperature for which the heat capacities hold; (2) the heat of reaction at some temperature within this temperature range; and (3) one value of the free energy of the reaction within the range of temperature for which the heat capacities are valid.

The determination of the heat capacity of ethylene gas through the temperature range 0° to 70°C., constitutes the experimental part of this investigation. The other required data for the computation of the free energy of formation of ethylene gas are taken from the work of other investigators.

Partington and Shilling[1] give a good account of the work on ethylene gas. The most recent determinations are given in Table I.

TABLE I

	Temperature	C_p
Scholer (1914)	20°C.	10.007
Schweikert (1915)	0	10.267
Scheel and Heuse (1919)[2]	18	10.22
	−36	9.19
	−68	8.81
	−91	8.65
Dixon and Greenwood (1924)[3]	12	10.25
	41.5	10.57
	63.5	10.84
	89.0	11.14

The Flow Method. The constant-flow method was used in this investigation. This method is fully described by previous investigators.[4,5] The apparatus was reconstructed after the completion of a similar problem on ethane gas,[5] and certain modifications were introduced.

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* Contribution No. 242 from the Department of Chemistry, University of Pittsburgh.

[1] Partington and Shilling: "The Specific Heats of Gases," 195 (1924).

[2] Scheel and Heuse: Ann. Physik, 59, 86-94 (1919).

[3] Dixon and Greenwood: Proc. Roy. Soc., 105A, 199 (1924).

[4] Scheel and Heuse: Ann. Physik, 37, 79 (1912); 40, 473, (1913); 59, 86 (1919).

[5] Victor R. Thayer: J. Phys. Chem., 35, 1505-1511 (1931).

Modifications. Six stopcocks were added in the specific heat apparatus, so as to facilitate the evacuation of the apparatus prior to introducing the purified gas. Mercury seals that were either movable, or that had some movable part operating in them, were extended in length so as to form a barometer column when the system was evacuated. A differential manometer containing mercury was inserted across the rate of flow device to give indication of any appreciable pressure changes during the pumping. The mercury seal in the calorimeter was replaced by a heavy-grease seal. The calorimeter lead-in tubing was lengthened by four feet to insure efficient heat transfer between calorimeter and bath.

A gear-and-chain drive was substituted for the pulley-and-belt transmission in the gas-circulating pump. In the earlier part of the work, considerable trouble was experienced due to failure or slippage in this driving mechanism. This defect was completely corrected and the rate of circulating gas was more constant than before.

A new constant-temperature bath, with redesigned thermoregulator of the toluene-mercury type, electrical heaters, relay, etc., was installed. The bath consisted of a 14 × 42 inches deep cylindrical, stoneware tank, with a lagging of double layer heavy hair felt, suitably enclosed in a case. With this equipment, it was not unusual to keep the temperature of the bath constant to 0.001° for eight to twelve hours.

The electrical equipment was similar to that used by Thayer.[5] A 25-ohm coil, certified by the Bureau of Standards, was the ultimate standard. A Weston cell served to standardize the potential measurements, and this unit was frequently checked against the 25-ohm coil and also against a standard resistance thermometer. A White Double Potentiometer was used for measuring all e.m.f's. The electrical heater in the calorimeter was checked for its resistance at least once for each temperature; in most of the determinations, however, this was done after each flow measurement. The physical constants of the two platinum resistance thermometers in the calorimeter were redetermined.

Purity of Ethylene. The ethylene gas used in this investigation was supplied by the Ohio Chemical and Manufacturing Company of Cleveland. Its purity, by the bromine adsorption test, was given as 99.8 per cent. Considering that this product is used in anesthesia, its high degree of purity and its freedom from toxic components must be assured to the consumer. The cylinder gas was further treated by passing it slowly over solid potassium hydroxide, phosphorus pentoxide and glass wool. It was then liquefied and solidified, pumped free from dissolved gases, and twice fractionated.

Experimental Results. The results of the heat capacity measurements are summarized in Table II. The mean specific heats recorded therein are based on at least three, and in most of the determinations, on seven to ten values for each temperature. Excepting the last two temperatures, the measurements apply to two, or three, and, at 46° to four different samples of gas.

TABLE II

Summary of Experimental Data

Temperature, °C	Specific Heat in Watt Seconds per Gram	Specific Heat in Cals. per Mol
2.50	1.4515	9.73
25.00	1.4998	10.05
31.50	1.5154	10.16
37.20	1.5375	10.31
46.00	1.5625	10.47
61.00	1.6131	10.81
66.80	1.6470	11.04

The heat loss factor of the vacuum-jacketed calorimeter was k = 0.000046.

Heat Capacity Equation. The molal specific heats listed in Table I were used for formulating an equation for the heat capacity of ethylene gas. This is given by

$$C_p = 4.064 + 0.02022\ T.$$

For the sake of comparison, the data of Dixon and Greenwood,[3] of Scheel and Heuse,[2] and of all investigators mentioned in Partington and Shilling,[1] were transformed into equations of the above form, and these equations were used for computing specific heats for the temperatures mentioned in Table II. The results are given in Table III. The values under "experimental" are reproduced from the foregoing table; and under "calculated" are given the values resulting from the application of the various heat capacity equations to the experimental temperatures.

TABLE III

Experimental		Calculated C_p			
Temp. °K	C_p Authors	Authors	D & G	S & H	Others
275.6	9.73	9.64	10.13	9.90	9.96
298.0	10.05	10.09	10.39	10.23	10.40
304.5	10.16	10.22	10.46	10.33	10.53
310.0	10.31	10.33	10.53	10.41	10.64
319.0	10.47	10.51	10.63	10.54	10.81
334.0	10.81	10.82	10.80	10.76	11.10
340.0	11.04	10.94	10.87	10.85	11.22

Fig. 1 shows the experimental specific heat values of Scheel and Heuse, of Dixon and Greenwood, and of this investigation, the last being expressed by the straight line.

Free Energy of Formation of Ethylene Gas. The free energy of formation of one mol of ethylene gas from the elements was calculated by the general free energy equation:

$$\Delta F = \Delta H_0 - \Delta\Gamma_0 T \ln T - \tfrac{1}{2}\Delta\Gamma_1 T^2 - \ldots\ldots\ldots\ldots + I\,T$$

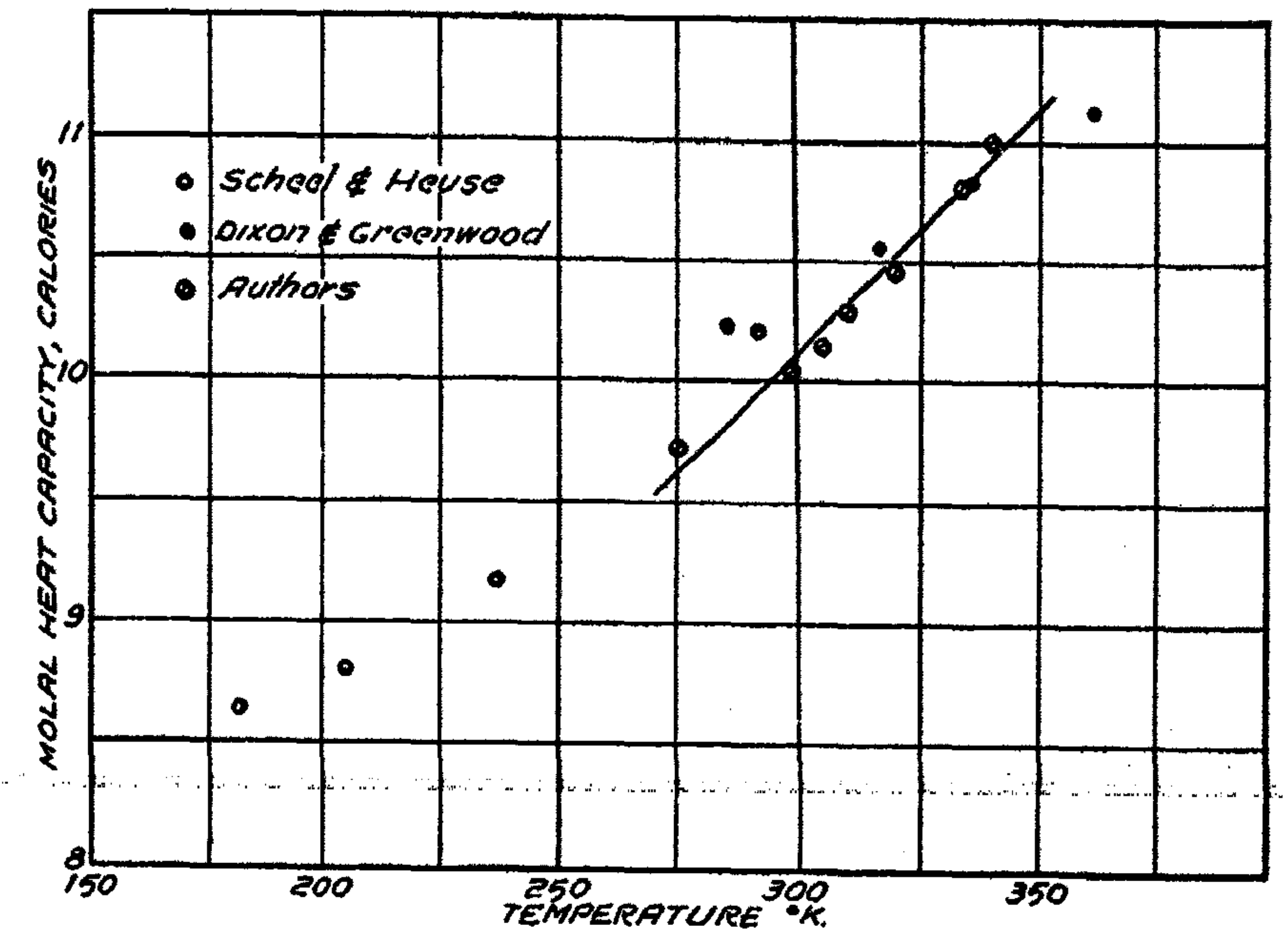

Fig. 1

Molal Heat Capacity of Ethylene

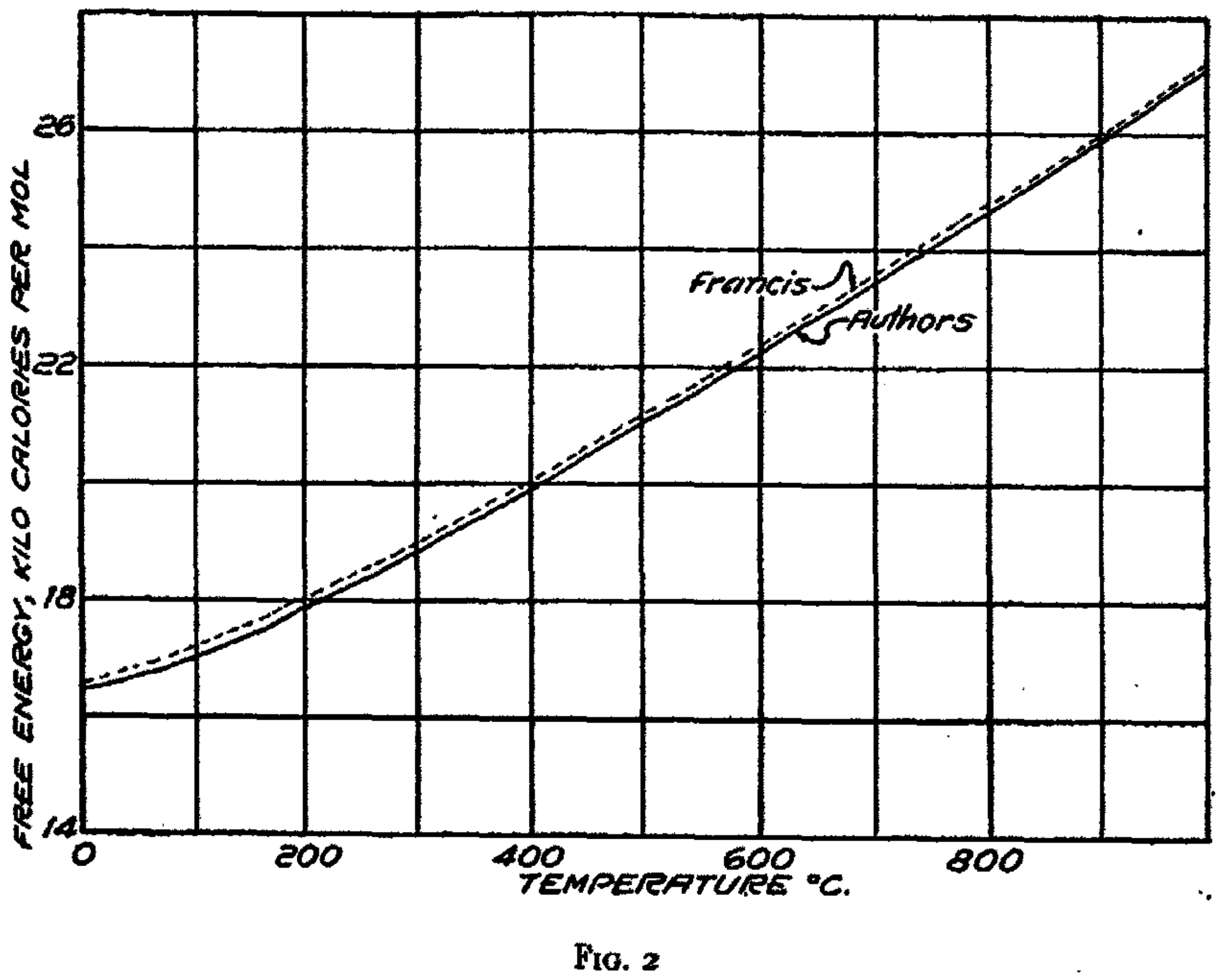

Fig. 2

Free Energy of Formation of Ethylene Gas in which the constants ΔH_0, Γ_0, and Γ_1 are defined by the equations:

$$\Delta H = \Delta H_0 + \Delta\Gamma_0 T + \tfrac{1}{2}\Delta \Gamma_1 T^2 + \ldots\ldots\ldots\ldots\ldots$$

$$\Delta C_p = \Delta\Gamma_0 + \Delta \Gamma_1 T + \ldots\ldots\ldots\ldots\ldots\ldots$$

$$C_p = \Gamma_0 + \Gamma_1 T + \ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

The values of $\Delta\Gamma_0$ and $\Delta\Gamma_1$ are obtained from the heat capacity equations for the reactants[6] and the resultant[7] of the chemical reaction:

$2\ C$ (graphite) $+ 2\ H_2 = C_2H_4$, as follows:

$$2\ C,\ C_p = 2\ (1.1 + 0.004\ T)$$

$$2\ H_2,\ C_p = 2\ (6.65 + 0.0007\ T)$$

$$C_2H_4,\ C_p = 4.064 + 0.02022\ T$$

from which, by taking the reactants as negative and the resultant as positive,

$$\Delta C_p = -11.436 + 0.0108\ T.$$

Using the value of ΔH_{298} as calculated by Francis,[6] namely, $\Delta H = 14{,}865$ calories, the equation for the heat of reaction becomes

$$14{,}865 = \Delta H_0 - 11.436\ (298) + 0.0054\ (298)^2,$$

from which $\Delta H_0 = 17{,}790$.

Substituting in the free energy equation, gives

$$\Delta F = 17{,}790 + 11.436\ T \ln T - 0.0054\ T^2 + \ldots\ldots + I\ T.$$

The constant *I* was calculated from the equilibrium data of Pring and Fairlie[8] in the same way as was done by Francis. The average of three values gave − 67.6. When introduced into the equation above, the free energy of formation of ethylene gas is given by

$$\Delta F = 17{,}790 + 11.436\ T \ln T - 0.0054\ T^2 - 67.6\ T.$$

Fig. 2 represents the free energy expression between 0° and 1000°C. The equation calculated by Francis from the data in the literature, shows close agreement with the results of this investigation.

The experimental specific heats reported in this work are considered to be accurate within one per cent.

The writers wish to express appreciation to the United States Bureau of Mines, Pittsburgh Experimental Station, for the loan of equipment, and to Dr. A. G. Loomis and Dr. Victor R. Thayer for suggestions and criticisms in this investigation.

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[6] A. W. Francis: Ind. Eng. Chem., 20, 277-279 (1928).

[7] This investigation.

[8] Pring and Fairlie: J. Ind. Eng. Chem., 4, 812, (1912).

Summary

Apparatus has been reconstructed with modifications, for the purpose of determining the specific heats of gases at atmospheric pressure by the Constant-Flow Method.

Measurements of the specific heats of ethylene gas at seven temperatures, from 0° to 70°C. have been made. The equation formulated from the results is given by

$$C_p = 4.064 + 0.02022\ T.$$

The free energy of formation of ethylene gas has been computed, using the specific heat equation given above.

CHEMICAL ACTION IN THE GLOW DISCHARGE

IX. Reaction in the Crookes Dark Space and Negative Glow*

BY A. KEITH BREWER AND P. D. KUECK

In the previous articles of this series it has been shown that an Electrochemical Equivalence Law, analogous to Faraday's Law for Electrolytes, holds for the chemical action in the electric discharge in gases. The definiteness of this law combined with the facts that the active states are easily identified, and that the reaction takes place in the gas phase without the presence of solvent, surface, or catalyst, makes the glow discharge an extremely fertile field for the study of chemical reactivity.

The principal difficulty at present in this type of research results from a lack of understanding of the physics of the discharge. Until this is solved an accurate estimation of the ratio of molecules formed to reactive centers (M/N) cannot be given. The present research was undertaken to clear up the uncertainty regarding the relative ability of the various regions of the discharge to incite reactivity, special attention being given to the Crookes dark space and to the negative glow. Also, a new method is suggested which permits a more accurate estimation of the number of positive ions formed than has heretofore been possible.

The Reaction

The reaction chosen for this work was the synthesis of nitrogen dioxide from an $N_2/2O_2$ mixture since the previous study of this reaction[1] yielded very clean cut results with no apparent complication. The technique was identical to that employed in the previous study.

The Method

The method of procedure employed was to measure the reactivity when various portions of the discharge were eliminated by moving the anode towards the cathode.

In the glow discharge as the anode is moved through the positive column toward the cathode the rate of change of potential between the electrodes is constant until the anode reaches the Faraday dark space where the change in potential per cm. is usually slightly increased. As soon as the anode enters the negative glow, however, no change in potential between the electrodes is observed until it has reached a point near the edge of the Crookes dark space, where the voltage rises suddenly, changing from about 300 for the average discharge to many thousand in a very short distance. The conditions

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* Fertilizer and Fixed Nitrogen Investigations, Bureau of Chemistry and Soils, Washington, D. C.

[1] J. W. Westhaver and A. K. Brewer: J. Phys. Chem., 34, 554 (1930).

existing in the discharge when the anode has reached the edge of the Crookes dark space are identical to those found in the gas-filled x-ray tube, similar voltages being necessary to maintain the current.

From these considerations it will be seen that no difficulty is to be expected in measuring the reactivity in various regions of the discharge by changing the electrode separation until the anode approaches close to the edge of the Crookes dark space where the cathode fall of potential is no longer characteristic of the ordinary type of discharge.

Apparatus

The discharge tube is illustrated in the insert in Fig. 1. It consisted of a Pyrex tube 3.5 cm. inside diameter and 20 cm. long sealed to a 3 liter bulb. The cathode was made of an aluminum block turned to fit tightly into the bottom of the tube in order to confine the discharge entirely to the top surface. The position of the anode was adjusted by a stopcock suspension. The anode itself was made of two thin aluminum discs placed 0.5 mm. apart. The lower disc was 3.5 cm. in diameter with a 1 cm. hole in the center; the upper disc was a solid plate 2.5 cm. in diameter. It was found necessary that the outer disc fit the walls of the tube tightly to prevent the discharge from passing up along the walls when the anode approached the Crookes dark space. The 0.5 mm. separation between the plates was to allow fresh gas to diffuse into the discharge.

The rates were measured at 0.3 mm. pressure with the electrode separations from 0.2 cm. to 2.5 cm. The discharge current was maintained at 5.0 m.a. The dark space measurements were made visually with a 2.5 cm. electrode separation, the distance between the cathode and the edge of the negative glow being taken as the dark space. The electrode separation, however, has no effect on the length of the dark space.

Results

The pressure vs. time curves for the various electrode separations are given in Fig. 1. The data show a decrease in the rate of reaction as the anode approaches the cathode. Especially it should be noted that there exists a definite pressure at which the rate becomes zero for each electrode separation; this pressure decreases for increasing separation. Further, the curves show that the reaction in each instance dropped to a negligible value when the dark space approached close to the anode.

The voltage curve for various electrode separations are shown in Fig. 2. The curves become practically asymtotic to the voltage axis where the dark space reached the anode. This is the same point at which the reaction rate became negligible.

The reactivity, however, never entirely ceased as it was not possible to confine the discharge completely between the electrodes. When the electrode separation was just slightly greater than the length of dark space the high

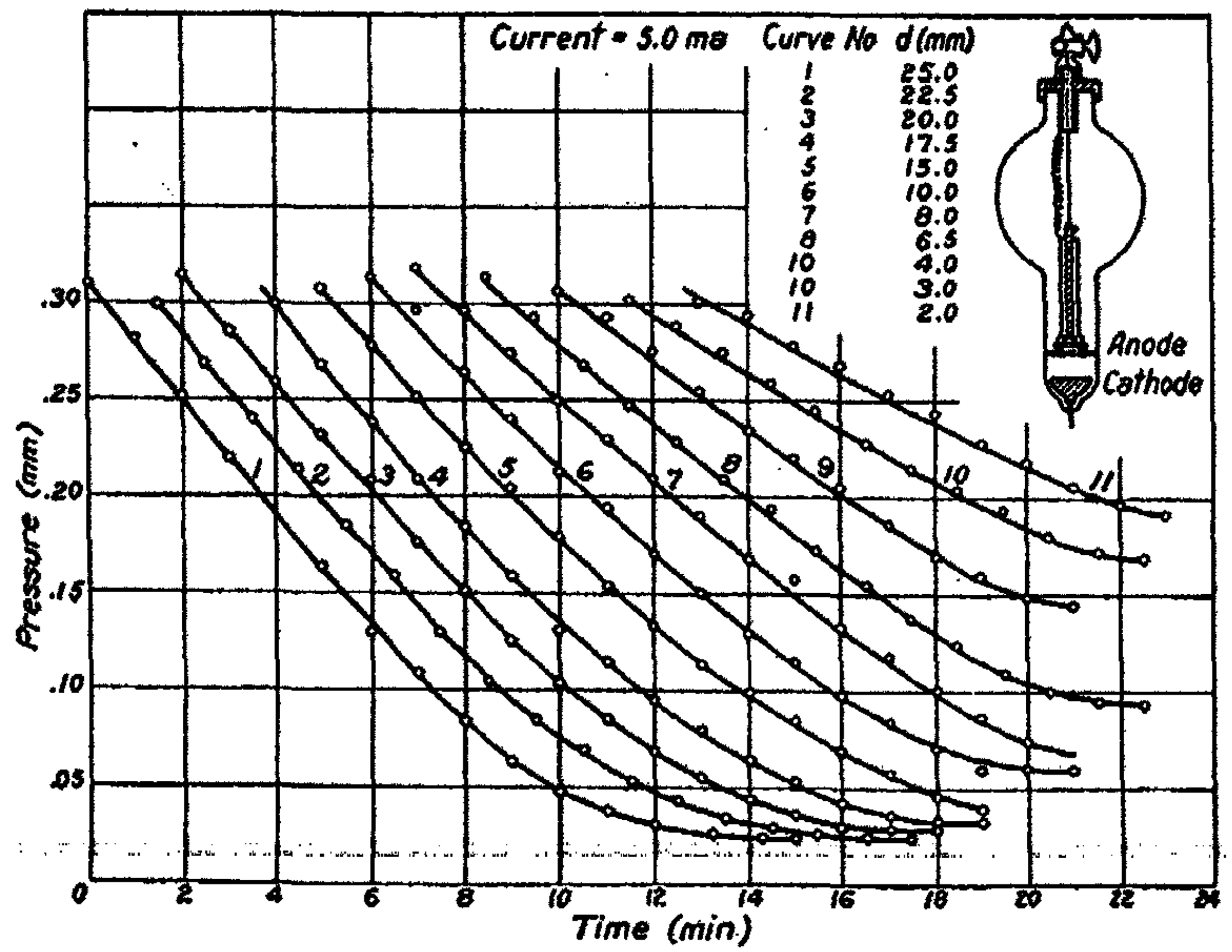

FIG. 1

Pressure vs. time curves for various electrode separations.

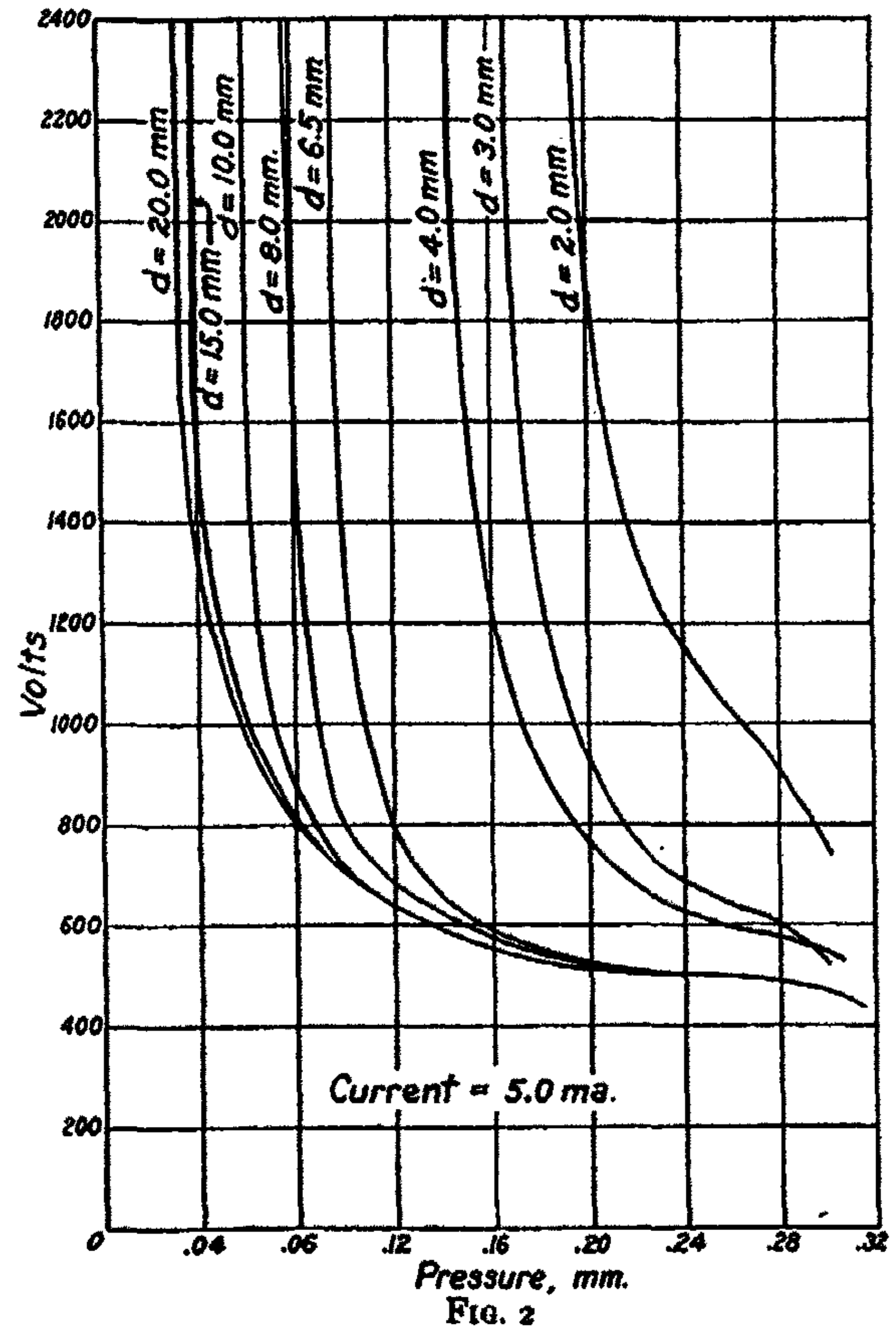

FIG. 2

Pressure vs. voltage curves for various electrode separations.

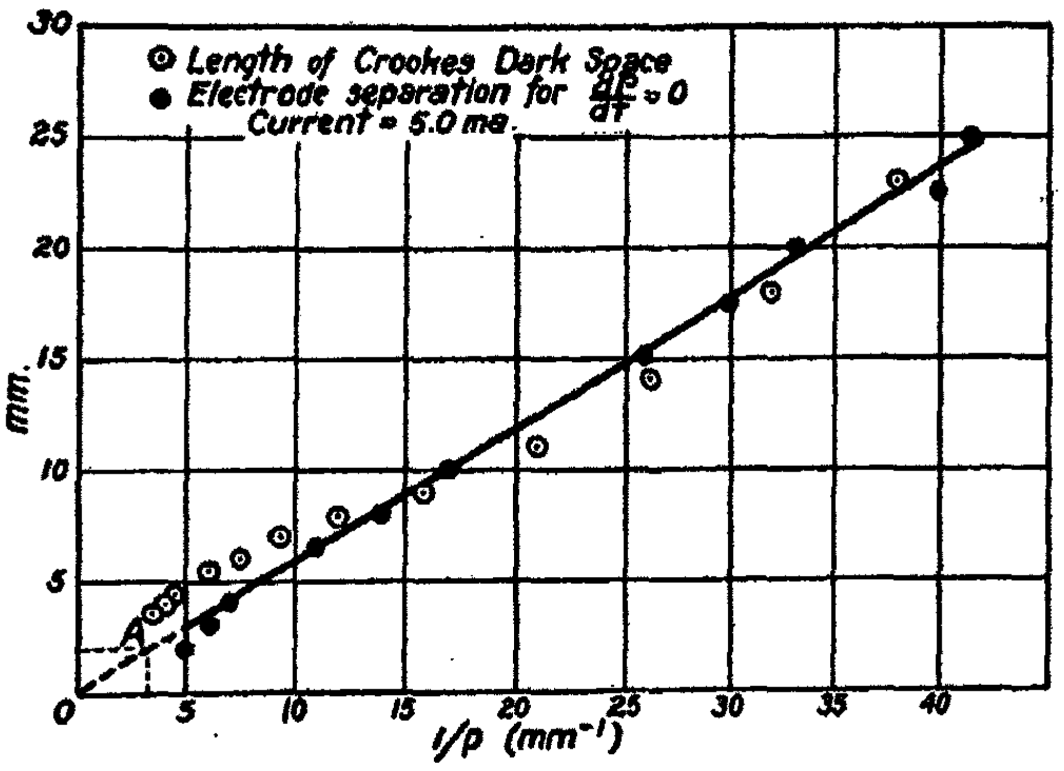

FIG. 3

Curve showing the relation between the length of the Crookes dark space and the electrode separation for zero rate as a function of pressure.

voltage necessary to maintain the current tended to cause the discharge to leak by the anode; the observed rates, therefore, are doubtless slightly high under these conditions.

The relationship between the Crookes dark space and the pressure at which the reaction ceases is shown in Fig. 3. The length of the Crookes dark space and the electrode separation at which the reaction becomes zero are plotted against the reciprocal of the pressure. It will be noted that the points fall close to the same straight line passing through the origin. The per cent error for short distances is necessarily higher than for greater distances; hence the observed deviations are not surprising. It should be mentioned that the dark space length was measured simply by visual observation; in another type of tube, designed for more accurate measurement, the hyperbolic relationship between length and pressure held accurately.

In Fig. 4 are plotted the rates measured at 0.3 mm. pressure for various electrode separations. The Crookes dark space at this pressure is very close to 2.0 mm. It will be observed that the rate decreases rapidly as the anode approaches the dark space.

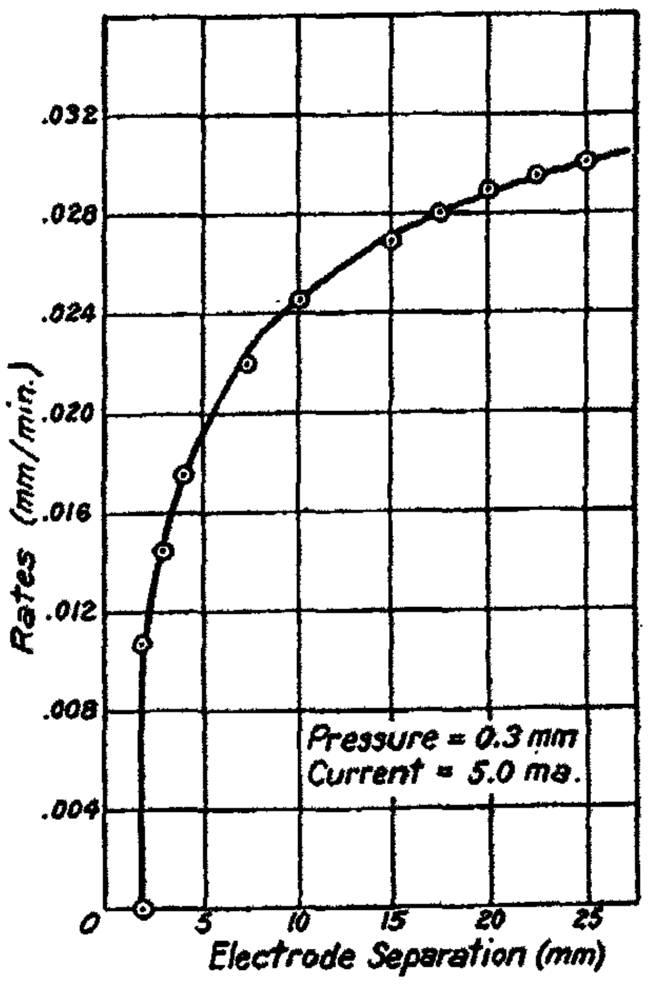

FIG. 4

Rate vs. electrode separation curve.

The rate of decrease in reactivity per unit volume of negative glow in moving from the Crookes dark space to the Faraday dark space is shown in Fig. 5. When the log of the decrease in rate (maximum rate minus the observed rate) is plotted against the electrode separation the points fall on a straight line except where the anode is very close to the Crookes dark space. 0.030 was taken as the maximum rate, since it represented the rate observed when the entire negative glow was included between the electrodes. Thus it will be seen that the reactivity in the negative glow decreases exponentially with distance from the edge of the dark space.

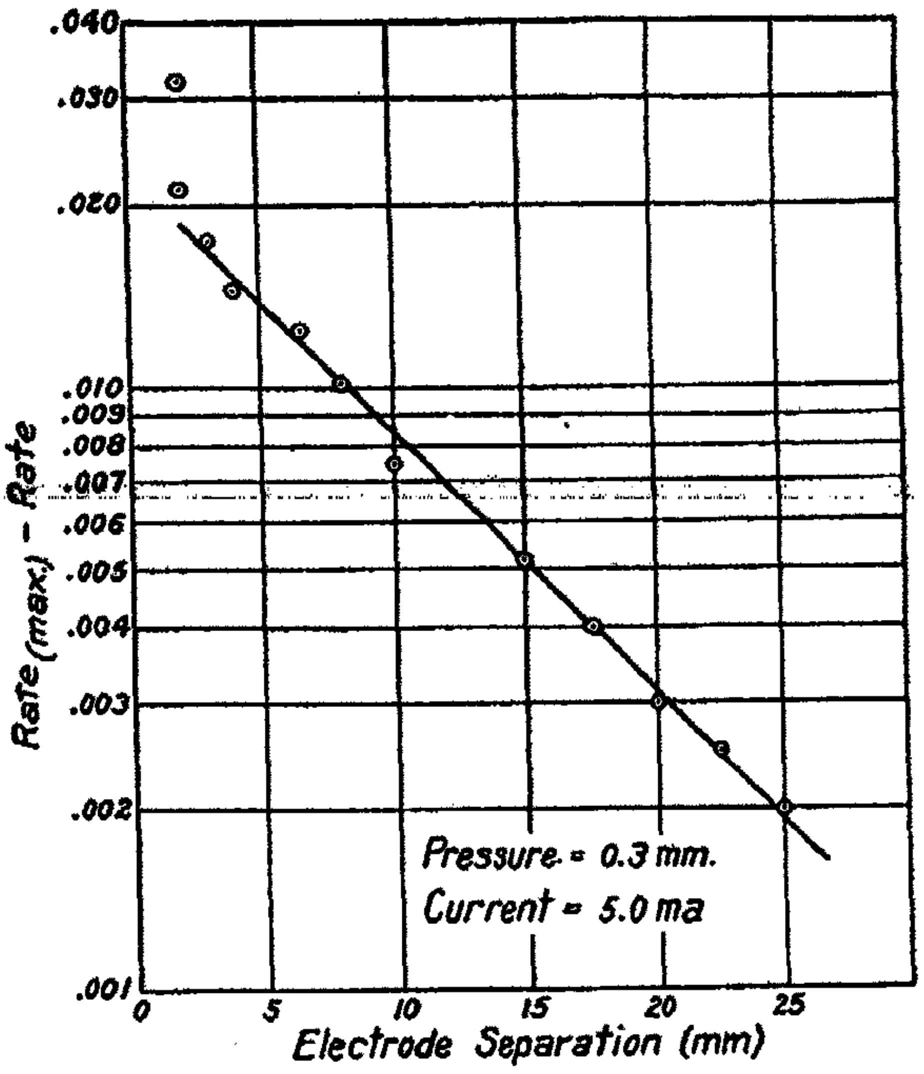

FIG. 5
Curve showing the rate of decay in reactivity through the negative glow.

Discussion of Results

Aston[1] has given the following expression for the Crookes dark space in the abnormal discharge,

$$d_a = \frac{A}{p} + \frac{B}{\sqrt{i}}$$

in which d_a is the length of the dark space in cm., p the pressure in mm. of mercury, i the current density, and A and B are constants. In the present experiments the current density was maintained constant so the relationship between length and pressure is expressed by

$$d_a = k_1/p + C$$

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[1] F. W. Aston: Proc. Roy. Soc., 87, 437 (1912).

From Fig. 3 it will be seen that the electrode separation at which dp/dt = 0 also obeys the relationship

$$l = k_2/p + C'$$

where l is the electrode separation. Since the points for both distances fall on the same line k_1 is equal to k_2, and C and C′ are equal and negligible at the low current densities used; hence $d_a = l$, i.e., the electrode separation at which the reactivity ceases is equal in length to the Crookes dark space. From this it follows that the reactivity in the dark space is negligible compared to that in the negative glow.

The mean path through which an electron is chemically active may be estimated from the rate of decrease of reactivity in the negative glow. Since the curve in Fig. 5 is exponential in character, except in the immediate neighborhood of the Crookes dark space, it follows from kinetic theory that for constant current and at a given pressure the decrease in the ability of an electron to induce reactivity can be expressed by

$$\frac{dp}{dt} = \int_{x=0}^{x=x} e^{-x/\lambda}\, dx$$

where x is the distance from the Crookes dark space, and λ is the mean path over which an electron is capable of inciting reaction. The value of λ obtained from the slope of the line is 2.5 mm. for 1 mm. pressure.

The fact that the exponential decay curve does not hold at the junction of the dark space may be due to several causes. When the anode is brought near the edge of the dark space the cathode fall of potential is not only materially raised, as is shown by Fig. 2, but the anode itself receives the direct impact of high-speed electrons. This bombardment gives rise to secondary electrons which produce an abnormal ionization in the gas adjacent to the anode. Another possible cause, inherent to the discharge itself, will be presented later on.

Interpretation of Results

The results that have just been presented can be interpreted readily from the physics of the discharge. In the discharge electrons are liberated from the cathode largely by metastable molecules and to some extent by positive ions and by photoelectric emission.[1] The electrons thus ejected are accelerated through the Crookes dark space by the cathode fall of potential. Very few positive ions are formed in the Crookes dark space since the length of the dark space is approximately equal to the mean free path of an electron between ionizing collisions. For instance, the dark spaces in nitrogen and oxygen at 1 mm. pressure are given by Townsend as 0.113 cm. and 0.114 cm., respectively. At this pressure the ionization mean free path of an electron is 0.113 cm. in nitrogen and 0.12 cm. in oxygen. These values as

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[1] Note. Linder and Davis (J. Phys. Chem., 35, 3649 (1931)) postulate that the current passing through the discharge is carried to the cathode almost entirely by positive ions falling in from the dark space. This conclusion apparently grew out of a misconception of the length of the dark space and the mean free path of an electron between ionizing collisions. Direct experimental measurements of the number of positive ions arriving at the cathode (to be published shortly) shows the positive ion current to be less than 3% of the total current in N_2 at 1 mm. pressure.

obtained from kinetic theory are equal to $4\sqrt{2}$ times the molecular mean free paths times the probabilities of ionization upon collision. From this it follows that the average electron does not begin to ionize until it reaches the edge of the negative glow.

In spite of the fact that the edge of the dark space comes within a mean free path of the cathode a fraction of the electrons, as given by probability, will ionize in this region. The ions formed near the cathode give rise to the positive ion current received by the cathode; the ions formed near the outer edge of the dark space where the field is weak are apparently driven into the negative glow by the momentum of the electrons and thus give rise to the known increase in pressure of the gas at this point. It is these ions driven into the negative glow from the dark space that may in part be responsible for the high reactivity observed at the beginning of the glow.

It does not seem probable that the positive ions arriving at the cathode can contribute materially to the chemical action. The lowest pressure to which this reaction can be carried shows that an ion must make between 10 and 15 collisions with neutral molecules for reaction to take place. The mean free path of an ion in oxygen is 0.082 mm. at 1 mm. pressure. Such an ion, therefore, would make less than 14 collisions in traveling completely across the dark space. However, as was just pointed out, it is doubtless only the ions formed near the cathode that ever reach that electrode; hence the probability of making the required number of collisions with neutral molecules is relatively small. For this reason it is not surprising that Fig. 2 shows the distance from the cathode where the reactivity becomes zero is equal to the length of the dark space.

The number of positive ions formed per electron of current can be estimated from the exponential decay of reactivity in the negative glow. In making this estimation it is necessary to assume that the rate of reaction is proportional to the rate of positive ion formation; the M/N ratio is not involved.

The slope of the line in Fig. 5 gives the value $\lambda = 0.25$ cm. for the mean distance over which an electron is chemically active in the negative glow. Since the electron has already traveled through the Crookes dark space or 0.11 cm. before entering the negative glow the total path of the average electron at 1 mm. pressure is 0.36 cm. The mean free path of an electron times the probability of ionization, as has been stated, is equal to the length of the dark space of 0.11 cm.; hence the average number of ionizing collisions made by an electron is $0.36 \div 0.11 = 3.3$.

The total number of positive ions formed per electron under conditions quite similar to those found in the discharge can be estimated from an extrapolation of the results of Langmuir and Jones[1] or from the values given by G. A. Anslow,[2] both observers obtaining substantially the same results. Miss Anslow gives 3.7 positive ions for a 400 volt electron which is in reasonable agreement with 3.3 derived from the present data.

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[1] Langmuir and Jones: Phys. Rev., (2) 31, 357 (1928).

[2] G. A. Anslow: Phys. Rev., (2) 25, 484 (1925).

These values assume that the energy of the electron is given by the entire cathode fall of potential. It may be, however, that the actual energy is slightly less than this, due to the space charge in the region through which the electrons are accelerated. In this connection it is interesting to note that Miss Anslow observed that an electron with 0.36 cm. range at 1 mm. pressure produced 3.4 ions, the required accelerating voltage being 347. Since 3.3 ions are obtained for a 0.36 cm. range in the present experiments, it might be inferred that the electrons in passing through the Crookes dark space failed by about 50 volts of receiving an acceleration corresponding to the entire cathode fall of potential.

The value of the M/N ratio can now be placed within reasonably narrow limits. The time vs. pressure curves for 2.5 cm. electrode separation indicate a yield at 0.3 mm. pressure of 1.5 molecules of NO_2 synthesized per electron of current. In the first paper on oxidation of nitrogen it was shown that this reaction is initiated by N^+_2 ions, O^+_2 ions being relatively inert. Since the stopping powers of oxygen and nitrogen are very nearly identical, the ratio of N^+_2 to O^+_2 ions is as 1:2. This gives an equivalent yield of 1.5 molecules formed per 1.1 N^+_2 ions, assuming positive ion current to be negligible. The positive ion current at 0.3 mm., however, has been found by direct measurement to be 15% of the total current; thus the number of electrons producing ions is reduced by 15%, and further the number of ions formed suffers an effective loss corresponding to 15% of the entire current since the positive ions arriving at the cathode do not contribute materially to the synthesis. Making these corrections the number of N^+_2 ions available for reaction is 0.73 per electron of current. The value of M/N, therefore, is 1.5/0.73 = 2, approximately.

Summary

The chemical action taking place in the Crookes dark space and the negative glow of the ordinary glow discharge has been measured for the synthesis of nitrogen dioxide. The distance from the cathode within which no appreciable reactivity occurs is shown to be equal to the length of the Crookes dark space. The reactivity per unit volume of discharge is a maximum at the beginning of the negative glow and thereafter decreases exponentially through the glow.

The average path at 1 mm. pressure over which electrons ejected from the cathode are capable of inciting reaction is shown to be 0.36 cm., the reactivity being confined entirely to the last 0.25 cm. of path. The total number of positive ions formed per electron is given by dividing 0.36 cm. by the mean free path of an electron between ionizing collisions. Thus the measurement of the mean free path over which the electrons are chemically active enables the number of positive ions formed in the negative glow to be computed by a new and independent method. The value of 3.3 ions so obtained agrees fairly well with 3.7 reported by Miss Anslow for 400 volt electrons.

The ratio of M/N = 2 for N^+_2 ions is obtained by correcting for the loss of N^+_2 ions to the positive ion current.

ELECTROKINETIC PHENOMENA

VIII. Surface Conductance of Cellulose and the Theory of Smoluchowski*

BY HAROLD A. ABRAMSON

In a recent series of papers dealing with the properties of the cellulose-water interface, Briggs[1] and Bull and Gortner[2] have described excellent methods for the measurement of surface conductance. They have, in addition, published most extensive and interesting reports of the effect of electrolytes on the specific surface conductance, $(\kappa_s - \kappa)$, of cellulose diaphragms. Briggs pointed out that electrolytes produced, in general, a continuous *increase* in the surface conductance but a *decrease* in the ζ-potential after a primary small increase. This was apparently completely contrary to the predictions of Smoluchowski[3] who postulated a concurrent increase of $(\kappa_s - \kappa)$ and ζ. It is the purpose of this communication to reconsider certain data of the authors mentioned above in the light of Smoluchowski's theory and that of Gouy[4] and of Debye and Hückel.[5] It will be shown that the general changes of $(\kappa_s - \kappa)$ and ζ are not inconsistent with the theory of Smoluchowski if the thickness of the double layer is considered, but that the theory is incomplete.

Theoretical

Consider with Smoluchowski[3] a cylindrical glass capillary having the property of surface conduction where the radius of the capillary is large compared with, d, the thickness of the double layer. The ratio of the current carried by the surface phase to that of the bulk is,

$$\frac{I_s}{I} = \frac{S}{Q\eta\kappa d}\left(\frac{\zeta D}{4\pi}\right)^2$$

where $\zeta \propto \frac{E}{P}(\kappa_s)$; S = circumference of capillary; D = dielectric constant; Q = cross-section; η = coefficient of viscosity of the liquid; κ = specific conductance of the liquid in bulk; E = streaming potential; P = the pressure difference; κ_s = specific conductance of the liquid in the capillary; units are c.g.s. electrostatic. Briggs developed a method for determining the specific conductance of the bulk liquid in cellulose diaphragms so that he could replace I_s/I by its equivalent $(\kappa_s - \kappa)/\kappa$, yielding

$$\kappa_s - \kappa = \frac{S}{Q\eta d}\left(\frac{\zeta D}{4\pi}\right)^2. \tag{1}$$

In order to compare $(\kappa_s - \kappa)$ and ζ when the concentration of electrolyte is changed, it is necessary to sort out the constants. In a given cellulose dia-

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phragm with small changes in concentration of salt $[S/Q\eta\ (D/4\pi)^2]$ can be taken as approximately constant, but ζ and d are variables.

The theory of Smoluchowski as here considered postulates that

$$(\kappa_s - \kappa) = C\ (\zeta^2/d). \qquad (1a)$$

C = a constant.

The specific surface conductance should increase not simply with ζ, but rather with the ratio (ζ^2/d). It is possible to calculate values of d in different salt solutions by the theories of Gouy and of Debye and Hückel. Both of these give essentially the same results. We employ the relationship of Debye and Hückel.

$$d = \frac{1}{\Gamma} = \frac{3.06 \times 10^{-8}\text{cm.}}{\sqrt{\mu}} \qquad (2)$$

where as usual the ionic strength, $\mu = \frac{1}{2} \sum_{1}^{s} n_i Z^2_i$, n = number of ions of the valence Z. Combining equations (1) and (2),

$$(\kappa_s - \kappa) = C(\zeta^2\Gamma) \qquad (3)$$

The ionic strength of the distilled water cannot be neglected because very dilute salt solutions are to be considered. A minimum value of μ was obtained by extrapolating $([E/P\ \kappa_s]^2\Gamma)$ to zero salt concentration considering the ionic strength as due to the salts alone. This extrapolation yielded $\mu = 25 \times 10^{-6}$.

Relationship of $(\kappa_s - \kappa)$ *and* $(\zeta^2\Gamma)$. To test equation (3) we have evaluated from the data of Bull and Gortner values of $(\zeta^2\Gamma)$ in different concentration of various salts for the cellulose-water interface. These values have been plotted as ordinates as closed circles in Fig. 1, against the concentration of electrolytes. On the same ordinate by converting the highest value of $(\kappa_s - \kappa)$ to the same scale $(\kappa_s - \kappa)$ has been also plotted. In every instance, for KCl, NaCl, $MgCl_2$, $CaCl_2$, K_2SO_4, K_2CO_3, K_3PO_4, $ThCl_4$, there is a general parallelism between $(\kappa_s - \kappa)$ and $(\zeta^2\Gamma)$, with, however, differences given by the areas and their shapes between the two sets of data which indicate that although the combined Smoluchowski and Debye theories as employed here give a qualitative expression of agreement it is evident definite differences exist between theory and experiment. This is brought out perhaps more clearly in Fig. 2, where $(\zeta^2\Gamma)$ has been plotted directly against $(\kappa_s - \kappa)$ for

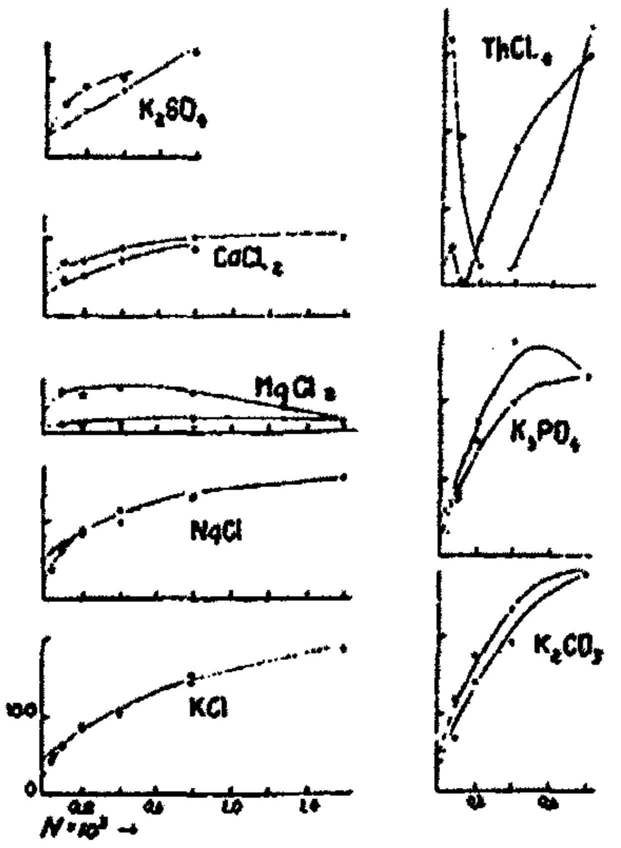

FIG. 1

Both $(\zeta^2\Gamma)$, closed circles, and $(\kappa_s - \kappa)$, open circles, increase as the salt concentration is increased, although the simple theory of Smoluchowski is evidently not followed. Data of Bull and Gortner.

LiCl, NaCl, KCl, CsCl, NH_4Cl and HCl (Briggs). The small black rectangle in the lower left-hand corner is the mean for values of $(\zeta^2\Gamma)$ in distilled water. The ordinate value of this rectangle is probably too low because of the low and uncertain value of μ for the distilled water. The dotted paraboloid curves starting at this rectangle fit the data fairly well. However, according to equation (3) when $(\kappa_s - \kappa) = 0$, $(\zeta^2\Gamma)$ should also be zero. If the theory were followed in an ideal case, the data should have extrapolated through the

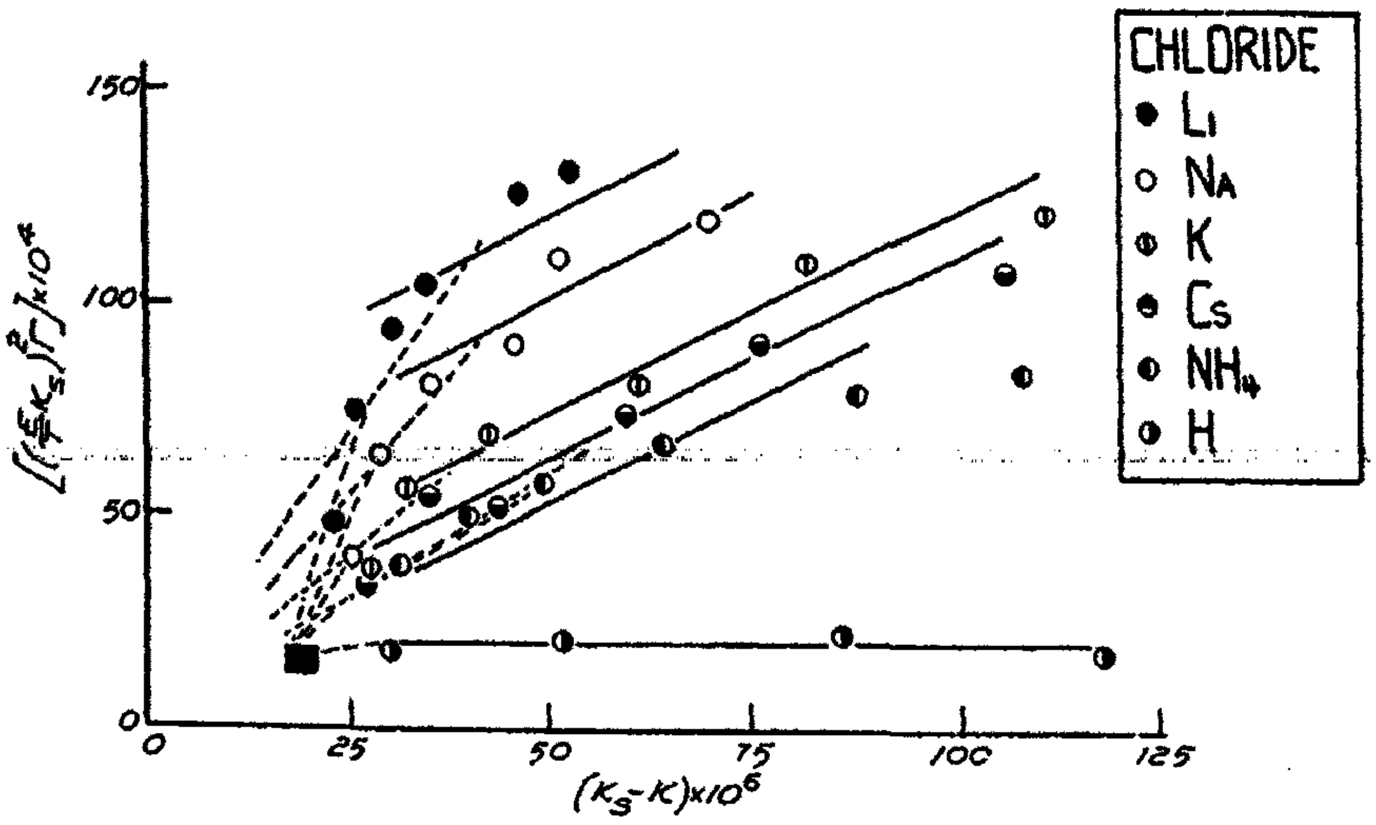

Fig. 2

origin as indicated by the broken straight lines. It must be remembered that the ions present in distilled water are different from those of each of the added salts. Since we are obviously dealing with changes due to the specific nature of the ions it is not logical to expect the simple theory to hold and the extrapolation through the origin to occur. The straight unbroken lines drawn through the data fit the latter portions of the curve poorly, the parabaloid plot being a closer fit. A clue which may lead to the correct theory has been given by Briggs who pointed out that $(\kappa_s - \kappa)$ for a given value of κ followed very closely the mobilities of the alkali halides. That is, the specific surface conductance was found to be simply related to the mobility of the cation alone. This is made clearly evident in Table I where values of (κ) and $(\kappa_s - \kappa)$ obtained from Briggs and Bull and Gortner are compared for a series of salts. If the surface conductance were to vary with the mobility of the cation, then for a given value of κ the ratios $\frac{\kappa_s - \kappa}{\text{mobility cation}}$ should be constant. This result is obtained for Li^+, Na^+ and K^+ but not for Mg^{++} and Ba^{++}. In the simple case of the alkali halides it would seem logical to expect a modification of the theory calling for a relationship of the sort given by Mooney[6] who considers the surface conductance as partially dependent upon the absolute mobilities of the positive and negative ions.

Professor R. A. Gortner has been kind enough to read and check parts of the calculations.

In Table I for various values of κ, the surface conductance $(\kappa_s - \kappa)$ is compared with the mobility of the cation for a series of salts. If the surface conductance follows the order of the mobilites of the cations with the same anion then for any given value of κ the ratios $\frac{\kappa_s - \kappa}{V_{\text{cation}}}$ should be constant. Note the excellent agreement with this assumption for lithium, sodium and potassium chlorides. It does not hold for divalent cations and those of higher valence. The values of $(\kappa_s - \kappa)$ are taken from smooth curves drawn from data of Briggs and Bull and Gortner.

TABLE I

κ	LiCl		NaCl		KCl		MgCl$_2$		BaCl$_2$	
$\times 10^5$ mhos	$\kappa_s - \kappa$ $\times 10^5$ mhos	$\frac{\kappa_s-\kappa}{V_{Li^+(33.3)}}$	$\kappa_s - \kappa$ $\times 10^5$ mhos	$\frac{\kappa_s-\kappa}{V_{Na^+(43.4)}}$	$\kappa_s - \kappa$ $\times 10^5$ mhos	$\frac{\kappa_s-\kappa}{V_{K^+(64.5)}}$	$\kappa_s - \kappa$	$\frac{2(\kappa_s-\kappa)}{V_{Mg^{++}(45.9)}}$	$\kappa_s - \kappa$	$\frac{2(\kappa_s-\kappa)}{V_{Ba^{++}(55.4)}}$
5	38	115	44	103	56	87	33	72	41	74
10	46	*139*	58	*134*	82	*127*	37	81	50	90
15	51	*155*	66	*152*	98	*152*	39	85	56	101
20	56	*170*	70	*161*	107	*166*	40	87	60	108
(40)	(60)	(*182*)	(82)	(*189*)	(122)	(*189*)	(40)	(87)	(68)	(123)

Professor K. S. Cole has been kind enough to discuss certain aspects of this problem with me.

Summary

It is shown that certain data on the effects of salts on the surface conductance of cellulose are not inconsistent with the combined theories of Smoluchowski and Debye and Hückel, but that the data indicate the incomplete form of the classical theory.

Bibliography

[1] D. R. Briggs: J. Phys. Chem., 32, 641 (1928).
[2] H. B. Bull and R. A. Gortner: J. Phys. Chem., 35, 308 (1931).
[3] M. von Smoluchowski: Physik. Z., 6, 529 (1905).
[4] L. Gouy: J. Phys., 9, 457 (1910).
[5] P. Debye and E. Hückel: Physik. Z., 24, 185 (1923).
[6] M. Mooney: J. Phys. Chem., 35, 329 (1931).

THE SOLUBILITY OF GOLD IN MERCURY. V*

BY JOSEPH T. ANDERSON

The object of the present investigation was to supplement the determinations of the solubility of gold in mercury already made in this laboratory[1,2,3,4] by advancing to higher temperatures. The range covered was from 280° to 400°C, a region concerning which existing evidence is rather discordant. For the most part the synthetic method was used.

The determination of solubility by the synthetic method consists in sealing up in a glass tube the system of which the solubility (liquidus) point is desired and, by properly heating, determining the temperature at which the last crystal of solid disappears. As used for non-metallic systems between 10° and 80°C the tubes are heated in a water bath with constant stirring and shaking, and if fine crystals are used and the heating is very slow over the last temperature range, the temperature at which the last crystal disappears can be determined with considerable accuracy.

To adapt this method to the higher temperature range it was necessary to find a substance for the bath which would be transparent fluid without objectionable properties at temperatures up to 400°C. The simplest kind of bath which can be used is an air bath. There are however disadvantages in the use of air due to its low specific heat and poor thermal conductivity, both of which tend to allow temperature differences to exist in the bath. After considerable casting about, no satisfactory liquid had been found and it was decided to use an electrically heated air bath.

Description of Furnace

The furnace used by Weiner[3] was redesigned as follows with the objects in view of improving the temperature uniformity and making it possible to see into the furnace readily in order to observe the disappearance of the solid. The four 500 watt nichrome elements which were in each of four corners of the furnace were replaced by B. and S. No. 30 Ni wire elements of which there were ten in parallel, wound side by side on four transit strips so that each of the elements went completely around the inside of the furnace eight times. This made the inside of the furnace surrounded on four sides (not the ends) by wires spaced about 3/16" apart, each tenth wire being part of the same element. Each of the elements developed about 250 watts on 110 volts a.c. They were connected so that two sets of two each could be put either in series or in parallel and a 50 ohm rheostat was provided which could be put in series with either or both of two elements. It was found possible to regulate the heat input to any desired value by these means.

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* Communication from the Chemical Laboratory of the University of Rochester, Rochester, N. Y.

After reaching the required temperature, it was never found necessary to use more than 1000 watts to maintain that temperature. In order to make it possible to get into the furnace without going through the heating elements one end of the furnace was made detachable. This end was provided with a 2" × 3" plate glass window.

Since there were found to be differences in temperature within the bath amounting to ten degrees it was necessary to stir the air. This was first done by large sheet metal vanes mounted on the shaft which rocked back and forth to stir the contents of the solubility tubes which were attached to it. More vigorous stirring was obtained by a large bent piece of sheet metal attached to a separate shaft which entered through a hole in the window and was rotated in such a way as to make the air move toward the center of the furnace as well as rotate. Later the stirring was done by an ordinary 6" air fan which also was attached to the shaft which entered through a hole in the window. With either of the two last mentioned fans there was probably not more than about a degree difference in temperature in the parts of the bath in which the tubes were.

Measurement of Temperature

The mercury thermometers used were of good grade, made by Taylor Instrument Company and by Hiergesell Brothers (see Table II) and were graduated in one-degree divisions. The bulb of the thermometer used was immersed in molten metal contained in an ordinary iron crucible. In order to eliminate stem correction and still allow it to be read, the thermometer was placed inside a heated chimney of pyrex glass which kept the mercury column at the same temperature as the bulb. The chimney was constructed as follows: Small glass drops were sealed every centimeter for 20 cm. on two opposite sides of the outside of a pyrex tube 5 cm. in external diameter. Nichrome ribbon, 4.1 ohms per foot, was then wound tightly on the tube so that the glass drops separated the windings. A large pyrex tube, 6 cm. internal diameter and long enough to cover the winding, was placed over the first leaving 6 cm. of the smaller tube projecting and the space between the tubes was closed at each end by asbestos which was moistened and forced into place. The portion of the smaller tube protruding fitted into a hole in the top of the furnace and this supported the chimney.

By means of a 50 ohm rheostat in series on 110 volts a.c. the temperature of the chimney could be kept at any temperature used in the furnace. The temperature of the chimney was read by an auxiliary thermometer the bulb of which was placed about half way up the chimney. Although the temperature of the chimney varied considerably from top to bottom, it seems very probable that by its use the stem correction for the main thermometer was reduced to less than 0.1°.

The thermometers used were standardized by comparing with a Hiergesell Brothers double-diamond 360° thermometer which was graduated in 1/2 degrees and had been standardized by the Bureau of Standards. The thermometers were standardized under the same conditions as those under which they were used, employing the fused metal bath and the chimney. The readings of the thermometers were taken every ten degrees from 280° to 360°C. At each point the temperature was held constant to within 0.2° for twenty minutes and readings were made to the nearest 0.1° using a small magnifying glass. Ice points were taken at the time of standardization and were checked frequently throughout the runs.

With continued use at temperatures over 300° the ice points of the thermometers were found to change in some cases as much as a degree. In order to eliminate the uncertainty thus introduced it was decided at about the midpoint of the investigation to change to a platinum resistance thermometer. The thermometer obtained was of the best grade made by Leeds and Northrup, having a resistance of 2.5 ohms cold. The bridge was of the semi-precision type being graduated to 0.01 ohms which corresponds to one degree and readable to 0.1°. The galvanometer was of the mirror type, having a self-contained light and ground-glass scale and was found to give a deflection of about 3 divisions per 0.1° thus making it possible to notice and correct very slight changes in temperature. Correcting small changes in temperature was further facilitated by the fact that, with the heating elements located as they were inside the furnace, the lag between the time when the current was increased and when the temperature started to rise was only 10 or 15 seconds.

The resistance thermometer was calibrated[13,14,15] at the ice point, steam point, and sulfur boiling point. During constant use over a period of about ten weeks the resistance of the thermometer at zero increased 0.009 ohms or the temperature for a given resistance fell 1.0°, the change being practically the same at all temperatures. Four calibrations were made and for the first, third, and fourth the changes were found to be fairly uniform as contrasted with the haphazard changes in the zero points of the mercury thermometers. The results of the second calibration were discordant with the others and therefore it was considered that there was a mistake in the calibration.

It has been found that the resistance (R) of platinum can be expressed to a high degree of accuracy as a parabolic function of temperature (t). The equation used is

$$R = R_0 + at + bt^2$$

in which the three constants R_0, a, and b are evaluated by determining R at the temperatures of melting ice, boiling water, and boiling sulfur. The change of boiling point with barometric pressure has to be taken into consideration and at the sulfur boiling point other factors also including radiation, condensation of vapor, and lagging of the vapor chamber. The methods have been standardized by the Bureau of Standards and are specified in the papers referred to above. The values of resistance found at zero and at the normal boiling point of water and sulfur in the four calibrations are given in Table I, along with the values for the constants in the resistance-temperature equation.

TABLE I

Constants* for L. & N. Resistance Thermometer No. 184209 for the equation $R = R_o + at + bt^2$

Calibration	R_o	$R_{100.00}$	a	$R_{444.60}$	b
1st	2.471	3.441	.009846	6.556	−.000001483
(2nd	2.473	3.437	.00977	6.558	−.00000132)
3rd	2.479	3.448	.009835	6.563	−.000001457
4th	2.480	3.450	.009850	6.565	−.000001488

* Using semi-precision bridge No. 207751 and galvanometer No. 219054.

In using the resistance thermometer in the furnace the metal bath and the heated chimney were done away with, the coil of the thermometer being placed as near as possible to the solubility tubes and at the level at which the amalgams were most of the time, namely about one inch below the center shaft.

Solubility Tubes

Since liquid amalgams are not transparent it is not possible to observe the disappearance of crystals simply by looking at the tube as is done with ordinary systems. Accordingly a tube was designed as shown in Fig. 1 made of pyrex glass tubing with a fine capillary C of the same bore as that previously used in solubility tubes in this laboratory, and a return tube E. The amalgam of desired composition is introduced into A and the tube is sealed off at B. The whole tube is evacuated to a few thousandths of a millimeter of mercury through the coarse capillary F and this is then sealed off near the bulb D. When the tube is turned counter clockwise 180 degrees the contents fall onto the capillary C and the liquid filters through, leaving the solid behind. When the tube is further rotated in the same direction (counter clockwise) the liquid runs back through the tube E into A. By continuously raising the temperature, filtering at frequent intervals, the amount of solid is observed to decrease and the temperature at which no more solid is found is the solubility temperature provided the rate of heating is slow enough and other conditions are such that the system is in equilibrium. In some of the later runs tubes were used which had about the same overall dimensions as that shown in Fig. 1 but only about half the volume since smaller tubing was used in making them. No difference in results was attributed to this change.

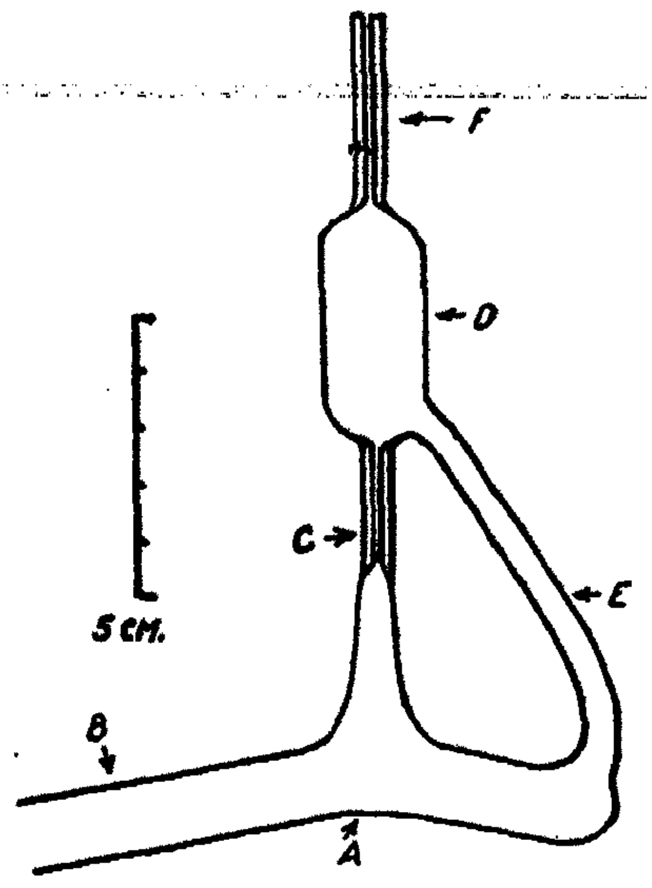

FIG. 1
Synthetic Tube. The capillary really has no constriction.

The tubes were supported by a shaft which was in the center of the furnace. Each tube was fastened to the shaft by two clamps, one of which held it about part A and one about part D. Two tubes could be run at the same time by placing the capillaries (C) of the two on opposite sides of the shaft so that the solid which filtered out could be seen in both. The shaft rocked back and forth so that the contents of the tube were transferred from one end of part A to the other about twenty times per minute. To furnish light a 50 watt show case bulb was partially inserted into the furnace through a hole in the end opposite to the window.

Synthetic Runs

The mercury used in the first part of the runs was the same used by Weiner[3] and that used later was purified by Mr. DeRight. Both lots were triple distilled in sealed glass systems. The gold used came from the United States Assay Office and was said to be at least 999.8 fine. In some of the runs gold was used which had been recovered from earlier runs by vaporizing the mercury at temperatures up to 550°C in a current of air. Knowns treated in this way show that the mercury is completely removed.

The tubes were evacuated in order to prevent oxidation of the mercury and also incidentally to keep down the total pressure in the tubes at high temperatures. Oxidation is objectionable not only because of the mercury removed but also because the solid oxide may interfere with the filtering, or may be mistaken for crystals of the solid phase, or may stick to the walls of the tube and hold with it crystals of solid. It is also very possible that the presence of the oxide may give a ternary system which has a solubility point different from that of the simple system gold-mercury. The pressure existing inside the tubes when cold was from 0.001 to 0.005 mm. of mercury as measured by a McLeod gauge.

In making a synthetic run the temperature of the furnace was raised rather rapidly, slowing down the rate of heating as the amount of solid left decreased, and the temperature of complete disappearance was determined within a degree or two with comparative ease. To obtain crystals again the furnace was cooled, the temperature of reappearance being generally two or three degrees lower than the temperature of disappearance. The temperature was then increased slowly and the solubility point determined.

The rate of heating at the solubility point was restricted by the fact that filtrations could not be repeated much more frequently than at two minute intervals. Since it was desired to determine the solubility point to the nearest tenth of a degree the average rate of heating at the solubility point could not be greater than 0.1° in 2 minutes or 1° in 20 minutes. Often the solubility temperature was approached much more slowly than this.

Tubes numbered up to XXXIV were made up and run according to this procedure and the results are shown in Table II and in Fig. 4 together with other data which will be described presently. In the case of tubes VI, IX, and X after the solubility point had been determined the tube was opened, a weighed amount of gold was added, and the tube was evacuated and sealed up and used as a new tube. The tubes so prepared were numbered VI-I, IX-I, and X-I respectively. It was finally decided to be better practice to start with fresh materials each time.

TABLE II

Results of Synthetic Runs

Tube No.	Gms. Au	Gms. Hg	At.% Au	Temp. °C	Thermometer	Remarks
II	3.875	34.647	10.22	286.3	T-1	one run, tube cracked and contents were transferred.
IV	5.444	36.502	13.17	288.2	"	several runs.
V	4.788	32.121	13.17	291.1	"	one run.
VI	4.771	31.927	13.19	290.8	"	one run.
VI-I	5.312	31.927	14.48	293.5	"	one run.
VII	5.264	31.551	14.51	293.9	"	one run, disappearance and reappearance.
VIII	5.152	30.915	14.50	293.9	"	do.
IX	5.678	30.174	16.07	297.9	H	one run.
IX-I	6.085	30.174	17.02	300.4	"	one run, ± 1/2°
X	6.272	31.135	17.01	300.7	"	one run.
X-I	7.838	31.135	20.40	307.2	"	3 runs, 2 checks.
XII	6.026	20.592	22.94	310.2	"	one run, possibly low.
XIII	5.767	19.888	22.78	309.4	"	2 runs, rather scanty, possibly low.
XIV	7.143	21.716	25.07	315.2	"	one run.
XVI	7.459	20.454	27.05	320.7	T-2	one run.
XVII	8.447	21.015	29.02	327.5	"	one run.
XVIII	8.746	21.740	29.04	328.6	"	one run.
XIX	9.493	21.503	31.00	334.5	"	2 runs, 1/2° difference.
XXII	6.709	21.640	23.97	315.4	"	2 runs, possible high, impurity suspected.
XXIV	7.251	19.978	26.97	321.7	"	one run, impurity suspected.
XXV	9.872	19.272	34.26	351.0	Pt(1,3)	one run.
XXVI	9.724	18.980	34.26	352.6	"	one run.
XXVII	11.824	19.659	37.96	373.4	"	one run. 2 disappearances.
XXVIII	12.252	20.368	37.96	374.8	"	do.
X-I		see above		308.9	"	one run.
XVII		see above		327.5	"	one run.
XIX		see above		335.9	"	one run.
XXIX	4.456	6.728	40.25	388.8	Pt(3)	5 runs varying over 3°, highest value given.
XXX	8.825	13.500	39.94	386.8	"	4 runs varying over 1°, highest value given.
XXXI	3.200	19.983	14.01	298.7	"	4 runs varying over 5°, highest value given.
XXXIII	1.986	14.139	12.50	286.5	"	2 runs, 4° difference, higher value given.

TABLE II (Continued)

Results of Synthetic Runs

Tube No.	Gms. Au	Gms. Hg	At.% Au	Temp. °C	Thermometer	Remarks
XXXIV	2.009	14.237	12.55	288.3	Pt(3)	2 runs, 4° difference, higher value given.
XVII		see above		329.6	"	one run.
XIX		see above		337.7	"	one run.
XVII		see above		326.7*	Pt(4)	one run, (two disappearances).
XIX		see above		331.8*	"	do.
X-I		see above		308.6	"	do.
XXVIII		see above		368.3	"	do.
XXXI		see above		296.9	"	one run.
XXXII	4.055	17.570	19.01	307.2	"	4 runs varying over 3°.
XXXV	2.910	15.548	15.99	300.2	"	2 runs, 1/2° difference, higher value given.
XXXVI	4.891	13.493	26.94	322.5	"	2 runs, 2° difference, higher value given.

Thermometers

T-1; Taylor 7A297924, nitrogen-filled mercury thermometer.
H; Hiergesell Bros. 3389, nitrogen-filled mercury thermometer.
T-2; Taylor 7A553812, nitrogen-filled mercury thermometer.

Pt (1,3); platinum resistance thermometer, average of the first and third calibrations.
Pt (3); platinum resistance thermometer, third calibration.
Pt (4); redesigned furnace; platinum resistance thermometer, fourth calibration; average of reading in holes J and K.

* These runs were made before the window was lagged with magnesia. A correction which was found for tube X-I by running it before and after installing the magnesia was applied to the results found to give the temperatures listed.

Analytical Runs—General Method

There is a great diversity of opinion among those who have worked on the system gold-mercury as to what compounds are formed. Therefore, in order to throw light on the nature of the crystals that separate from a saturated solution of gold in mercury, it was decided to attempt to determine the composition of the solid phase in equilibrium with the saturated solution at a few temperatures in the region of this investigation.

The tube used is shown in Fig. 2. Mercury and an amount of gold more than enough to saturate the mercury at the temperature to be used were sealed in part A and the tube was evacuated through D and sealed off as the other tubes were. The tube was fastened to the shaft by means of clamps around part A and part C in such a manner that the shaft was just below part A of the tube in the position shown in Fig. 2. The tube was then rocked back and forth, over a large enough angle to transfer the materials from one end of A to the other, for a long time at the required temperature. When it was certain that the system had attained equilibrium the tube was inverted by turning the shaft 180 degrees, causing the contents of the tube to fall on the porous glass disc[16] B. The shaft was then quickly started revolving at about 2000 r.p.m. and the centrifugal force held the solid amalgam against the glass disc, forcing the liquid through the disc into part C of the tube. After whirling for one or two minutes the tube was cooled and the crystals left on the glass disc were removed, put in a weighed crucible, and analyzed by evaporating the mercury and reweighing. The part of the amalgam which had gone through the filter was also analyzed, since this gave a value for the solubility of gold in mercury as well as a check on whether any of the materials put into the tubes had been lost in removing from the tube or in analyzing.

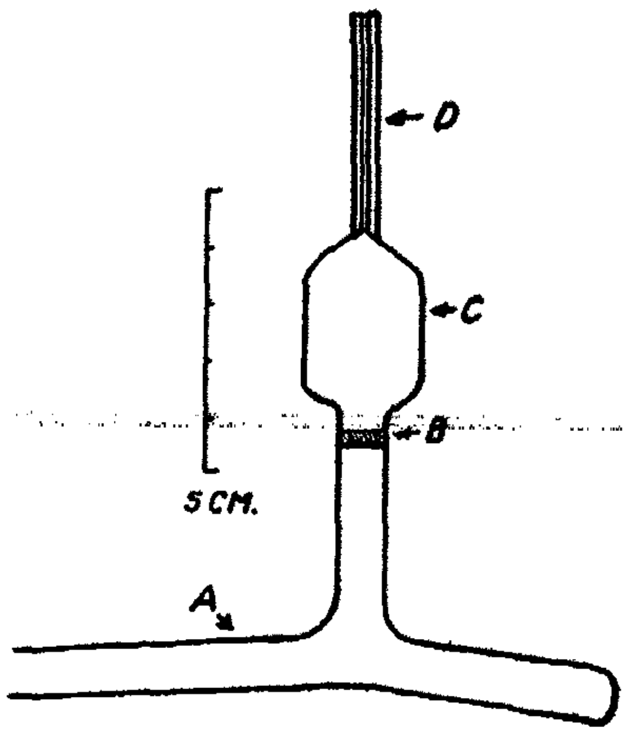

Fig. 2
Analytical Tube.

Description of the Redesigned Furnace

Since the furnace used in the synthetic runs did not have as good temperature uniformity as might be desired (there were variations of about a degree in the region of the tubes) it was redesigned to allow the tubes to be whirled, an effort being made at the same time to improve the uniformity. The rebuilt furnace is shown in Fig. 3. All the heating elements were removed from inside the copper shell A and six new nichrome ribbon elements were wound around the outside of the electrobestos which covered the copper. The elements were wound side by side as before but each one went around the furnace only five times. The ribbon had a resistance of about 2 ohms per foot and each element was about 19 feet long and developed about 320 watts on 120 volts a.c. Outside of the heating elements were a 1 1/2" layer of super-x and a 1 1/2" layer of 85% magnesia. Outside of all was a shell of galvanized sheet iron which held the magnesia and super-x in place. Following the design of Kracek[19] the fan was mounted on a tubular shaft and a second smaller shaft entered the furnace through the hole in the tube. The shaft B of 1" brass tubing was supported outside the furnace by two Smith self-aligning bearings entered through a hole in the left end. The shaft carried an 8" air fan C and was driven by an electric motor at about 3000 r.p.m. Through the brass tube was inserted a longer shaft D, 5/8" in diameter, which was supported outside the furnace by two Smith self-aligning bearings and inside by a third E. To this shaft the tubes were fastened by means of the clamps F and G. The shaft could either be rocked back and forth to stir the contents of the tubes or whirled to make the liquid filter through the porous glass discs. The counterweight H was adjusted so as to prevent excessive vibration when the tubes were being revolved. With the tubes held in the clamps as described the radius from the center of the shaft to the glass disc was about 4 cm. This distance was limited by the size of the furnace. When making synthetic runs the counterweight was removed and the collar holding the clamps G was put in its place. This brought the center of the tubes (Fig. 1) near the shaft and therefore kept the tubes always near the center of the furnace when they were being turned around to filter off the liquid. Keeping the tubes in one part of the furnace is essential to obtain uniformity of temperature as they are rotated. That this condition was not fulfilled and therefore the temperature may have varied in the analytical runs during whirling is not considered important since the precision of the analytical runs is considerably lower than that of the synthetic runs.

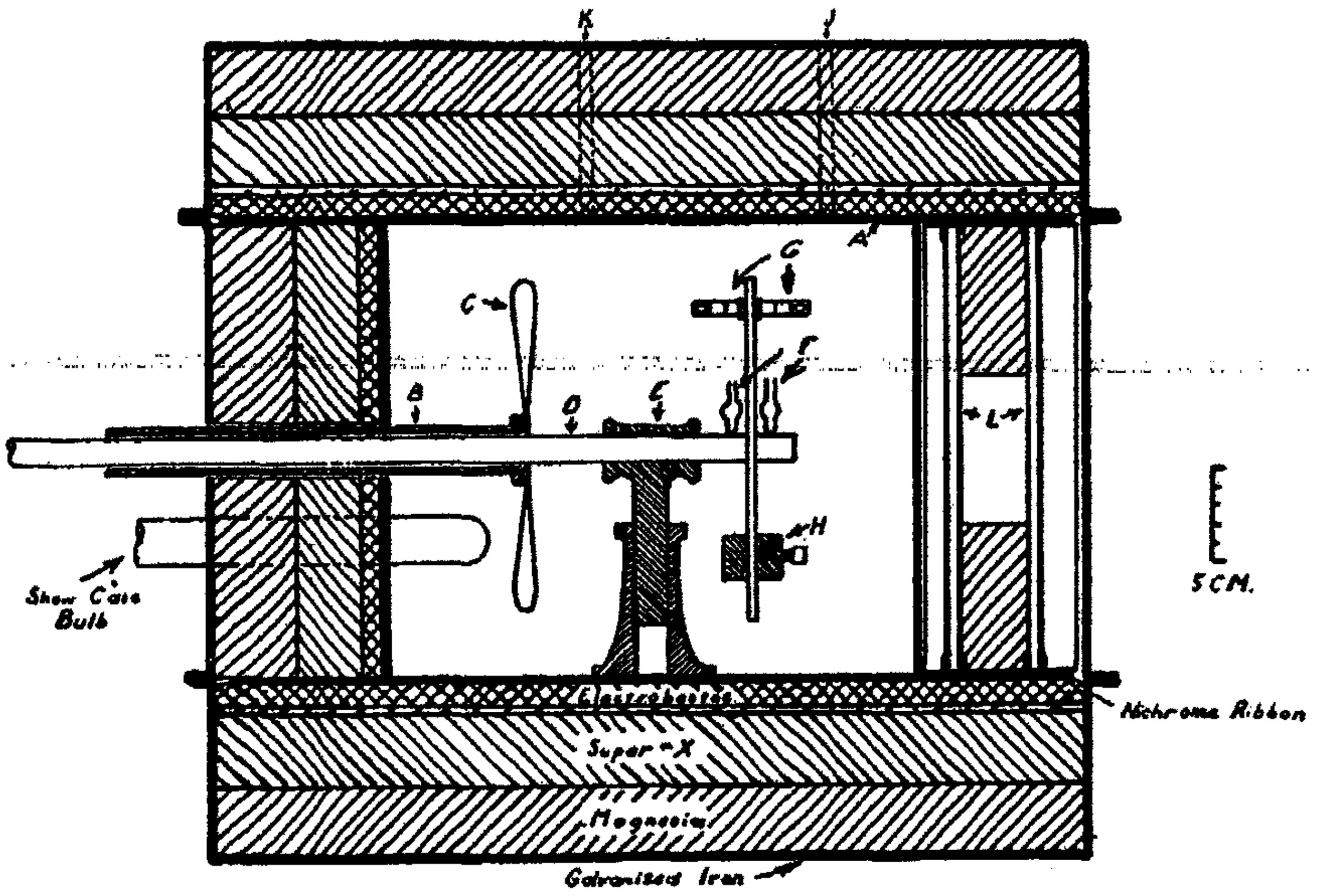

Fig. 3

The resistance thermometer was placed in either hole J or K and the sensitive coil of the thermometer was placed at the same level as that at which the amalgams were when the tubes were being rocked. The temperature recorded was generally an average of the temperatures indicated in the two holes since the tube was between them and the chief cause of temperature variation in the direction of the shaft was considered to be the loss of heat through the double plate glass window L. After use for some time this loss was cut down by filling the space between the glasses with magnesia except for a 3 1/2" hole in the center. The difference in temperature between points of equal level below holes J and K seemed to change also with the speed of the fan. For a number of runs the difference was found to be 2°. Vigorous stirring helps to correct differences in temperature but also may aggravate the condition by sucking in cold air if the rate of stirring is high enough and there are any cracks in the furnace walls. All the holes behind the fan were filled with furnace cement but the indication was that air entered in some way at least when the speed of the fan was great. With the thermometer in the same hole, the variation of temperature with height seemed to indicate that the center was the coolest part of the furnace and that the temperature increased toward the walls. Within the region occupied by the tubes the variation of temperature was probably not one degree. It had been hoped to obtain better uniformity than was found. It would appear that for much better uniformity than that obtained, a bath of some fluid other than air would have to be used.

Procedure in Analytical Runs with Gold and Mercury alone

In some of the analytical runs the equilibrium temperature was approached from the high side and in some from the low side. The temperature of the furnace was held at least within about 10° of the final temperature for from three hours to eight hours and usually it was held within 0.1° for an hour or more before the solid and liquid were separated by whirling. As the tubes cooled after filtering some mercury condensed on the inside of the outer walls in the parts of the tube on both sides of the glass disc. The amount condensed seemed more than the amount of mercury which would be expected to be in the vapor form in the tube and it was feared that the mercury might have vaporized from the mercury rich portion below the disc (part C Fig. 2) and passed through the disc to condense on the walls of part A and also on the solid crystals and so have changed the composition of the solid. In one run the bottoms of the tubes (parts C) were quickly cooled with water after whirling to prevent vaporization of mercury from that part of the tube and in other runs a coarse capillary was included in the tube between the porous disc and part C and this capillary was sealed off as soon as possible after the whirling. Since these procedures did not apparently change the amount of condensed mercury in part A, the mercury condensed on the outer walls of part A must either have been present in that part as vapor or have come from the solid phase, distilling to the walls, because they cooled first. Apparently, therefore, no error was introduced by mercury vapor passing through the porous glass disc during cooling.

The analysis of the gold-mercury mixtures was accomplished by heating them in porcelain or sillimanite crucibles in a current of air, thereby vaporizing the mercury. The greater portion was vaporized slowly at or below 300°C. to avoid spattering, and the temperature was then raised to about 500° to remove all but the last traces of the mercury. The last traces were then driven off by heating the crucibles with an oxygen-gas flame rather poor in oxygen, until the gold was just melted. The crucibles were then cooled in a desiccator and weighed. These weights, together with the weights before heating and the weights of the empty crucibles, give the compositions of the samples.

The contents of tubes XXIX and XXX were analyzed by this method and the resulting amounts of gold and mercury found checked the amounts put into the tube to within 1/5 of a part per thousand for both tubes. The results indicate that the method of analysis is more than accurate enough for the purpose. The weights taken and found are given in Table III.

TABLE III

Analysis of Knowns for Gold and Mercury

		Taken	Found	Error
XXIX	g.Au	4.4557	4.4560	high 0.3 mg.
	g.Hg	6.7276	6.7288	high 1.2 mg.
XXX	g.Au	8.8249	8.8161	high 1.2 mg.
	g.Hg	13.4995	13.4968	low 2.7 mg.

Analytical Runs using Third Component

The solid phase is however likely to retain a certain amount of the saturated solution which will not be separated from the solid by the centrifugal force employed and the presence of the solution will decrease the percentage of gold in the solid phase below the true value. The amount of solution remaining on the solid can be determined by a method mentioned by Bancroft[17] and also described and used by van Heteren,[18] namely the addition of a third component which will not be in the crystals but will be in the solution. Then from the amount of the third component found in the solid phase, the amount of solution retained can be calculated and so the true value for the composition of the crystals can be calculated.

The substance chosen as a third component must be present only in the liquid phase. If the component is not to be in the solid phase it must not form a solid solution with the solid phase nor may it form a compound which is stable at the temperature used. The only way possible to choose such an element is to suppose that a metal which does not form solid solutions in gold and does not form a stable compound with gold probably will not form solid solutions or compounds with the solid phase whatever it may be. Thallium[12a] is a metal which fulfills these requirements since pure gold separates from liquid gold-thallium solutions of concentrations up to 72% thallium and at all temperatures down to the eutectic which is 120°C. Lead[12b] is also of interest since pure gold separates from gold-lead solutions from 0 to 45% lead above 436°C, which is the temperature of decomposition of the compound Au_2Pb. Lead does not form solid solutions in gold and if the eutectic of the compound Au_2Pb with the solid phase of the gold-mercury system is at a temperature below 300°, the solid phase in equilibrium with solutions containing only small amounts of lead with gold and mercury at 300° would contain no lead.

In order to use this method it was necessary to develop a method of analyzing mixtures for the three metals used. A sample of thallium was obtained which was said to contain about 2% of carbon and seemed also to contain some volatile matter. Since it did not alloy properly with gold and mercury its use was abandoned. Lead from a certified Bureau of Standards sample, stated to contain less than 0.05% impurity, was used and knowns were prepared by heating the ternary systems in sealed glass tubes until they were completely fused. The knowns were then cooled and transferred from the tubes to weighed porcelain crucibles. The mercury was removed from the gold and lead by heating the crucibles for several hours at from 300° to 350°C, thus slowly vaporizing most of the mercury and avoiding spattering, and then continuing the heating at 550°C for several hours. It was necessary to use a non-oxidizing atmosphere (such as hydrogen) to prevent the formation of lead oxide which is more volatile than lead and would probably vaporize. Lead is not lost since its vapor pressure reaches 0.001 mm. of mercury only at 636°C.[12c]

The first method tried for removing the lead was to volatilize it from a porcelain crucible using an oxygen-gas flame. Upon heating with the flame the lead oxidized and while some of the oxide volatilized more of it fused into the porcelain and could not be removed. It was however found possible to get rid of all the lead by heating the gold-lead residue on a bone-ash cupel up to the melting point of gold. Here again the heating had to be done carefully to prevent spattering. The lead oxide formed during the heating was absorbed by the bone ash, leaving a button of pure gold. If the gold was heated very much above its melting point it volatilized but by heating just to the melting point good results were obtained. The data for two knowns analyzed in this way are given in Table IV.

TABLE IV

Analysis of Knowns for Gold, Mercury, and Lead

		Taken	Found	Error
I	g.Au	2.9537	2.9528	low 0.9 mg.
	g.Hg	1.0606	1.0584	low 2.2 mg.
	g.Pb	0.0254	0.0271	high 1.7 mg.
II	g.Au	2.1796	2.1808	high 1.2 mg.
	g.Hg	0.8464	0.8444	low 2.0 mg.
	g.Pb	0.1160	0.1161	high 0.1 mg.

Since the amount of lead present in the solid phase, which is used to calculate the amount of saturated solution left behind on the crystals, is small (15 to 20 mg. in our runs) a small absolute error in the determination of the amount of lead results in a large error in the calculated amount of solution left behind and therefore a sizable error in the corrected percentage of the solid phase. Thus for one tube it was calculated that a difference of one mg. in the amount of lead found in the solid phase would cause a difference of 3/4% in the calculated gold concentration of that phase. The percentages given for the composition of the solid should not therefore be considered any more precise than plus or minus one even if the assumption that the pure solid phase contains no lead is true. There is nothing, however, to indicate that this assumption is not true.

The runs in which lead was used were carried out in exactly the same manner as the earlier runs, except for the method of analysis. A check on the accuracy of the analyses was made by comparing the total amount of each constituent found in both phases with the amount put in the tube at the beginning. The greatest differences in the four tubes in which lead was used were as follows: for gold 19.6 mg. low, for mercury 23.3 mg. low, and for lead 9.4 mg. low. All of the results for gold and mercury were low but for lead half were high. The average errors (not regarding sign) were as follows: gold 17.5 mg., mercury 14.6 mg., and lead 4.0 mg. Despite the fact that the lead was determined by difference the absolute accuracy of its determination was greater than that for gold or mercury.

Analytical Runs—Results

The results of the analytical runs are given in Table V. Runs A through E using gold and mercury alone seem to show that at temperatures from 295 to 359°C the solid phase in equilibrium with saturated solutions of gold in mercury has a composition somewhere between 60 and 80% gold. There is no indication of a change in the composition of the solid phase in the temperature range investigated.

TABLE V

Gold and Mercury alone

Run no.	Temp. °C	Liquid Phase Au gms.	Liquid Phase Hg gms.	Liquid Phase At.% Au	Solid Phase Au gms.	Solid Phase Hg gms.	Solid Phase At.% Au
A-I[a]	307.9*	2.4561	9.6403	20.58	0.9608	0.9069	51.87
A-II[a]	do	2.1580	8.7699	20.01	2.0269	1.0632	65.98
B-I[b]	359.3*	2.9379	5.2585	36.24	2.5454	0.8701	74.84
B-II[b]	do	2.0289	3.4864	37.17	1.8300	0.8444	68.80
C-I[a]	359.2*	2.5896	4.1770	38.69	1.5241	1.0198	60.33
C-II[a]	do	1.7517	2.8032	38.87	1.0221	0.7196	59.10
D-I[c]	297.2*	2.0697	12.0023	14.92	1.1274	0.2305	83.27
D-I[c]	do	(2nd part of solid phase)			0.8300	0.5374	61.11
D-II[c]	do	0.6292	3.4231	15.75	0.5895	0.1173	33.83
E-I[d]	295.8	1.0064	5.9344	14.71	1.1173	0.7003	61.88
E-II[d]	do	0.9598	5.8167	14.37	1.1556	0.3777	75.68

Gold, Mercury, and Lead

Run. no.	Temp. °C	Liquid Phase Au gms.	Liquid Phase Hg gms.	Liquid Phase Pb gms.	Solid Phase Au gms.	Solid Phase Hg gms.	Solid Phase Pb gms.	At.% Au Corrected
F-I[b]	317.1	2.5091	3.7221	0.5657	0.4319	0.2021	0.0146	77.89
(F-II[b]	do	2.0844	2.9922	0.5251	1.4024	0.2292	0.0179	91.4)
G-I[a]	317.1	1.9718	2.7920	0.5422	1.7271	0.6118	0.0162	76.25
G-II[a]	do	2.5216	3.6239	0.6941	2.0138	0.5730	0.0268	81.82
					Average (F-II out)			78.65
					Average deviation: 26.8			p.p.t.

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* See footnote to Table II.

[a] From high side.

[b] From low side.

[c] Some strips of gold were never dissolved.

[d] The shaft showed a tendency to stick which made the centrifuging poor.

Runs F and G using gold, mercury, and lead gave much more concordant results for the composition of the solid phase corrected for the amount of solution retained. If we leave out F—II (the deviation of which from the average of the other three is more than four times the average deviation of the other three) the results give an average value of 78.65 at.% with an average deviation of 26.8 parts per thousand which is about what might be expected from the precision of the analytical method.

Synthetic Runs with the Reconstructed Furnace

A number of runs of the synthetic type were also made with the reconstructed furnace as is indicated in Table II. The main difference in procedure caused by the change in the furnace was that in determining the solubility point the bath was adjusted so that the temperature was rising slowly and filtrations were made periodically rather than keeping the temperature constant at each tenth of a degree for several minutes and then moving up a tenth of a degree when it seemed clear there was solid left. The change in procedure was necessitated by the fact that the lag in the new furnace from the time the heat was increased until the temperature started to rise was of the order of ten minutes.

It happened regularly with a few tubes and once in a while with most of the rest that, after inverting the tube the liquid would not completely filter off through the capillary, leaving the solid behind. When some of the liquid remained above the capillary it was almost impossible to tell whether or not any solid was left. After the furnace had been changed so that the tubes could be whirled it was found that the last part of the liquid could be forced through the capillary by revolving the tubes. Since the whirling left the solid in a rather packed condition, which was moreover practically the same after each filtration, it was possible to estimate the solubility temperature from the amounts of solid left in the tube at two temperatures below the solubility point. These estimates speeded the accurate determination of the solubility point.

Some of the difficulties in applying the synthetic method of solubility determination to this system should be pointed out. The difficulties encountered if any mercury oxidizes have been mentioned. Any small foreign bodies in the tubes such as pieces of glass are also objectionable because they may get caught in the capillary and retard or entirely prevent filtration.

If any considerable number of fine crystals which pass through the capillary are present the solubility temperature determined will be too low. In runs made by the analytical method the systems are held for a long time at constant temperature and undoubtedly the crystals all grew to such a size that they would not pass through a capillary. Since the results of the synthetic method check those of Weiner[3] and of Mees[4] determined by the analytical method and since the present analytical results lie at lower rather than higher temperatures than the synthetic curve it does not seem probable that an error was introduced by fine crystals passing through the capillary.

If temperature differences exist in the parts of the furnace through which the tube passes as it is rotated, the possibility arises that parts of the tube may be at times hotter than other parts. It might then happen that by some particular manipulation of the tube the contents would be heated for a time enough to dissolve all the solid (when the amount of solid present is small) without any change having occurred in the temperature of the bath. If on subsequent cooling, which would result when the rocking was resumed, the system persisted in a supercooled liquid state, the result would be that the temperature found as the solubility point would be too low. The different results obtained in running the same tube on different days was attributed at least in part to this cause. For that reason the highest result was in general considered the nearest to the correct value.

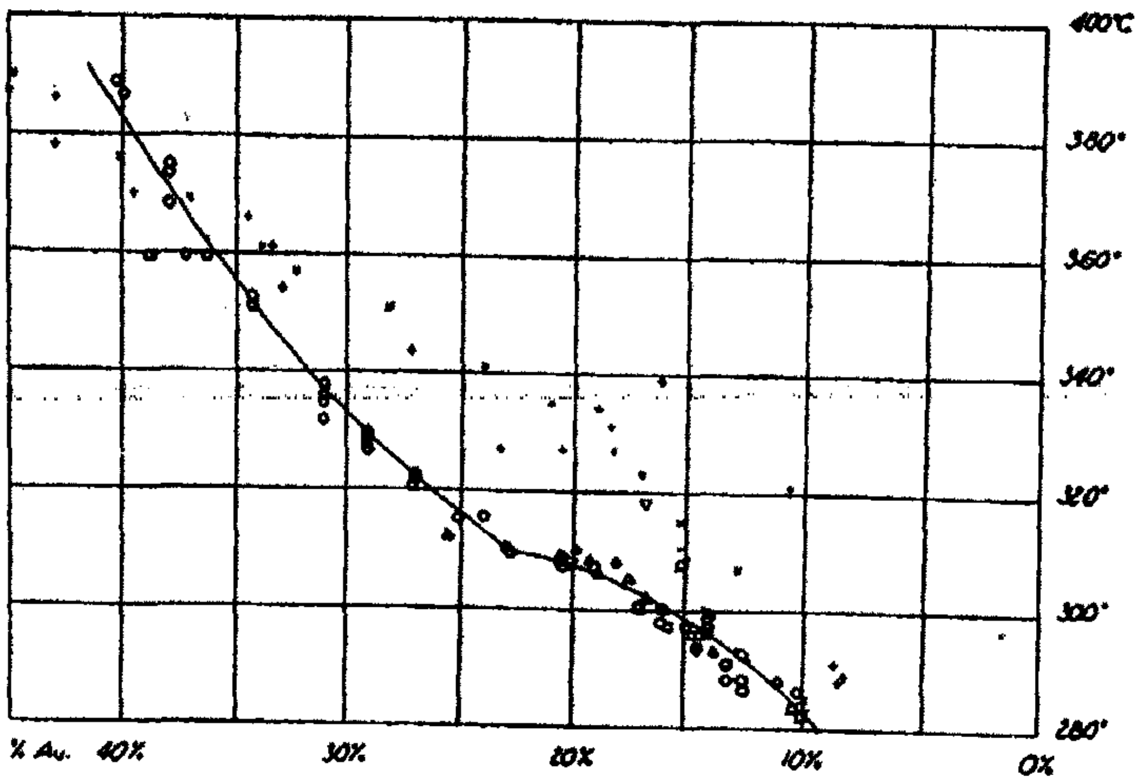

Fig. 4

⊙ Anderson, synthetic; □ same, analytical; ϕ Sunier and Mees; ♁ Sunier and Weiner; Δ Parravano; + Britton and McBain; × Plaksin; ▽ Eastman and Hildebrand.

Discussion of Results—Solubility

The solubility of gold in mercury has been determined at temperatures up to 300°C in this laboratory by Weiner[3] and by Mees.[4] The results of the present investigation below 300° agree well with theirs, as can be seen on the graph Fig. 4. Another set of determinations which are in substantial agreement with those found in this laboratory are those of Parravano,[6] determined by the cooling curve method. The solubility over the entire range covered has also been determined by Britton and McBain[8] and by Plaksin.[11]

Britton and McBain made their determinations by an analytical method. They find a maximum in the solubility curve at about 14.3% of which there is no indication in the present results. At that concentration their curve is 40° higher than the curve of Fig. 4. Plaksin found the solubility by the method of cooling curves. His solubility curve does not have a maximum but is a smooth curve lying partly above and partly below that of Britton and McBain. Both the curves of Britton and McBain and of Plaksin lie above the curve of Fig. 4 from 280° to about 370° and below at higher temperatures.

Eastman and Hildebrand[5] investigated the vapor pressures of solutions of gold in mercury at about 318°C and found that the vapor pressure decreases as the concentration of gold increases up to 16.8 at.% gold and thereafter remains constant. This means that a saturated solution of gold in mercury at 318° contains 16.8 at.% gold. This value agrees best with Plaksin's results, lying more than 10° higher than the curve of Fig. 4.

The greatest difference in temperature for a given composition in the present data is about 6° and the average deviation of the synthetic points from the curve is 2.2°C. The nature and precision of the data allow some freedom in locating the break in the curve. The temperature of the break, which is the temperature of some change in the solid phase, is to be considered accurate only to within plus or minus 10°.

Discussion of Results—Compounds existing

Parravano[6] investigated the gold-mercury system below 312° by the method of cooling curves and found a compound Au_2Hg_3 (40 at.% Au) which decomposes at about 100°C forming Au_3Hg (75 at.% Au). Braley and Schneider[7] working also by the method of cooling curves found the compounds $AuHg_4$ (20 at.% Au), Au_2Hg_5 (28.6 at.% Au), and AuHg (66.7 at.% Au). They found a thermal effect at about 100° as Parravano did and also one at about 380°. If we assume that their rate of cooling was much too rapid to allow equilibrium to be established (they state that the longest arrest was 180 sec.) their results giving a maximum in the liquidus curve might possibly be interpreted as being due to a thermal effect at about 300°C. The results given by Braley and Schneider for the liquidus curve for low gold concentrations are not even in the right neighborhood. There is evidently something very wrong with their work and the existence of the compounds reported by them is not well established.

Britton and McBain[8] determined the solubility curve for gold in mercury by an analytical method and found a maximum in the curve at about 14.3 at.% Au which led them to postulate the compound $AuHg_6$ with a congruent melting point of 342°C.

Plaksin[11] by the method of cooling curves in a research apparently of considerably greater precision than either that of Braley and Schneider or of Parravano found the compounds $AuHg_2$ (33.3 at.% Au) and Au_2Hg (66.7 at.% Au). He states that $AuHg_2$ has transition points at −36° and at 122° and decomposes into Au_2Hg and a liquid phase at 310°. Au_2Hg undergoes a polymorphic transformation at 402° and breaks up into a liquid solution of gold in mercury and a saturated solid solution of Au_2Hg in gold at 420°. This means that there are thermal effects at 420°, 402°, 310°, 122°, and at −36°. These are to be compared with the effects found by Parravano and by Braley and Schneider at 100° and by the latter authors also at 380° and possibly at 300°. The break in the solubility curve found in this investigation at about 310° is also an indication that there is at that temperature a change of some kind in the solid phase involving a heat change. Plaksin confirmed his conclusions by metallographic methods.

Biltz and Meyer[9] investigated the vapor pressures of gold-rich amalgams of varying compositions at three temperatures, 253°, 300°, and 315°. They interpreted their results as showing the existence, in addition to the solid solution in pure gold upon which all investigators agree, of a solid solution of compositions from 75.6 to 79.3 at.% Au. This would seem to necessitate the existence of a compound in that composition range, the simplest formula for which would be Au_7Hg_2. If the lowest gold concentration were 75.0% instead of 75.6% the probability would be that the compound Au_3Hg (75.0 at.% Au) exists and forms solid solutions with gold but not with any constituent containing less than 75% Au. Fixing the limit of the solid solution range appears to depend on locating the point of inflection of the vapor pressure-composition curve and therefore might be wrong by a small amount. Biltz and Meyer further state that mixtures having less than 75% Au have the vapor pressure of pure mercury. This seems to disagree with the results of Eastman and Hildebrand[5] who found that at 318°C the vapor pressure of a saturated solution of gold in mercury is only about 0.93 of the vapor pressure of pure mercury. Nevertheless the results of Biltz and Meyer may be interpreted as showing that between 253° and 315° only one compound of gold and mercury exists and that it has a composition between 75 and 80 at.% Au and forms a solid solution.

Pabst[10] investigated the gold-mercury system by the powder method of x-ray analysis. He found a hexagonal phase at about 75% Au which he believes is the same as the solid solution phase which Biltz and Meyer say exists between 75.6 and 79.3 at.% Au. He also found evidence of compounds existing at room temperature of the formulas Au_2Hg_3 (40 at.% Au) and $AuHg_2$ (33.3 at.% Au). That the latter compound exists seems improbable since he states that by putting an amalgam of less than 33% Au in a leather bag and squeezing with a screw clamp, mercury is removed to such an extent that the compound Au_2Hg_3 is formed. With regard to the usefulness of the x-ray analysis method it is of interest that in the related system silver-mercury Murphy[20] found that this method gave results when no conclusions could be drawn from photomicrographs and the cooling curve method failed because of the slowness of attainment of equilibrium.

The present results as well as those of Biltz and Meyer, of Pabst, and of Parravano indicate that the gold rich compound formed is probably Au_3Hg instead of Au_2Hg as reported by Plaksin and by Braley and Schneider. Both the present investigators and Biltz and Meyer fail to find evidence of a second compound poorer in gold below 310°, the present work going down to 295° and that of Biltz and Meyer down to 253°. That a second compound is formed at lower temperatures seems likely but whether it is $AuHg_2$ as found by Plaksin or Au_2Hg_3 as reported by Parravano and by Pabst is not clear. The existence of more than two compounds in the system at room temperature or above does not seem probable.

A Suggested Phase Diagram for the System Au-Hg

Fig. 5 gives the phase diagram for gold and mercury constructed by Plaksin[11] and Fig. 6 presents a new phase diagram suggested for the same system. It is really an extension of the diagram constructed by Parravano[6] who gave the compounds shown but did not say anything about solid solution formation nor about anything in the region above 300°C. Parravano gave the temperature of decomposition of Au_2Hg_3 (40 at.% Au) as 100° but his individual values varied over more than 10°. The value of 122° used in Fig. 6 is the temperature given for a thermal effect by Plaksin[11] who, however, says that the effect is caused by an allotropic change in the compound $AuHg_2$ (33.3 at.% Au). That the compound reported by Parravano, Au_2Hg_3, is the one existing is supported by the results obtained by Pabst using the x-ray analysis method. The temperatures of the other thermal effects are those given by Plaksin and the one given at 310° is also indicated by the break in the curve of Fig. 4.

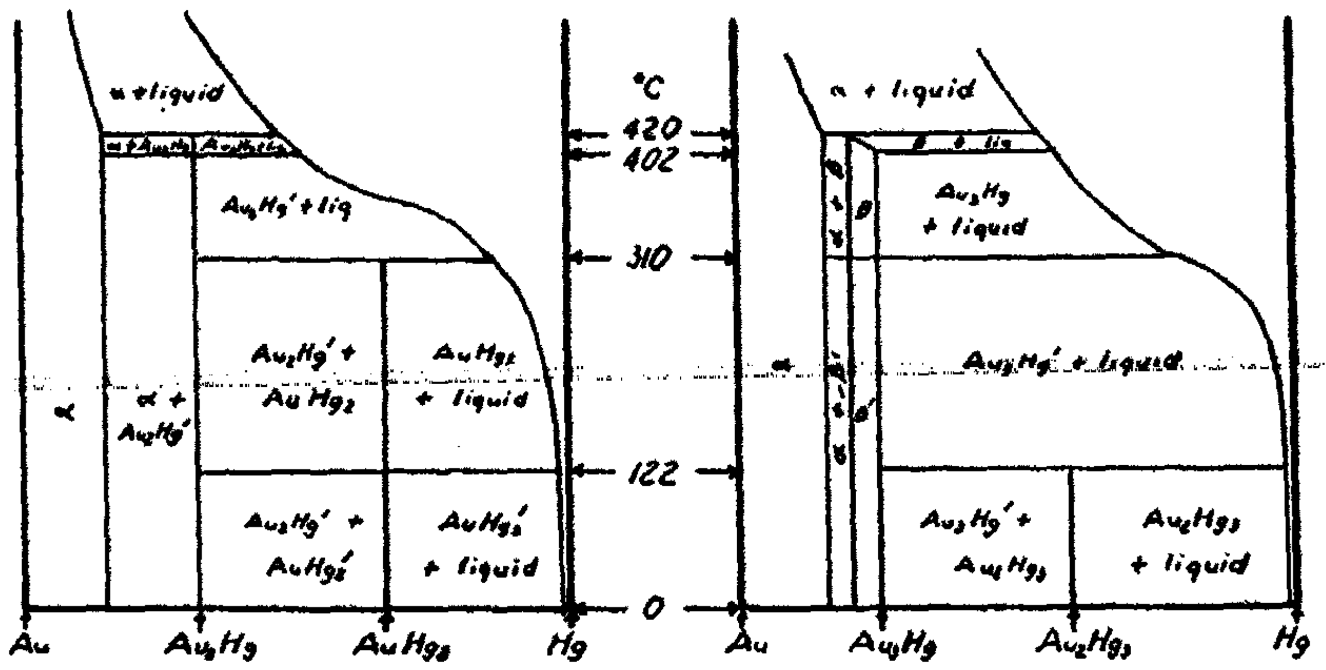

Fig. 5
According to Plaksin

Fig. 6
A Suggested Phase Diagram

Phase Diagrams of the System Au—Hg.

Fig. 6 also differs from Plaksin's phase diagram in showing the compound Au_3Hg and indicating that it dissolves gold to form the beta solid solution. The existence of the compound Au_3Hg (75 at.% Au) instead of that reported by Plaksin, Au_2Hg (66.7 at.% Au), is supported by the work of Parravano, of Biltz and Meyer,[9] and of Pabst[10] as well as by the results of the analytical runs as given in Table V. The thermal effect at 310°, which Plaksin interprets as caused by the decomposition of the compound $AuHg_2$, is shown as caused by an allotropic change of the compound Au_3Hg. This effect will therefore extend through all the regions in which the compound itself or the solid solution of gold in it (the beta solid solution) occurs. The temperature of the change must be constant through the two phase areas (alpha plus beta) and (Au_3Hg plus liq.) but would in general change in passing through the beta solid solution area instead of being constant as shown, since the transformation temperature would in general be a function of the gold concentration of the solid solution.

The transformation in the beta area probably would take place also over a range of temperature and the shape of the curves might have any of the forms found in the corresponding change from liquid solution to solid solution. It will be noticed that the phase diagram of Fig. 6 is in accord with the results of the analytical runs given in Table 5 in that no change in the composition of the solid phase in equilibrium with the saturated solutions is indicated at 310°. Plaksin's diagram demands that the composition change at that temperature from 33% Au to 67% Au. It is also evident that the two diagrams demand different values for the composition at which the cooling curve break at 310° is maximum. Fig. 5 has the maximum break come at 33.3 at.% corresponding to a complete change of solid and liquid into the compound $AuHg_2$, while Fig. 6 places it at 75 at.% at which composition the whole system, being the compound Au_3Hg, undergoes the polymorphic change.

The thermal effects at 402° and at 420° Plaksin's diagram shows are due, respectively, to a polymorphic transformation and the decomposition of the compound Au_2Hg. Fig. 6 shows that, starting with the compound Au_3Hg and heating, the decomposition of the solid phase into beta solid solution and liquid begins at 402° and continues gradually, with no invariant point, to 420°, where the remaining beta solid solution being now saturated with gold decomposes at constant temperature into saturated alpha solid solution and liquid. It will be noticed that, if the diagram is correct, when a sample is being cooled the change in the solid phase at 402° is not a discontinuous one accompanied by a heat change, which according to the phase rule must take place at constant temperature, as is the case at 420°, and at 310°, and at 120°. Rather the change in the solid phase, the beta solid solution, lies in the fact that at 402° its composition reaches that of the compound Au_3Hg at which value it ceases to change, thereafter remaining constant as the temperature is lowered. The break found in a cooling curve therefore would not be a horizontal line, but simply a change in slope such as occurs at the liquidus point. There is no experimental evidence which indicates that the break at 402° should be as shown in Fig. 6 rather than as shown in Fig. 5. The form of diagram shown in Fig. 6 is however, a possibility.

Plaksin's phase diagram, Fig. 5, rests on cooling curve and metallographic results. When using the cooling curve method and even more particularly when using the metallographic method it is important that equilibrium be attained in the process, otherwise the results can not in general be interpreted. Murphy[20] in his work with the system silver-mercury found with one sample that it was necessary to anneal for three days at 100°C in order that equilibrium be attained, as indicated by a maximum liberation of heat at the invariant point at 127°C. With another sample he found that the complete formation of the beta phase in a good crystalline form from the alpha phase and liquid required annealing at 100° for four weeks (as shown by photomicrographs). If the gold-mercury system is like the silver-mercury system in this respect it seems likely that to successfully analyze the system by these methods would require uncommon care.

Fig. 6 is to be considered as a phase diagram which seems to fit the results of Parravano, Biltz and Meyer, Pabst, and of the present investigation better than does the diagram given by Plaksin. The two highest singular points, however, are given only by the evidence of Plaksin whose work stands alone in the region except for the point at 380° advanced by Braley and Schneider.[7]

The present knowledge about the system gold-mercury can not be considered satisfactory. An independent determination of the liquidus curve above 300° would be valuable. More evidence as to what compounds exist and what their regions of stability are is to be desired. Additional carefully conducted thermal and microscopic experiments very likely would help solve the problem.

The writer wishes to express his thanks to Prof. Conley for his aid in the explanation of the work of Plaksin, and to acknowledge his indebtedness to Prof. Sunier, who has so charitably and inspiringly directed this investigation.

Summary

(1) The application of the synthetic method of solubility determination to a metallic system has been made. A form of solubility tube with a capillary filter has been developed which enables the disappearance of the solid phase to be detected when the solution is not transparent.

(2) Using this method 42 determinations of the solubility of gold in mercury have been made between 280° and 400°C.

(3) The uniformity of temperature in an air bath at temperatures of 300° to 400°C has been investigated and the variations of temperature in the center part found to be about one degree.

(4) Methods of analysis have been found for mixtures of gold, mercury, and lead.

(5) A tube has been designed in which the liquid phase is separated from the solid by filtering through a porous glass disc. The tube is mounted on a shaft and whirled and the centrifugal force causes the filtering. Using this tube ten analytical runs have been made with gold and mercury between 295° and 360°C in which the solid and liquid phases were separated and the composition of each determined.

(6) Four similar analytical runs have been made in which some lead was added to the gold and mercury and, by assuming that all the lead found in the solid phase represents an equivalent amount of solution which has not been removed by the centrifugal force, a corrected composition of the solid phase has been calculated.

(7) The solubility results agree with the results of Sunier and Weiner, Sunier and Mees, and Parravano but do not agree well with those of Britton and McBain and of Plaksin. The solubility curve shows a break at about 310°C, at which temperature Plaksin also reports a thermal effect.

(8) The results found for the composition of the solid phase indicate that the gold-rich compound is probably Au_3Hg instead of Au_2Hg as found by

Plaksin. A suggested phase diagram is given which seems to agree with the results of Parravano, Biltz and Meyer, Pabst, and the present work better than does the phase diagram given by Plaksin.

References cited

The system gold-mercury

[1] Sunier and Gramkee: J. Am. Chem. Soc., **51**, 1703 (1929).
[2] Sunier and White: J. Am. Chem. Soc., **52**, 1842 (1930).
[3] Sunier and Weiner: J. Am. Chem. Soc., **53**, 1714 (1931).
[4] Sunier and Mees: Unpublished work.
[5] Eastman and Hildebrand: J. Am. Chem. Soc., **36**, 2020 (1914).
[6] Parravano: Gazz., **48** II, 123 (1918).
[7] Braley and Schneider: J. Am. Chem. Soc., **43**, 740 (1921).
[8] Britton and McBain: J. Am. Chem. Soc., **48**, 593 (1926).
[9] Biltz and Meyer: Z. anorg. allgem. Chem., **176**, 23 (1928).
[10] Pabst: Z. physik. Chem., **3B**, 443 (1929).
[11] Plaksin: J. Russ. Phys.-Chem. Soc., **61**, 521 (1929).

Other references

[12a] Int. Crit. Tables, **2**, 426 (1927).
[12b] Ibid., **2**, 414 (1927).
[12c] Ibid., **3**, 205 (1928).
[13] Foote, Fairchild, and Harrison: "Pyrometric Practice," Bur. Standards Tech. Paper, No. 170.
[14] Mueller and Burgess: "Standardization of the Sulfur Boiling Point," Bur. Standards Scient. Paper, No. 339.
[15] Glazebrook: "Dictionary of Applied Physics," I, 693 (1929).
[16] Bruce and Bent: J. Am. Chem. Soc., **53**, 990 (1931).
[17] Bancroft: J. Phys. Chem., **6**, 178 (1902).
[18] Van Heteren: Z. anorg. Chem., **42**, 129 (1904).
[19] Kracek: J. Am. Chem. Soc., **53**, 2609 (1931).
[20] Murphy: J. Inst. Metals, **46**, 507 (1931).

THE DIFFUSION OF SODIUM CHLORIDE IN AQUEOUS SOLUTIONS

BY L. J. BURRAGE

I. Introduction

The main object of the present investigation was to test the accuracy with which the diffusion coefficients of electrolytes could be measured as a preliminary to work on the diffusion of mixtures. Comparison was made with the results of Öholm, which form the most accurate and extensive work on the subject so far available. The experimental comparison was carried out on sodium chloride, partly in order to ascertain whether there was a definite minimum in the diffusion coefficient-concentration curve similar to those found in the cases of HCl, KCl and LiCl. Whereas Öholm[1] found such minima to be well marked with these electrolytes, the curve for sodium chloride was practically linear between 1 M and 6 M, and parallel to the concentration axis, exhibiting no upward movement. Its course in this concentration region was, however, determined by two points only, at 2.8 M and 5.5 M, and these are scarcely sufficient for so large a concentration range. In the experiments recorded below the diffusion coefficient has been determined for six solutions falling within the same range; the curve can consequently be drawn with greater accuracy. Figures have also been obtained for the diffusion coefficient of 0.1 M HCl in water and these have been made use of in a later paper where experiments on the rate of diffusion of 0.1 M HCl in solutions of alkali metal halides are described.

II. Experimental

An examination of the previous workers' methods and the difficulties which they experienced, shows that there are three important factors which must be taken into account to ensure the success of the practical work.

(a) Temperature Variation.

(b) Vibration Effects.

(c) Mixing during the filling or emptying of the apparatus.

Although, strictly speaking, these three factors come under the one category, since they all cause a false movement of the diffusing substance, it will be advantageous to consider them separately and to show what precautions have been observed to eliminate each.

(a) *Temperature Variation.*

A sudden rise or fall in the temperature tends to cause mixing of the solution even though that variation be comparatively small. A much greater temperature change will be far less serious if it takes place over a long period of time.

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[1] Z. physik. Chem., 50, 309 (1904).

In order to reduce this temperature effect to a minimum the experiments were carried out in a large vault, the door of which was felted to prevent any possibility of draughts. The vault itself had a fairly constant temperature, the maximum range covered being 12°C. in Winter to 18° in Summer.

The vault was lit by a single electric lamp which was used as little as possible during the experiments, an electric torch also being used when a strong local illumination was needed. The author remained in the vault for as short a time as possible during an experiment.

Inside this vault, whose only outlet was the door, was a large wooden box six feet in height and three feet square in cross-section, papered throughout internally and then painted, thus ensuring that all cracks and pinholes were covered. The parts of the box which opened were felted, both inside and outside, to prevent any slight external temperature change from being communicated. The box was provided with maximum and minimum thermometers.

(*b*) *Vibration Effects.*

In order to ensure that the vibration effects should be reduced to a minimum the following precautions were taken.

A vibration-free concrete block was constructed which stood about 3 feet above the ground level and was 2½ ft. square in cross-section. On this a stout wooden platform was securely bolted and so arranged as to be exactly horizontal.

This block was entirely encased by the constant temperature box to which reference has already been made. A portion of the front, the whole width and 18 inches high, was hinged at its lower end and thus allowed of access to the apparatus when emptying the latter. In order to avoid opening this door unnecessarily it was fitted with a long mica inspection window about 3 inches in height and running the whole length near the bottom.

(*c*) *Convection effects during the filling or emptying of the apparatus.*

A full description of the apparatus employed will be given at this point, as the design is a matter of importance when discussing convection effects during filling or emptying.

An examination of previous workers' apparatus has brought to notice the following points:

(1) That a very accurate control of the rate of flow of the liquid is necessary when filling or emptying, and

(2) That it is preferable to fill from above and empty from below.

The method employed in this investigation was based upon that of Graham as modified by Svedberg and Öholm. In general outline it consisted of placing a certain volume of solution below three times that volume of pure water and allowing diffusion to take place. At the close of the experiment the liquid was separated into four equal portions which were referred to as layers. These were analysed and the distribution of substance in each of the layers obtained.

The apparatus used in these experiments was essentially that of Öholm.[1] It consisted of a diffusion cylinder D about 20 cms. long and 3.5 cms. in cross-

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[1] Z. physik. Chem., 50, 309 (1904).

section, fitted with a ground glass joint at the upper end and a capillary tube, 1.5 mm. in diameter, with tap, at the lower. A is a pipette of about 20 ccs. capacity between the marks x and y, and fitted with taps above and below these points. Below the lower tap was a ground glass joint B, which fitted into the diffusion cylinder. In this ground glass joint there was a small hole C to allow of the free passage of air during filling or emptying.

The length of capillary tubing below E was 0.5 mm. in diameter. This was an improvement on previous designs, which did not employ a sufficiently narrow capillary. A second point of difference between this apparatus and that used by Öholm was the incorporation of a tap at the top of the pipette. This tap was so adjusted as to let air pass very slowly indeed. Both these improvements were designed to minimize mixing of the solution when the diffusing liquid first entered the diffusion cylinder. Unless very careful control is exercised when the lower tap is first turned the diffusing liquid will run down into the cylinder too rapidly and convection will result.

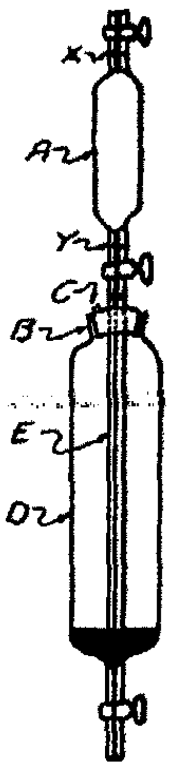

Fig. 1

(d) *Method of Operation.*

(1) *Filling.* Four pieces of apparatus were arranged side by side near the front of the box and mercury poured into each until it was 0.5 mm. — 1.0 mm. below the end of the pipette. Each pipette was then filled to the upper mark with distilled water placed in the apparatus, and allowed to run in until the liquid reached the lower mark. This was repeated twice. The diffusion cylinders were now corked and the pipettes put on a stand at the back of the box, which was closed and left for about 24 hours to allow of temperature equalisation.

Each pipette was then rinsed out with the solution whose diffusion coefficient was about to be determined, filled to the top mark, the stem being carefully dried with a dry cloth, and inserted in the apparatus. The door of the box was closed and the apparatus left for 3 hours to allow the disturbing effects of slight change of temperature, due to opening the door of the box, and liquid disturbances, caused by the withdrawal of the pipette, to disappear.

After a three-hour interval the door of the box was opened and the lower tap turned very slowly, the time being simultaneously noted, for diffusion starts from this moment. The speed of running-in was such that the total 20 ccs. should take about 2 hours. The rate was noted by the movement of the liquid column, observation being made through the upper of the mica windows. When the liquid had reached the lower mark the tap was turned and the door of the box closed. The vault was not entered again until the time for the withdrawal of the liquid had arrived. The length of a single run varied from case to case, but generally fell between one and seven days.

(2) *Withdrawal of the Liquid.* A narrow platform, fitted inside the box, ran parallel to the front, underneath the exit tubes at the bottom of each piece of apparatus. It was attached to the sides of the box, was quite independent

of the concrete block, and served as a tray to carry the flasks which were filled with liquid during emptying.

The liquid was drawn off into flasks of similar design to those used by Öholm, each one having a graduation mark on the neck corresponding to the volume of the pipette, between the marks x and y. In this way the liquid column could be separated into four equal portions, which were subsequently analysed.

The time was noted when each flask was filled, the period of diffusion being counted up to this point. It was most essential that the four layers should be separated as accurately as possible, since a very slight error at this point caused a large variation in the determined value of the diffusion coefficient.

The rate at which the withdrawal of the liquid was carried out was approximately 1 cc. per 10 mins., although considerably longer times have been taken in some cases.

(e) Materials employed.

The following chemicals were involved in this investigation:—

(1) Potassium and Sodium Chlorides. These were of A.R. quality and were used as such after heating strongly until all decrepitation had ceased.

(2) Hydrochloric Acid. Analytically pure acid was distilled under constant boiling conditions. This was then diluted until a concentration of exactly 0.1 M was obtained.

(3) Lithium Chloride. This was not obtainable as A.R. quality. The impurities, other than water, were, however, only a few hundredths of 1%, the chief being ferric chloride.

(f) Calibration of the Apparatus.

The calibration of each portion of the apparatus was carried out with water, by weighing in the case of the pipette and volume measurements for the cylinder.

For the success of the experiments it is essential that the diffusion column should be as nearly as possible of constant cross-section. This means that the diffusion cylinder must be of constant cross-section as must also be the external dimensions of the capillary of the pipette.

The cylinder was calibrated in the following manner. It was set up in the stand, as for an experiment, mercury being run in until there was about a millimetre gap between this and the end of the pipette. The height of this mercury level was read off, the measurements being made to 1/100 mm. by a cathetometer. A known volume of water – 9.94 ccs. – was then added and the level of the water measured with the pipette in position and when it had been removed. This was carried out eight times successively. The results showed that in every case, the condition of constancy of cross-section was sufficiently fulfilled.

III. Results

The diffusion coefficient has been calculated for each of the four layers from the tables of Kawalki and Stefan.[1] In Table I a few results are given showing the agreement between the coefficients for the four layers for sodium chloride solutions.

The vertical columns have the following significance:—

1. Concentration of sodium chloride.
2. Temperature of experiment.
3. The Diffusion coefficient for the lowest layer.
4. The Diffusion coefficient for the next layer and similarly for 5 and 6.
7. The average diffusion coefficient of all four layers. Each horizontal set of figures shows the complete results for one single experiment.

TABLE I

1 Conc.	2 T	3 K_1	4 K_2	5 K_3	6 K_4	7 *av* K
0.498 M.	13.6°	0.936	0.931	0.933	0.932	0.933
		0.937	0.917	0.948	0.945	0.937
		0.931	0.943	0.938	0.930	0.935
		0.935	0.946	0.943	0.927	0.938
5.810 M.	13.5°	0.952	0.945	0.953	0.949	0.950
		0.954	0.960	0.952	0.949	0.954
		0.951	0.952	0.952	0.946	0.950
		0.954	0.955	0.952	0.955	0.952

Table II comprises the full results and the symbols have the following significance.

M. Weight molality.

A. Apparatus used.

T. The temperature of the experiment °C.

Δt. The extreme temperature variation.

K. The average diffusion coefficient for the four layers.

K^1. The average diffusion coefficient for a given concentration at a definite temperature.

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[1] Wied. Ann., 52, 166 (1894).

TABLE II

M	A	T	Δt	K	K^1
0.1012	A	14.7	− .7	0.989	
	B	14.7	− .7	0.989	
	E	14.7	− .7	0.977	
	F	14.7	− .7	0.990	0.986
0.198	D	13.6	− .5	0.936	
	A	13.6	− .5	0.952	0.944
	C	14.4	− .5	0.969	
	F	14.4	− .5	0.964	
	B	14.4	− .5	0.970	0.968
0.498	D	13.6	− .2	0.933	
	F	13.6	− .2	0.937	
	A	13.6	− .3	0.935	
	B	13.6	− .3	0.938	0.936
1.005	C	13.6	− .3	0.927	
	F	13.6	− .3	0.926	
	B	13.6	± .0	0.929	0.927
	A	13.0	± .0	0.912	0.912
1.501	A	13.7	− .3	0.930	
	D	13.7	− .3	0.928	
	C	13.7	− .3	0.937	
	B	13.7	− .3	0.926	0.930
2.072	D	15.0	+ .4	0.972	
	E	15.0	+ .4	0.974	
	F	15.0	+ .4	0.954	
	A	15.0	− .6	0.992	0.973
	D	12.8	+ .1	0.897	
	F	12.8	+ .1	0.913	0.905
2.936	C	13.5	± .0	0.917	
	D	13.5	± .0	0.918	0.918
	A	13.8	+ .1	0.954	
	C	13.8	+ .1	0.947	0.950
4.259	D	13.3	+ .3	0.930	
	F	13.3	+ .3	0.920	
	C	13.3	+ .3	0.947	
	B	13.3	+ .3	0.925	0.930

Table II (continued)

M	A	T	Δt	K	K'
5.503	A	16.0	+ .3	1.026	1.026
	B	17.0	+ .6	1.075	1.075
	D	13.3	+ .05	0.940	
	F	13.3	+ .05	0.939	0.940
5.810	A	13.5	± .0	0.950	
	B	13.5	± .0	0.954	
	F	13.5	± .0	0.950	
	C	13.5	± .0	0.954	0.952
		Hydrochloric Acid			
0.1004	B	16.2	− .1	2.153	
	A	16.2	+ .3	2.157	
	B	16.2	+ .3	2.156	
	C	16.2	+ .5	2.148	2.153
	F	16.6	− .3	2.166	2.166

The variation in the temperature during the course of the experiment (Δt) only amounted to 0.1 − 0.2°C., the increase above this value being caused by the opening of the box at the close of the experiment, thereby exposing the apparatus to the change in the temperature of the vault. The Δt values quoted in the table represent the change which had occurred at the close of each experiment and that amount due to the opening of the box cannot affect the result to any serious extent as the diffusion had already proceeded for a period varying from 1 to 7 days, and the gradient must be small, hence there is little danger of any sudden connection effect due to this cause, since it only occurs during the withdrawal of the liquid.

IV. Discussion

Discussion of Sources of Errors affecting the Results.

(a) The first possibility is that the amount of diffusing substance in the column may be increased during a run by diffusion out of the end of the pipette. This, however, does not take place since the lowest section of the bottom layer in the diffusion column does not change in concentration during the course of the experiment, and there is therefore no tendency for the pipette contents to diffuse outwards. However, if any did diffuse, it would not cause serious error since the volume of liquid contained in the pipette below the lower tap is exceedingly small.

(b) It will be noted that the value of K derived from the second layer of an experiment sometimes appears high. This is undoubtedly due to a very slight amount of mixing. A reference to Kawalki's figures will show how serious is the effect of a slight error in the determination of the amount of diffusing substance in this particular layer. There will be seen that the value of v^1, the amount of substance expressed as parts per 10,000, for the second layer very slowly increases and then falls just as slowly. This gives a very flat curve corresponding to a large range of x values, where $x = h'^2/KT = \frac{1}{4}$ height of a layer squared, divided by the diffusion coefficient multiplied by the time. It is thus easy to see that a very slight error in v' may give rise to a very serious error in the value of x and thus cause the value of K to be somewhat inaccurate.

(c) In some cases the value of the K for the fourth layer is somewhat uncertain. This happens when the experiment has only proceeded for a short space of time and there is an insufficient amount of diffusing substance in the top layer to give a really accurate analysis.

Comparison of Results at 18°

The results in Table II have been calculated to 18°C. by means of the temperature coefficients given by Öholm[1] and these final figures are collected in Table III together with those obtained by Öholm. Fig. 2 contains the data (circles) for NaCl plotted in the form of diffusion coefficient against molality. Öholm's data are shown by crosses.

TABLE III

Substance	M	K 18°	Öholm K 18°
NaCl	0.101	1.094	1.117
	0.198	1.086	1.089
	0.498	1.078	1.077
	1.005	1.069	1.074
	1.501	1.067	—
	2.072	1.071	—
	2.936	1.074	1.064
	4.259	1.083	—
	5.503	1.097	1.065
	5.810	1.100	—
HCl	0.100	2.227	2.229

Agreement with Öholm is seen to be moderate throughout the whole concentration range. In contrast to his results, however, the present curve shows a distinct minimum at a concentration of 1.5 M.

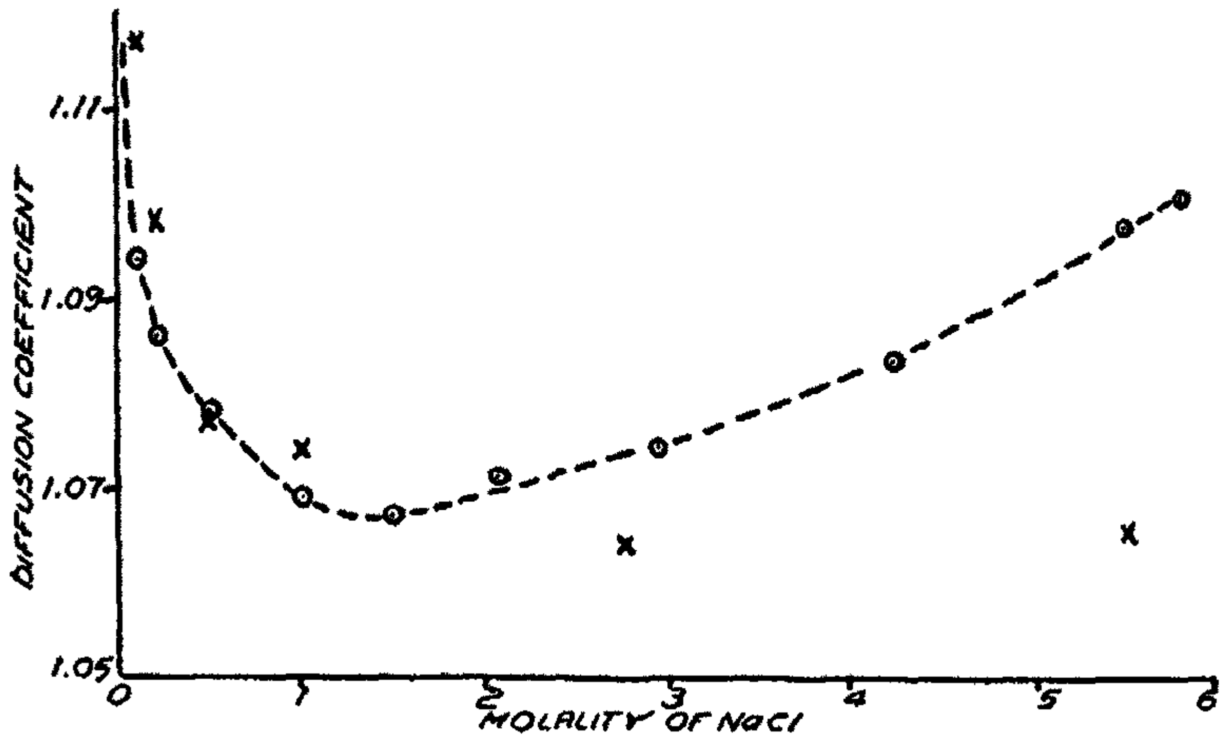

FIG. 2

Summary

I. A detailed account has been given of the precautions taken to prevent vibration and mixing.

II. The diffusion coefficient of NaCl has been measured over a large concentration range.

III. The diffusion coefficient of 0.1 M HCl has been measured.

IV. Comparisons have been made with existing data.

The author desires to express his thanks to Prof. A. J. Allmand, under whose direction this work has been carried out.

King's College,
University of London.
March 17, 1932.

ELECTRODEPOSITED ϵ-BRASS

BY H. KERSTEN* AND JOSEPH MAAS†

Introduction

The crystal structure of brass made by fusing together zinc and copper has been the subject of a number of investigations[1] which have shown that such brass probably has five different structures (known as α, β, γ, ϵ, and η), all stable at room temperature.

Alloys of zinc and copper have been electrodeposited from mixtures of their cyanides dissolved in a solution of potassium or sodium cyanide, since 1841.[2] It has recently been shown that α-brass having a structure agreeing with that of a fused alloy of like composition may be deposited from such a solution.[3] This paper shows that ϵ-brass, agreeing reasonably well in composition and structure with fused ϵ-brass may also be deposited from a cyanide bath.

Experimental

The electrolysis was carried on in a one-liter beaker with stainless steel anode and cathode, each 5 × 10 cm in size, 5 cm apart. The sides of the anode and cathode not facing each other were covered with a thick sheet of celluloid so that no current could flow from the back of the anode or to the back of the cathode. Stainless steel was used as an anode because it was practically insoluble in the electrolyte and as a cathode because the deposit did not adhere well and could be stripped for analysis.

A bath having the following composition was made:

Zinc cyanide	40 gm,
Sodium cyanide	50 gm,
Sodium carbonate (anhydrous)	30 gm,
Water, to make	1 liter

To this was added small quantities of copper cyanide to determine a region in which the ϵ-brass could be deposited. A new bath was used for each sample plated. For all the experiments the current density was held at 2 amperes per square decimeter and the bath temperature at 50°C.

The x-rays were supplied by a gas tube[4] having an iron target. The samples were clamped in the reflection spectrograph[5] shown in Fig. 1, in which the x-rays, after passing through the slits in the tube at the left, strike the

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sample clamped at the center of the ring, diffract into smaller beams, and blacken a photographic film in a paper envelope held on the circumference of the large ring by means of a rubber band.

FIG. 1
X-ray spectrograph.

Conclusions

The percentage of copper in the deposit from a number of baths made by adding copper cyanide to the bath given in a previous paragraph is given in Table I.

TABLE I

Bath number	Gm of CuCN in the bath	Percentage of copper in the deposit	Bath number	Gm of CuCN in the bath	Percentage of copper in the deposit
1	0.75	5.9	5	1.70	18.7
2	1.25	9.4	6	1.70	21.4
3	1.50	11.4	7	1.80	25.1
4	1.50	19.6	8	2.00	20.5

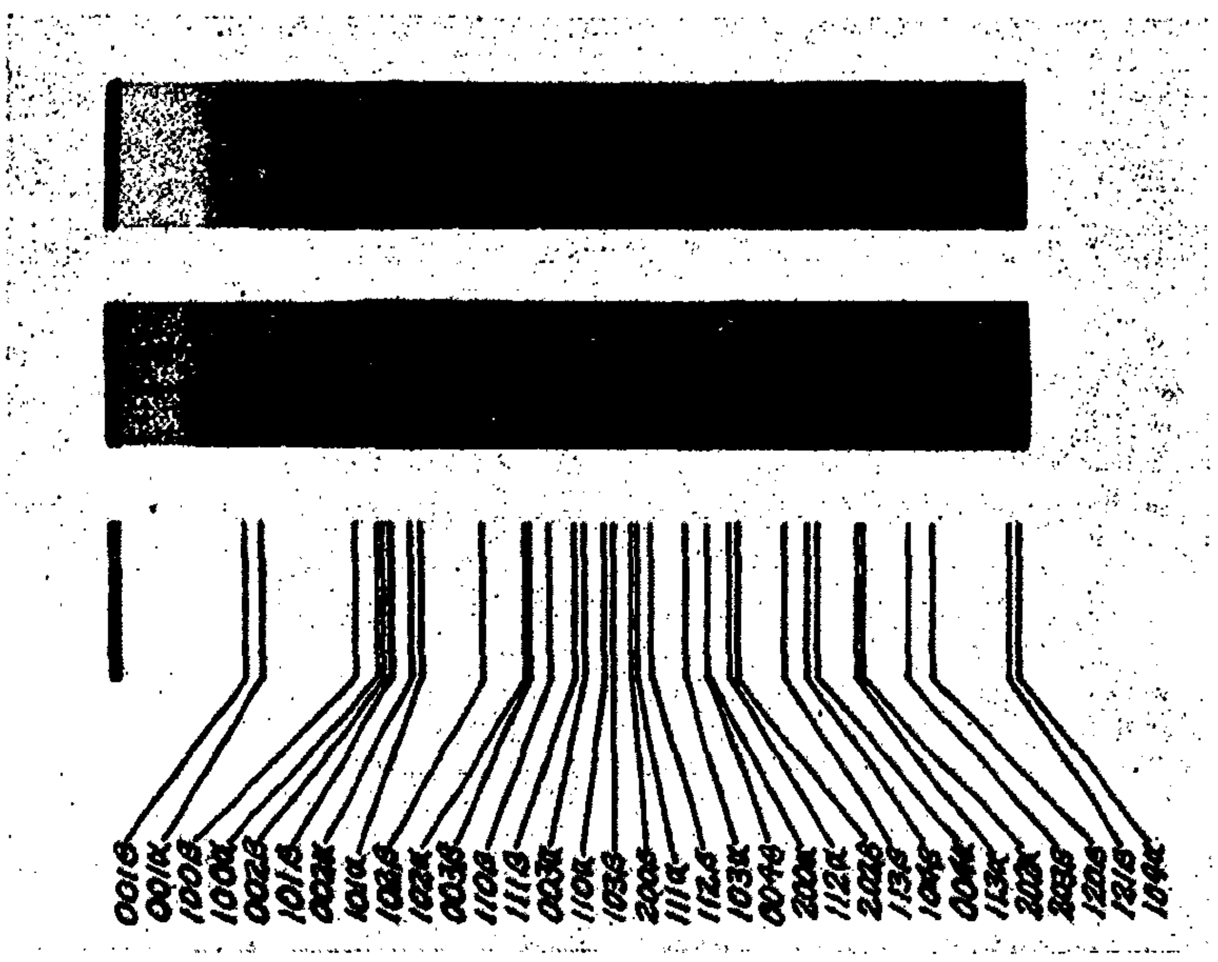

FIG. 2
Electrodeposited ε-brass compared with fused ε-brass.
Top: Electrodeposited sample containing 18.7% copper.
Middle: Fused sample containing 16.13% copper.
Bottom: Computed position of the lines for 19.7% copper.

Samples 3, 4, 5 and 6 showed the ϵ-structure. Fig. 2 shows the reflection photograph for sample 5 compared with fused ϵ-brass of nearly the same composition and with the computed positions of the diffraction lines. The fused ϵ-brass was annealed for 9 days at 360°C, before the picture was taken.

It is evident that the two photographs show structures nearly the same. The electrodeposited sample did not give as sharp lines as the annealed fused sample. Some of the lines to be seen on the original negatives have been lost in the reproduction.

The authors wish to express their thanks to Dr. Earl F. Farnau for the loan of samples of fused brass of various compositions.

References

[1] References are given in Wyckoff: "The Structure of Crystals," 2nd. Ed., 212 (1931).
[2] Gore: "The Art of Electro-Metallurgy," 278 (1877).
[3] Nakamura: Sci. Papers Inst. Phys. Chem. Research (Tokyo), 2, 287-92. (1925).
[4] Kersten: Rev. Sci. Inst., 3, 145-50. (1932).
[5] Kersten: Rev. Sci. Inst., 3, 384 (1932).

THE MECHANISM OF THE COAGULATION OF SOLS BY ELECTROLYTES

III. Exchange Adsorption during the Coagulation of Hydrous Oxide Sols

BY HARRY B. WEISER AND GEORGE R. GRAY

"Superequivalent" Displacement of Chloride

In recent communications[1] a method of procedure has been given which enables one to follow the displacement of chloride ion from the micelles of hydrous oxide sols during the stepwise addition of coagulating electrolyte. The method of titration previously described in detail consists essentially in mixing separate portions of sol, in which is suspended a small amount of calomel, with gradually increasing amounts of electrolyte and determining the chloride concentration potentiometrically after the mixture has stood in a thermostat for at least 48 hours to allow equilibrium conditions to be established. The significance of these observations and of the accompanying change in hydrogen ion concentration, for the precipitation process, have received detailed consideration in the earlier papers and will not be reviewed here.

Rabinowitsch[2] followed a much simpler method of titration: A definite portion of sol containing suspended calomel was placed in a beaker containing mercury, thus making one-half of a calomel concentration cell. The other half was a standard calomel electrode. The difference in potential was measured at the outset and shortly after each addition of a small amount of coagulating electrolyte. This procedure, which has the advantage of being more rapid than the one we adopted, leads to entirely different results as indicated by the two curves shown diagrammatically in Fig. 1. The lower curve *W* representing the displacement of chloride by sulfate was obtained with a hydrous Fe_2O_3 sol by the method used in this laboratory[3] while the upper curve *R* was obtained on a similar sol by Rabinowitsch and Kargan.[4] It will be noted that the former curve follows a smooth course well below the straight line showing the amount of sulfate added, while the initial portion of the Rabinowitsch curve lies above the sulfate line indicating that with low concentrations of coagulating agent, appreciably more chloride is displaced than corresponds to the sulfate added. Similar observations were made by Wassiliev and Rabinowitsch with Al_2O_3 sol but the phenomenon appeared less frequently than with Fe_2O_3 sol.

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[1] Weiser: J. Phys. Chem., 35, 1, 1368 (1931).

[2] Rabinowitsch and Kargan: Z. physik. Chem., 133, 203 (1928); Wassiliev and Rabinowitsch: Kolloid-Z., 56, 306 (1931).

[3] Weiser: J. Phys. Chem., 35, 16 (1931).

[4] Z. physik. Chem., 133, 203 (1928).

The so-called "superequivalent" displacement of chloride ion during the titration process was at first believed by us to be a delusion resulting from the slowness with which the calomel electrode comes to equilibrium. Rabinowitsch, on the other hand, is of the opinion that this factor is relatively unimportant and defends his experimental method. After stating that he has confirmed the experimental results reported by us, he writes:[1]

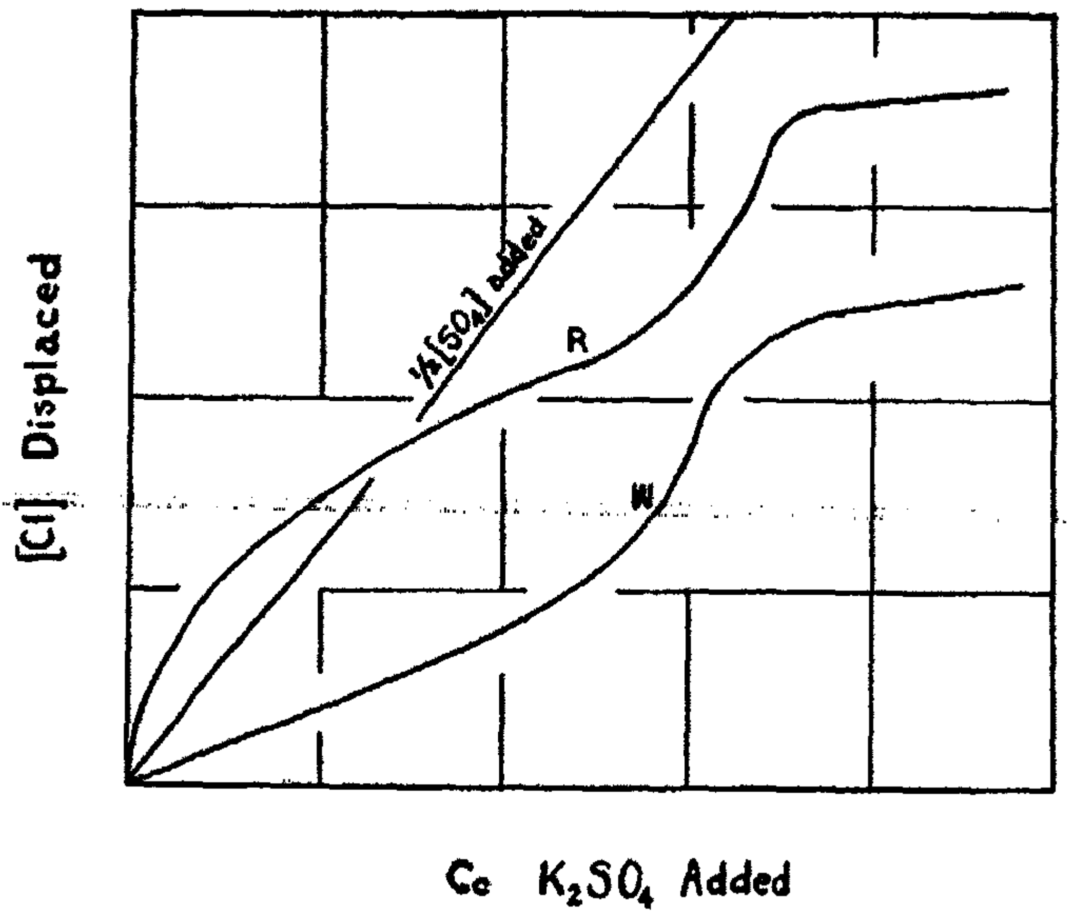

Fig. 1

Diagrammatic Representation of Chloride Displacement Curves obtained on "Titrating" Fe_2O_3 Sols with K_2SO_4 by the Method of Weiser (W) and Rabinowitsch (R).

"There is only one point of discrepancy between your views and those of my laboratory. It regards the question of legitimacy of the procedures used in our respective laboratories. I think that both are equally legitimate. Of course yours presents a more close approximation to the equilibrium in each point of the curve. But ours, which has the advantage of rapidity and simplicity, is no less satisfactory. It only gives the picture of the changes which take place in the first minutes and hours after the addition of each portion of electrolyte, whereas yours tends to find the final state of the system.

"The irregular trend of the potentiometric titration curve in our experiments which you ascribe to the calomel electrode not attaining the state of equilibrium, we understand as the picture of the stormy processes of ionic interchange following immediately the addition of concentrated electrolyte solutions to the colloid."

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[1] Private communication to Harry B. Weiser. A similar point of view is expressed in an article which appeared after this paper was written. [Rabinowitsch and Fodiman: Z. physik. Chem. 159A, 403 (1932)].

This is not convincing for it leaves altogether unanswered the nature of the "stormy process of ionic interchange" which brings about the alleged superequivalent displacement of chloride ion.

Adsorption of Precipitating Ions

In the investigations above referred to, attention has been given especially to the stepwise displacement of chloride resulting from the adsorption of the precipitating ion. The converse of this procedure consists in determining the actual amount of precipitating ion adsorbed during the stepwise addition of electrolyte both above and below the precipitation value. This has been done by Peterson and Storks[1] for the adsorption of chromate by hydrous alumina. A series of samples of the Al_2O_3 sol was prepared by the addition of varying amounts of K_2CrO_4 and the adsorption determined by the change in concentration. Below the precipitation value, the sol was ultrafiltered and the ultrafiltrate analyzed, while above the precipitation value, an aliquot part of the supernatant solution was withdrawn for analysis. A curve showing three distinct parts was obtained. The first part, below the precipitation value, was characterized by decreasing adsorption with increasing concentration of electrolyte while above the precipitation value the curve had a form similar to that of the usual adsorption isotherm but with a distinct point of inflection. Peterson and Storks believe that the first portion of the curve represents a neutralization adsorption, the last portion a surface adsorption non-electrical in type, and the intermediate portion a combination of the two types.

Since the adsorption of the precipitating ion by hydrous Al_2O_3 prepared from the chloride is an exchange adsorption process throughout most, if not all, of the concentration range investigated, the observations of Peterson and Storks may be open to question. Indeed both the choice of precipitating reagent and the experimental method appear to be somewhat unfortunate. In the first place, it is known that the following equilibrium is set up in chromate solutions: $2CrO_4^{--} + 2H^{\cdot} \leftrightarrows H_2O + Cr_2O_7^{--}$. In such solutions we are dealing with two ions and when they are mixed with the sol there will be a shift in the equilibrium depending on the change in pH value.[2] In the second place, nothing can be told about the true adsorption equilibrium after ultrafiltration. The process causes a gradual change in the amount of intermicellar solution in contact with the micelles and results in more or less coagulation and agglomeration of the micelles, especially if it is carried very far. A potentiometric method which does not involve ultrafiltration may give a fairly accurate measure of the concentration of ions in equilibrium with those adsorbed in the micelles; but the true equilibrium will be shifted by ultrafiltration.

In this investigation attention will be given to the two questions raised in the above survey: (1) the alleged superequivalent displacement of chloride

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[1] J. Phys. Chem., 35, 649 (1931).

[2] Cf. Weiser and Middleton: J. Phys. Chem., 24, 648 (1920); Ishizaka: Z. physik. Chem., 83, 97 (1913); cf., also, Weiser: J. Phys. Chem., 35, 1368 (1931).

ion from a hydrous oxide sol by a precipitating electrolyte; and (2) the interrelation between adsorption of a precipitating ion and displacement of chloride during the stepwise addition of electrolyte to a hydrous oxide sol.

I. "Superequivalent" Displacement of Chloride Ion

The hydrous oxide sols of aluminum, chromium and iron were "titrated" with K_2SO_4 by means of the Rabinowitsch method. The observations disclose the causes of the observed superequivalent displacement of chloride and indicate the unsatisfactory nature of the rapid Rabinowitsch procedure.

General Method of Procedure

Preparation of Sols. Al_2O_3 Sol I was obtained by adding 1.5 N NH_4OH from a dropping funnel to 1 liter of a solution containing 100 g $AlCl_3 \cdot 6H_2O$ stirred by a mechanical stirrer, until the precipitate which first formed just failed to redissolve. The mixture was diluted to 3 liters, boiled for 30 minutes and dialyzed in a Neidle[1] dialyzer at 75° until a satisfactory ratio of $Al_2O_3 : Cl$ was obtained, after which it was evaporated to the desired concentration and allowed to age. Al_2O_3 Sol II was formed by the method of Wassiliev and and Rabinowitsch:[2] 75% of the theoretical amount of 7.5 N NH_4OH was added with constant stirring to 1 liter of solution containing 100 g of $AlCl_3 \cdot 6H_2O$. The mixture was diluted to 1750 cc and dialyzed as above described.

The Cr_2O_3 sol was prepared by adding to 1 liter of solution containing 55 g $CrCl_3$, small portions at a time of NH_4OH containing 25 g of concentrated base diluted to 800 cc. The mixture was diluted to 3.5 liters, boiled for 30 minutes, and dialyzed in a Neidle dialyzer at 75°.

The Fe_2O_3 sol was made by adding dilute NH_4OH in small portions to 500 cc of a solution containing 100 g $FeCl_3 \cdot 6H_2O$, until 75% of the amount necessary for complete precipitation was used. The sol was diluted to 3.5 liters, dialyzed at room temperature to remove the excess $FeCl_3$ and finally at 75° until the desired ratio of Fe_2O_3 to Cl was obtained.

TABLE I

Age and Composition of Hydrous Oxide Sols

Sol	Age before use	Composition	
		M_2O_3 g/l	Cl equivalents/l
Al_2O_3 I	3 months at room temperature	5.08	0.0206
Al_2O_3 II	3 months at room temperature	3.53	0.0268
Cr_2O_3	2 months at room temperature	6.02	0.0140
Fe_2O_3	2 weeks at 80° + 1 month at room temperature	5.91	0.0096

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[1] J. Am. Chem. Soc., 38, 1270 (1916).

[2] Kolloid-Z., 56, 306 (1931).

The oxide content of the several sols was determined by precipitating with a slight excess of NH_4OH, filtering, washing, and igniting in the usual way. The chloride content was gotten by adding a slight excess of $AgNO_3$ and then a large excess of HNO_3 followed by digestion in the dark for 24 hours at 80°. This dissolved the hydrous oxide and after dilution, the AgCl was filtered into a Gooch crucible, washed, dried and weighed. The age before use and the composition of the several sols are summarized in Table I.

Method of Titration. The change in chloride ion concentration during the stepwise addition of 0.5 N K_2SO_4 was determined by the method of Rabinowitsch and Kargan[1] using the same potentiometer set-up and electrode vessels previously described.[2] In all cases, 15 cc of sol were used and 0.5 N K_2SO_4 was added from a micro burette graduated in 0.01 cc. The potential was measured against a 0.1 N calomel electrode and the chloride activity as KCl was calculated by means of the Nernst equation. The molar concentration was obtained from activity by means of a graph prepared from data given by Lewis and Randall.[3] The chloride concentration was corrected for dilution by the added electrolyte.

Preliminary experiments showed that electrodes prepared with sols not previously saturated with calomel required 12 to 15 hours before constant potentials were obtained, while sols which had stood in contact with calomel overnight usually gave constant potentials within 3 hours. Accordingly the electrodes were prepared at least 12 hours before the titration was begun.

The titration proceeded as follows: The electrolyte was added from the burette to the sol in the electrode vessel and the mixture stirred thoroughly with a stirring rod. The potential against the 0.1 N electrode was read at 10-minute intervals for 30 minutes and then at 15-minute intervals until the potential was constant for three consecutive readings. In general, the alumina sols gave a constant potential after 30 minutes to one hour, while a somewhat longer time was required for the chromic oxide sol and a still longer time for the ferric oxide sol. Above the coagulation point the potential became constant after 10 to 30 minutes.

Experiments with Alumina Sol

Preliminary observations with alumina sol disclosed that there was no superequivalent displacement of chloride if the sol was thoroughly mixed with electrolyte and a reasonable time allowed for the electrode to come to equilibrium conditions. Rapid mixing of sol and electrolyte in an all-glass mixing vessel gave mixtures which showed no evidence of superequivalent displacement of chloride ion at any concentration.

It was observed that the dropwise addition of the relatively strong electrolyte to the sol causes localized coagulation. If stirred sufficiently vigorously, the precipitated hydrous oxide is peptized completely; but if the

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[1] Z. physik. Chem., 133, 203 (1928).

[2] Weiser: J. Phys. Chem., 35, 8 (1931).

[3] "Thermodynamics," 344, 362 (1923).

TABLE II

Titration of Al_2O_3 Sol I with 0.5 *N* K_2SO_4

	K_2SO_4 0.5 N cc	milli-volts	(αCl) $\times 10^3$	[Cl] $\times 10^3$	[Cl] corrected $\times 10^3$	[Cl] displaced $\times 10^3$	$\frac{1}{2}[SO_4]$ added $\times 10^3$
	0.00	57.1	8.46	9.05	9.05	0.00	
A	0.05	44.0	14.14	15.62	15.67	6.62	1.67
B	0.05	51.4	10.58	11.54	11.57	2.52	1.67
C	0.05	54.5	9.18	9.92	9.95	0.90	1.67
A	0.10	41.3	15.72	17.48	17.62	8.57	3.33
B	0.10	51.2	10.66	11.68	11.76	2.71	3.33
C	0.10	53.4	9.78	10.62	10.69	1.64	3.33
A	0.20	40.8	16.03	17.86	18.09	9.04	6.67
B	0.20	48.6	11.81	12.96	13.13	4.08	6.67
C	0.20	49.5	11.40	12.50	12.66	3.61	6.67
A	0.30	42.6	14.94	16.54	16.86	7.81	10.00
B	0.30	45.0	13.60	15.00	15.30	6.25	10.00
C	0.30	46.1	13.02	14.35	14.64	5.59	10.00
A	0.40	45.8	13.18	14.48	14.86	5.81	13.33
B	0.40	44.6	13.81	15.25	15.64	6.59	13.33
C	0.40	44.9	13.65	15.02	15.41	6.36	13.33
A	0.50	45.3	13.44	14.85	15.30	6.25	16.67
B	0.50	44.0	14.14	15.62	16.18	7.13	16.67
C	0.50	42.5	15.00	16.62	17.12	8.07	16.67
A	0.60	41.4	15.66	17.40	18.09	9.04	20.00
B&C	0.60	41.4	15.66	17.40	18.09	9.04	20.00
A	0.70	40.2	16.41	18.30	19.14	10.09	23.33
B&C	0.70	40.9	15.97	17.78	18.52	9.47	23.33
A	0.80	40.0	16.54	18.44	19.39	10.34	26.67
B&C	0.80	40.7	16.10	17.90	18.85	9.80	26.67
A	0.90	39.9	16.61	18.50	19.58	10.53	30.00
B&C	0.90	40.3	16.35	18.18	19.26	10.21	30.00

mixture is not well stirred or if sufficient time is not allowed before making the chloride ion measurement, a value appreciably above the normal equilibrium value would be expected. That such is the case is indicated by the following experiments.

Effect of the Nature of the Stirring following the Dropwise Addition of Electrolyte. The 0.5 N K_2SO_4 was allowed to drop into 15 cc of sol from a micro burette and the following observations made at 23°: A. The mixture was stirred gently for a few seconds after which it was allowed to stand 10 minutes and the potential measured against an $N/10$ calomel electrode.

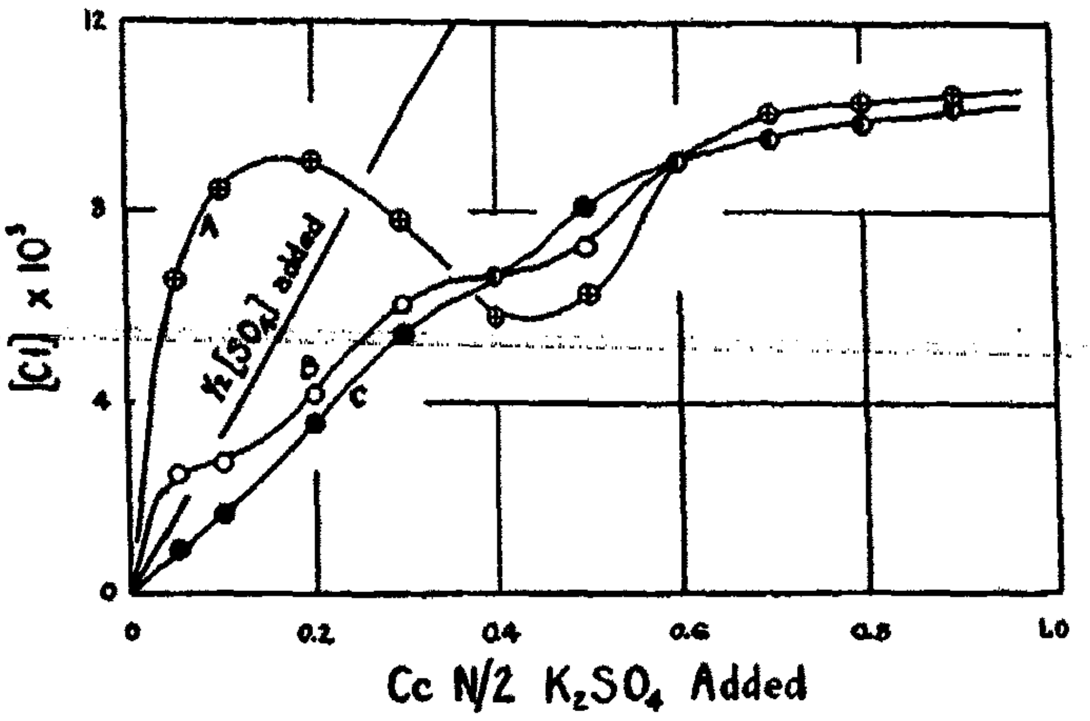

FIG. 2
"Chloride Displacement" Curves with Al_2O_3 Sol I (A) after 10 minutes, (B) after 20 minutes and (C) at equilibrium.

B. The mixture was then stirred vigorously for 30 seconds, allowed to stand for 10 minutes and the potential read once more. C. The mixture was again stirred thoroughly and potential readings taken at 10 minute intervals until three consecutive readings were the same. The observations on Al_2O_3 Sol I are given in Table II and shown graphically in Fig. 2. Line A shows the values obtained on the first reading, line B on the second, and line C the final value.

Observations with Al_2O_3 Sol II are given in Fig. 3. The results are similar to those of Sol I in all essential respects.

It is apparent that the chloride concentrations calculated from the first potential readings show very erratic variations from the equilibrium conditions. The observed superequivalence is the result of two errors inherent in the method, which render it of questionable value. First, the partial coagulation accompanying the addition of strong electrolyte results in a proportionately greater displacement of chloride than if no coagulation takes place. This relatively greater displacement of chloride in the zone of coagulation accounts for the marked change in direction of the equilibrium chloride displacement curve in this region.[1] Second, a few minutes is insufficient time

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[1] Cf. Weiser: J. Phys. Chem., 35, 10, 1374 (1931).

for the sol-calomel-electrolyte mixture to come to equilibrium. Accordingly the curve obtained by adding the relatively strong solution to the sol, stirring gently, and measuring after 10 minutes, is meaningless.

The second curve obtained after thorough stirring and waiting for an additional 10 minutes is more regular and the observed superequivalence is much less. Here also the superequivalence results chiefly from partial electrolyte coagulation which is not completely reversed and from delay in setting up equilibrium at the electrode. The final equilibrium curve is similar in form to those obtained by Weiser's method but the true amount of chloride displaced is uniformly higher. The reason is obvious. In the Rabinowitsch method, partial coagulation always takes place below the precipitation value, while this is avoided in Weiser's procedure. The excess chloride displaced by the partial coagulation is never taken up completely since the coagulation is not completely reversible.

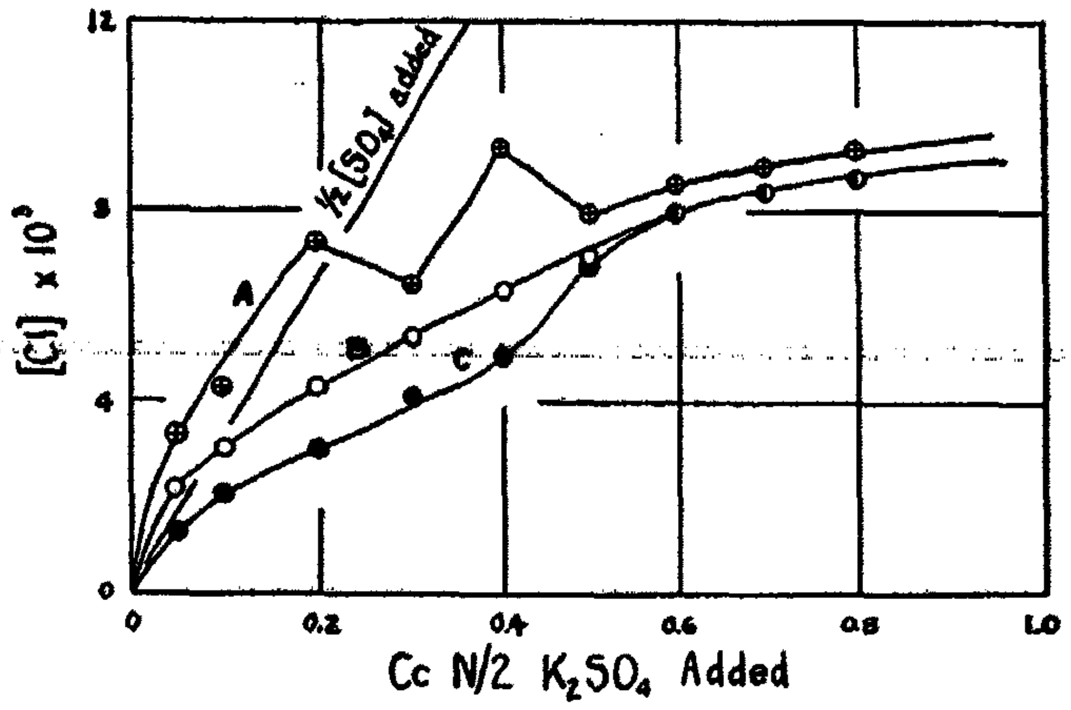

Fig. 3

"Chloride Displacement" Curves with Al_2O_3 Sol II (A) after 10 minutes, (B) after 20 minutes and (C) at equilibrium.

From these observations it is clear that the Rabinowitsch method of procedure has little to commend it. Initial coagulation is distinctly objectionable and the titration curves are meaningless unless an approximate state of equilibrium is attained. If time is allowed for this, the procedure is much more time consuming than the Weiser method. Thus, starting with the sol saturated with calomel, approximately 15 hours elapsed from the beginning of the titration until the last point in the *C* curves of Figs. 2 and 3 were obtained. In the Weiser method about two hours are required to prepare the series of electrodes containing the varying amounts of electrolytes and after these have stood for 2 days to attain equilibrium, the potentiometric measurements are made in a few minutes. Moreover, the method of mixing avoids the complication of localized coagulation below the precipitation value.

Effect of Concentration of Sol. Since the so-called superequivalent displacement of chloride ion results in part from an inherent error in the experi-

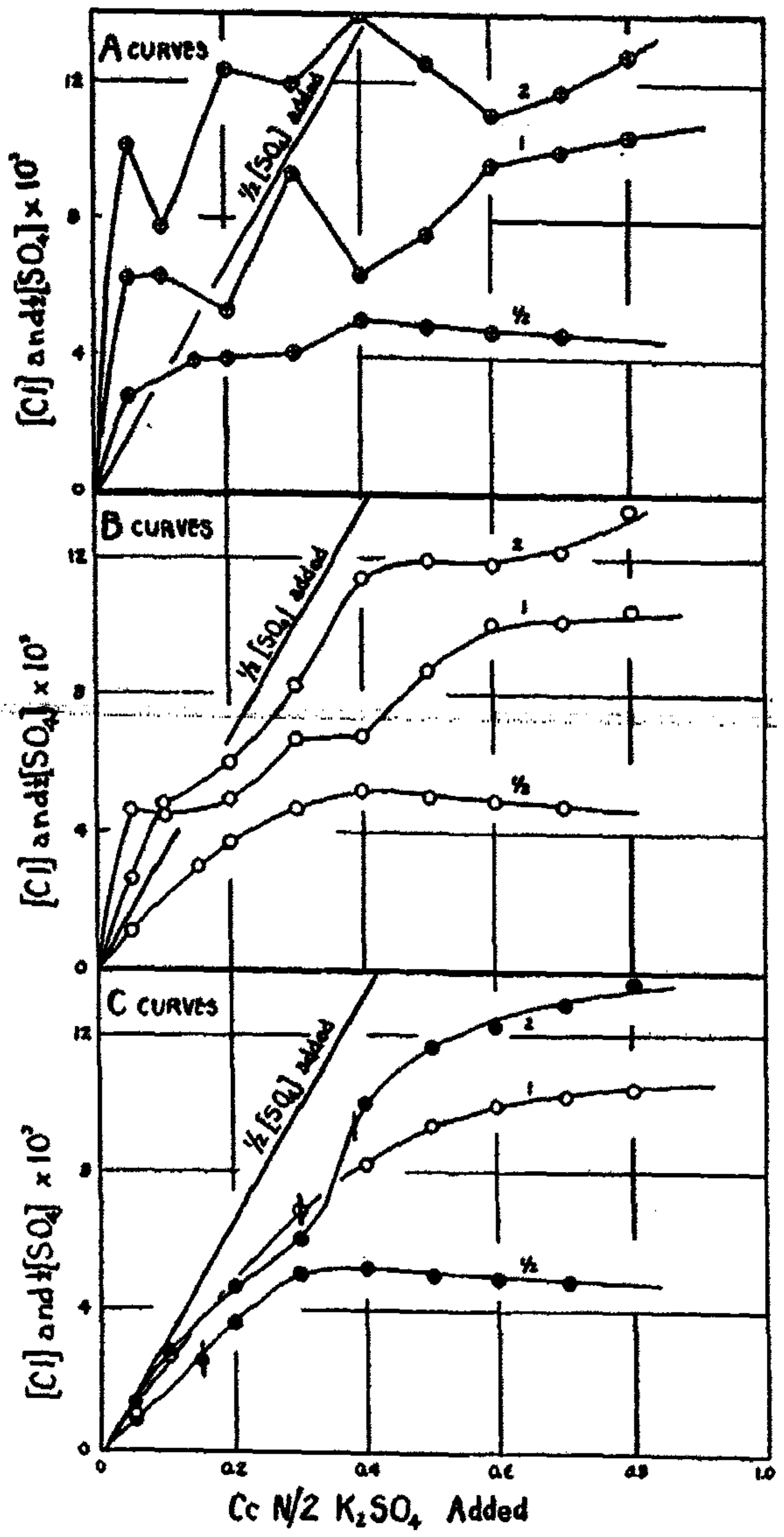

FIG. 4

"Chloride Displacement" Curves with Al_2O_3 Sols of Varying Concentration (A) after 10 minutes, (B) after 20 minutes and (C) at equilibrium.

mental method, namely, partial electrolyte coagulation, it follows that the effect would be least marked the greater the dilution of sol. This is borne out by the following experiments: Al_2O_3 Sol I was evaporated in a vacuum desiccator over H_2SO_4 until its concentration was approximately doubled. Titration experiments similar to those described in the preceding section were then made on (1) the concentrated sol (2) the concentrated sol diluted with one part of water and (3) the concentrated sol diluted with three parts of water. In order to conserve space the lengthy tables of data are omitted but the results are shown graphically in Fig. 4. To avoid confusion the *A*, *B* and *C* curves for three different sols are plotted separately. The results speak for themselves. There is no "superequivalent" displacement with the most dilute sol if the sol electrolyte mixture is thoroughly stirred before making the potentiometric reading. This merely confirms the earlier observations in this laboratory that there is no indication of superequivalent displacement when the sol is mixed rapidly with the highly diluted precipitating electrolyte.

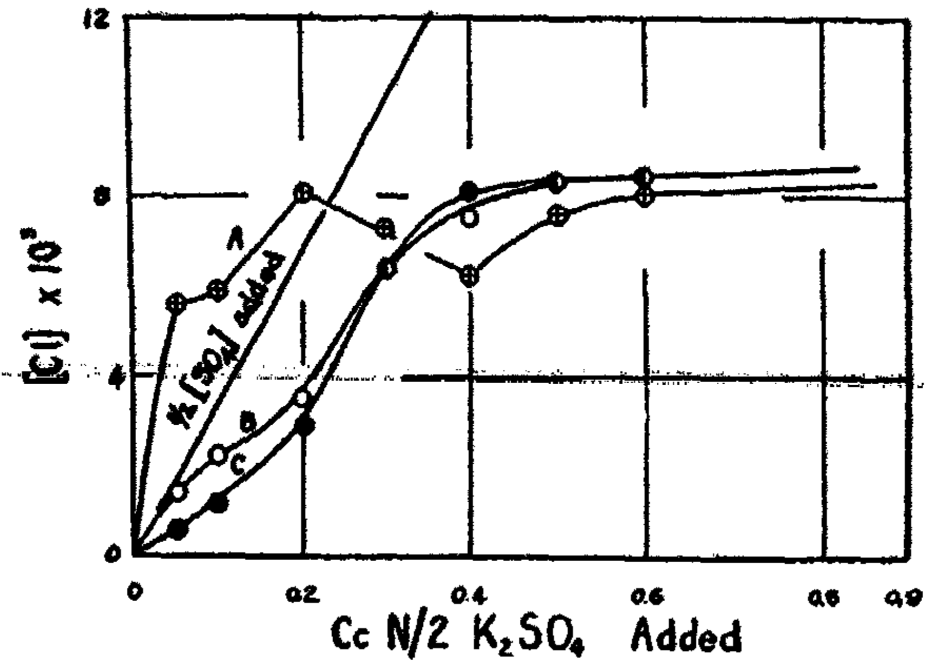

Fig. 5

"Chloride Displacement" Curves with Cr_2O_3 Sol (A) after 10 minutes, (B) after 20 minutes and (C) at equilibrium.

In this connection attention should be called to the observation of Rabinowitsch and Kargan[1] that the excess of chloride ion displaced, falls off with dilution of sol and disappears entirely with five-fold dilution of a Fe_2O_3 sol whose original concentration was 5.76 grams per liter. This is as it should be but the reason for this behavior was apparently overlooked.

Experiments with Chromic Oxide Sol

Observations on the Cr_2O_3 sol were made by the same procedure used with alumina and the results are shown graphically in Fig. 5. The similarity of curves obtained under similar conditions with the two different sols is at once apparent.

Experiments with Ferric Oxide Sol

The observations with Fe_2O_3 sol are so similar to those with Al_2O_3 and Cr_2O_3 that no comment is necessary. The data are shown graphically in Fig. 6. Since the chloride content of the sol is less than in the other two sols the chloride displacement is correspondingly less. For this reason the scale in Fig. 6 is made twice as large as in the other figures.

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[1] Z. physik. Chem., 133, 224 (1928).

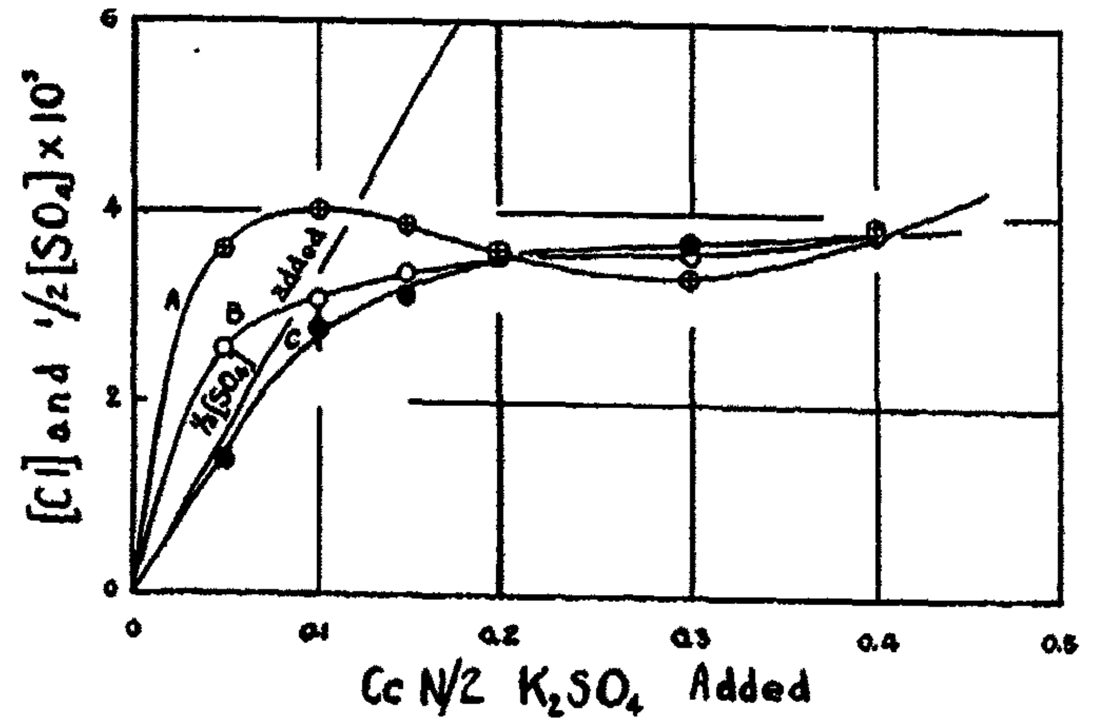

FIG. 6

"Chloride Displacement" Curves with Fe_2O_3 Sol. (A) after 10 minutes, (B) after 20 minutes and (C) at equilibrium.

Conclusion

The conclusion from these observations is that the so-called superequivalent displacement of chloride ion during the "rapid" titration of hydrous oxide sols by the dropwise addition of a relatively strong precipitating electrolyte according to the method of Rabinowitsch, is the result of an unsatisfactory experimental procedure which produces localized coagulation of a portion of the sol and does not allow time for equilibrium conditions to be approached. It is not typical of any one sol and the experimental conditions cannot be developed uniformly in any case. For this reason the chief value of the rapid procedure is in emphasizing the experimental conditions which should be avoided in studying the change in the adsorption equilibria which follow the stepwise addition of precipitating electrolytes to sols.

II. Adsorption of Precipitating Ions

It will be recalled that Peterson and Storks obtained a curve showing three distinct parts for the adsorption of chromate added in gradually increasing amounts to alumina sol. Since the equilibrium curves showing the displacement of chloride from hydrous oxide micelles by adsorption of sulfate and other ions including chromate, show no breaks,[1] there was no reason for believing that breaks would occur in the adsorption curve of the precipitating ion. The following experiments indicate that there are no breaks in the adsorption curves for sulfate added stepwise to the hydrous oxide sols of aluminum, chromium and iron.

General Procedure. It was found by preliminary experiments that all of the precipitation concentration of sulfate was adsorbed by the several oxides. Since none of the precipitating electrolyte was left over at the precipitation point, it is apparent that none would remain unadsorbed below the precipitation value. Accordingly, it was necessary to make the adsorption measure-

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[1] Weiser: J. Phys. Chem., 35, 1, 1368 (1931).

ments above the precipitation value only. This was fortunate since, as we have seen, it is not permissible to ultrafilter the sol and since the lead sulfate electrode was found to be unsatisfactory for the potentiometric estimation of low concentration of sulfate.

A definite amount of 0.5 N K_2SO_4 was added from a micro burette graduated in 0.01 cc to 15 cc of sol contained in a test tube. The tube was stoppered and the mixture shaken thoroughly. After standing 24 hours the precipitated hydrous oxide was thrown down by centrifuging for 30 minutes at 3000 r.p.m. in an International Equipment Company Centrifuge. The supernatant liquid was poured off and centrifuged 15 minutes more, after which an aliquot part was analyzed for sulfate by the nephelometric method which was found by preliminary experiments to be quite satisfactory.

To a mixture of 5 cc of 1% $BaCl_2$ solution, 5 cc of 0.1 N HCl and 1 cc of 5% sulfate-free gelatin,[1] was added an amount of liquid (not exceeding 5 cc) which contained not over 0.5 mg of SO_4 ion as determined by preliminary experiment, and the final volume was made up to 16 cc with water. This sample was compared with a standard prepared at the same time using 5 cc of K_2SO_4 solution containing 0.24 mg SO_4. The comparison was made after the sample had stood 15 minutes, using a Dubosque-Leitz nephelometer. In each case the mean value of 10 readings was taken.

Adsorption by Alumina. The measurements of adsorption by alumina was accomplished without difficulty except at concentrations just above the precipitation value. In this region traces of alumina that are shaken up during the centrifuging process remain in suspension persistently. Accordingly, the determination of unadsorbed sulfate after the addition of 0.3 and 0.35 cc of K_2SO_4 was made by the following modification of the procedure described above: A 2 cc sample of the supernatant liquid was added to a mixture of 5 cc of 0.1 N HCl, 5 cc H_2O, and 0.5 cc 1% $BaCl_2$ solution. Another 2 cc portion was added to a similar mixture in which water was substituted for the $BaCl_2$

TABLE III

Adsorption of Sulfate by Al_2O_3 Sol I
(15.0 cc of sol with 0.5 N K_2SO_4)

K_2SO_4 0.5 N cc	SO_4 added mg	SO_4 in solution mg	SO_4 adsorbed mg	$\frac{1}{2}[SO_4]$ adsorbed $\times 10^3$	$\frac{1}{2}[SO_4]$ corrected $\times 10^3$	$\frac{1}{2}[SO_4]$ added $\times 10^3$
0.30	7.20	0.61	6.59	8.98	9.16	10.00
0.35	8.40	1.23	7.17	9.73	9.95	11.67
0.40	9.60	1.48	8.12	11.00	11.29	13.33
0.50	12.00	1.74	10.26	13.80	14.21	16.67
0.60	14.40	2.44	11.96	15.97	16.60	20.00
0.70	16.80	3.30	13.50	17.92	18.76	23.33
0.80	19.20	4.31	14.89	19.63	20.67	26.67
0.90	21.60	5.80	15.80	20.70	21.94	30.00

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[1] Denis and Reed: J. Biol. Chem., 71, 193 (1926).

solution. These samples were compared with a standard prepared at the same time containing 0.12 mg SO_4. The samples were allowed to stand 15 minutes before making the comparison. A correction for the turbidity due to dispersed Al_2O_3 was applied to the calculated SO_4 concentration.

The observations are recorded in Table III and shown graphically in Fig. 7, together with the chloride displacement curve from Fig. 2.

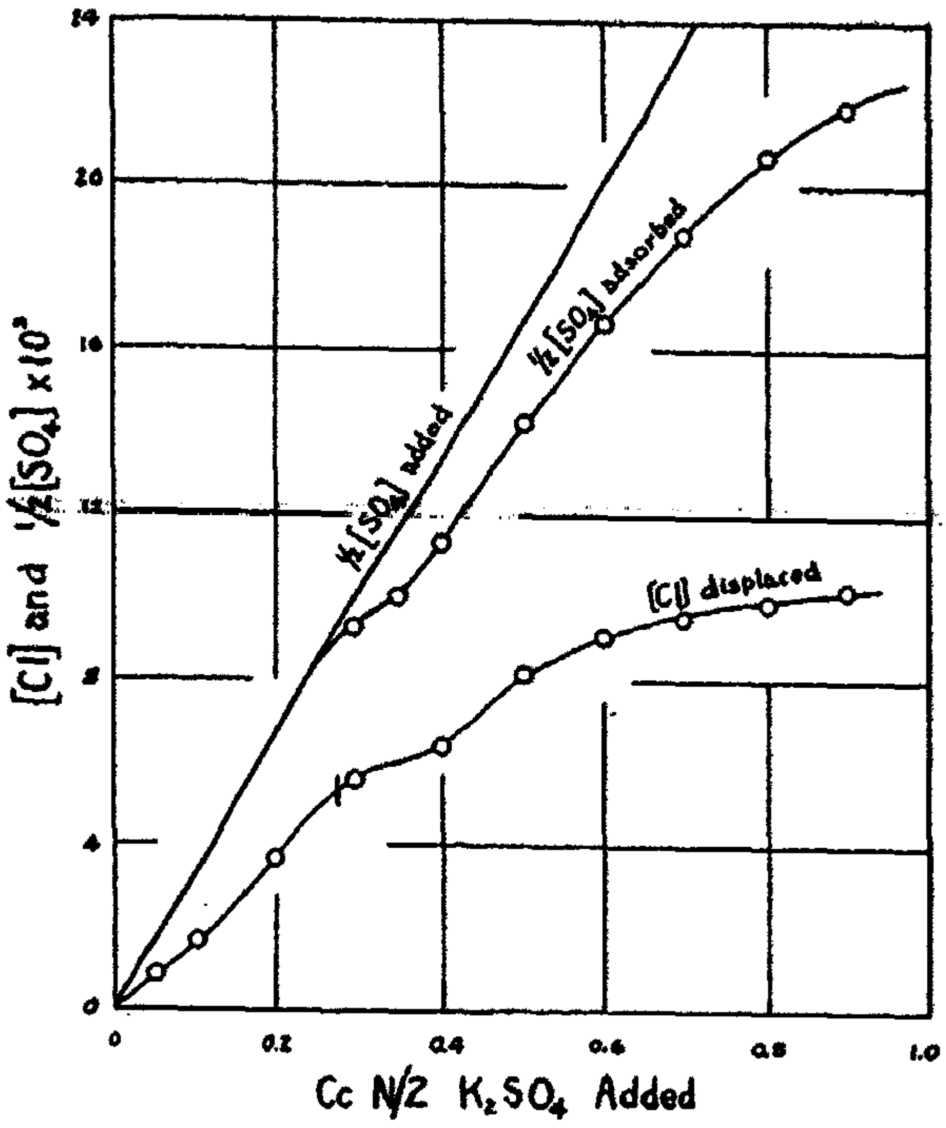

Fig. 7

Curves for the Simultaneous Displacement of Chloride and Adsorption of Sulfate by Colloidal Al_2O_3 Sol. I.

The sulfate concentration was corrected to the same basis as the chloride displaced, *i.e.*, to 15 cc volume. The adsorption curve follows an unbroken course through the entire concentration range, but there appears to be a slight point of inflection just above the precipitation value corresponding to a similar bend in the chloride displacement curve. The sulfate adsorption is appreciably greater than the amount of chloride displaced. The reason for this is that a part of the sulfate which is taken up corresponds to chloride measurable potentiometrically in the intermicellar solution.[1]

Adsorption by Chromic Oxide. No difficulty was encountered in the adsorption measurements with Cr_2O_3 sol since the supernatant solution above the precipitation value was entirely free from suspended matter. The adsorption data are given in Table IV and the adsorption is shown in Fig. 8 together with the chloride displacement curve from Fig. 5.

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[1] Cf. Weiser: J. Phys. Chem., 35, 23, 1392 (1931).

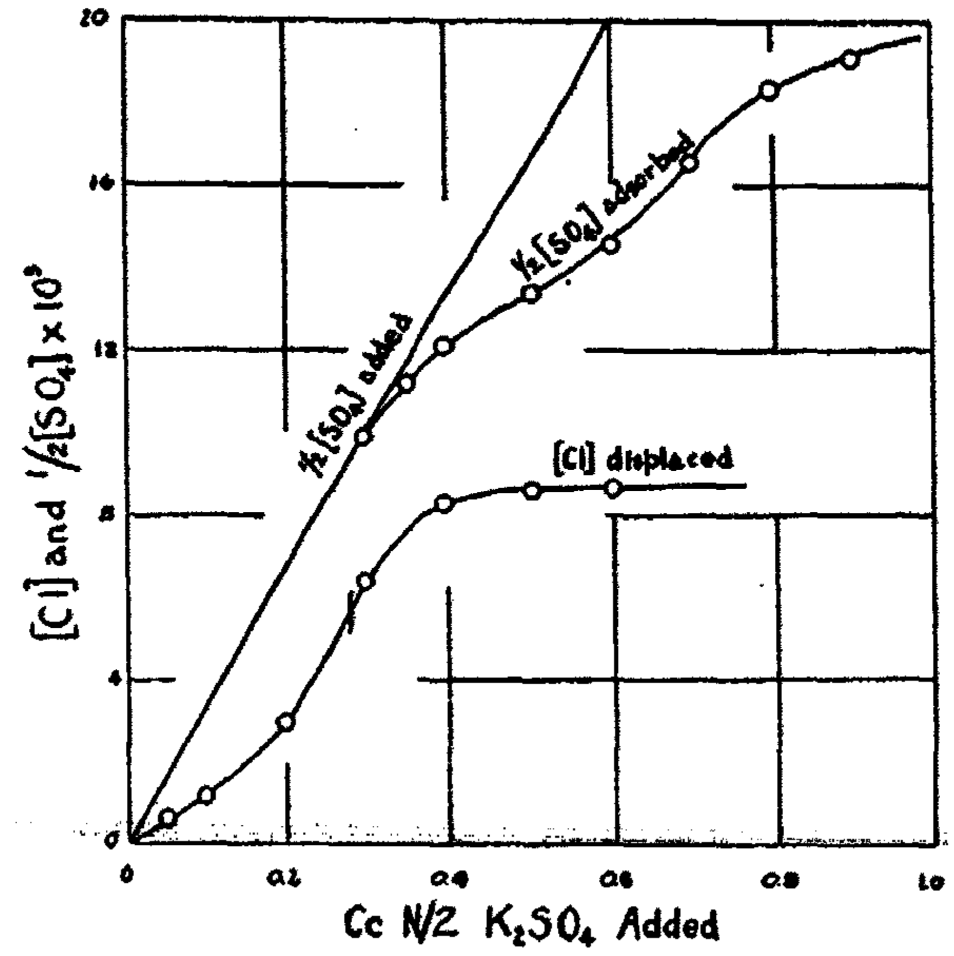

Fig. 8

Curves for the Simultaneous Displacement of Chloride and Adsorption of Sulfate by Colloidal Cr_2O_3 Sol.

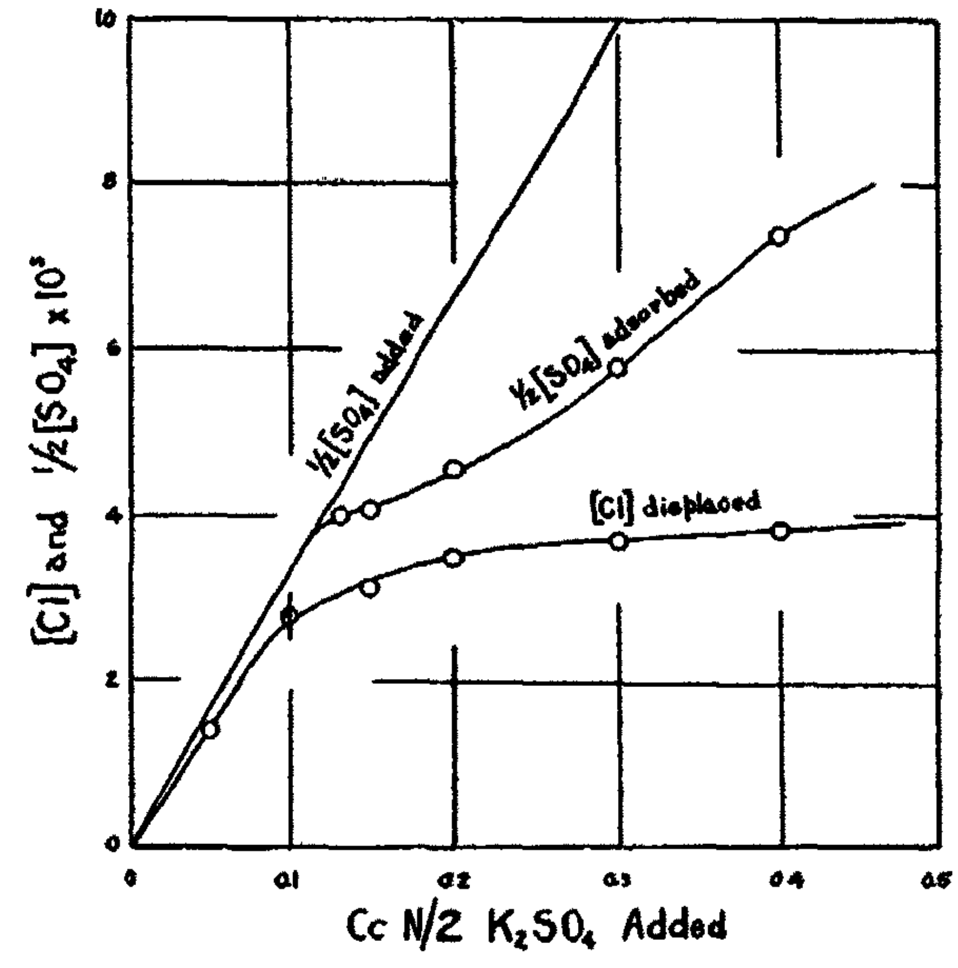

Fig. 9

Curves for the Simultaneous Displacement of Chloride and Adsorption of Sulfate by Colloidal Fe_2O_3 Sol.

TABLE IV

Adsorption of Sulfate by Cr_2O_3 Sol
(15.0 cc of sol with 0.5 N K_2SO_4)

K_2SO_4 0.5 N cc	SO_4 added mg	SO_4 in solution mg	SO_4 adsorbed mg	$\frac{1}{2}[SO_4]$ adsorbed $\times 10^3$	$\frac{1}{2}[SO_4]$ corrected $\times 10^3$	$\frac{1}{2}[SO_4]$ added $\times 10^3$
0.30	7.20	0.10	7.10	9.67	9.86	10.00
0.35	8.40	0.34	8.06	10.94	11.19	11.67
0.40	9.60	0.88	8.72	11.80	12.11	13.33
0.50	12.00	2.31	9.69	13.03	13.42	16.67
0.60	14.40	3.95	10.45	13.96	14.52	20.00
0.70	16.80	4.88	11.92	15.82	16.56	23.33
0.80	19.20	6.00	13.20	17.41	18.33	26.67
0.90	21.60	7.90	13.70	17.95	19.02	30.00

Adsorption by Ferric Oxide.—The adsorption data with ferric oxide sol are given in Table V and Fig. 9.

TABLE V

Adsorption of Sulfate by Fe_2O_3 Sol
(15.0 cc of Sol with 0.5 N K_2SO_4)

K_2SO_4 0.5 N cc	SO_4 added mg	SO_4 in solution mg	SO_4 adsorbed mg	$\frac{1}{2}[SO_4]$ adsorbed $\times 10^3$	$\frac{1}{2}[SO_4]$ corrected $\times 10^3$	$\frac{1}{2}[SO_4]$ added $\times 10^3$
0.13	3.12	0.24	2.88	3.97	4.00	4.33
0.15	3.60	0.68	2.92	4.02	4.06	5.00
0.20	4.80	1.49	3.31	4.54	4.60	6.67
0.30	7.20	3.03	4.17	5.68	5.79	10.00
0.40	9.60	4.23	5.37	7.27	7.46	13.33
0.50	12.00	5.77	6.23	8.38	8.63	16.67

Conclusion

At all concentrations both above and below the precipitation value, sulfate ion enters into exchange adsorption with chloride ion present in the diffuse outer layer of the hydrous oxide particles. The sulfate adsorption curve follows a smooth course above that of the chloride displacement curve through the entire concentration range.

Summary

The following is a summary of the results of this investigation.

1. A comparison is made of the methods employed by Weiser and by Rabinowitsch for following the stepwise displacement of chloride ion from hydrous oxide sols during the dropwise addition of electrolyte to the sol.

2. The so-called superequivalent displacement of chloride observed by Rabinowitsch by his method of "rapid titration" is the result of an unsatisfactory experimental procedure which (a) produces localized coagulation of a portion of the sol below the precipitation value and (b) does not allow time for equilibrium to be approached.

3. The final equilibrium concentration of chloride following localized coagulation of the sol is higher than in the absence of coagulation since the coagulation process is not completely reversible in a reasonable time.

4. At all concentrations both above and below the precipitation value, sulfate ion enters into exchange adsorption with chloride ion present in the diffuse outer layer of the hydrous oxide particles.

5. Contrary to observations of Peterson and Storks on the adsorption of chromate by hydrous alumina both above and below the precipitation value, the sulfate adsorption curve follows a smooth course above that of the chloride displacement curve throughout the entire concentration range. The most marked break in the adsorption curve obtained by Peterson and Storks is probably due to a displacement of the adsorption equilibrium by ultrafiltration.

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STUDIES ON SILICIC ACID GELS

II. The Time of Set as a Function of the Temperature*

BY CHARLES B. HURD AND P. SCHUYLER MILLER

Introduction

In the preceding paper of this series of studies on the setting process of silicic acid gels[1] a series of determinations of the time of set as a function of the temperature was given. Aqueous solutions of one commercial brand of water glass were mixed with solutions of acetic acid at various temperatures. The time of set was determined by the tilted rod method.

It was pointed out in the article that if certain simple assumptions were possible, the time of set could be treated according to the ordinary laws for the velocity of a chemical reaction. By the use of Arrhenius' equation, a series of values for the heat of activation were obtained. The mean value, 16,940 calories, comes well within the limits for the heat of activation for ordinary reactions. The value was reasonably constant for various mixtures of solutions of the same water glass with acetic acid.

It was, of course, immediately apparent that a further study should be made of this phenomenon, in order to ascertain if the same value would be obtained with solutions of other samples of water glass and acetic acid. The next step would be to substitute other acids for the acetic acid. The third study should include the results where deliberate attempt had been made to modify the composition or structure of the original silicate.

The work reported in the previous paper was carried out with a water glass which can no longer be obtained. The silicates used in the work reported in the present paper and in the work now under investigation can be secured at any time, and their soda-silica ratio can be obtained from the maker, the Philadelphia Quartz Company.[2]

The present paper includes the results of a series of determinations on six brands of sodium silicate. Acetic acid only was used. The results appear interesting and will, we believe, assist somewhat in obtaining a useful picture of the process of setting of silicic acid gels.

Historical

As previously mentioned in this article, Hurd and Letteron have shown that it is possible, by means of certain simple assumptions, to treat the process of the setting of a silicic acid gel according to the laws for the velocity

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* Contribution from the Chemical Laboratory of Union College, Schenectady, N.Y.

[1] C. B. Hurd and H. A. Letteron: J. Phys. Chem., 36, 604 (1932).

[2] The writers wish to acknowledge their gratitude to the Philadelphia Quartz Company for their courtesy in supplying not only all of the silicates used in these studies, but also for supplying analyses, methods of analysis, and other valuable information.

of ordinary chemical reactions. No other measurements of this kind have been found in the literature.

It has also been found, by a search of the literature, that little is known concerning the heat of setting of silicic acid gels. Thomsen[1] has reported that he found no heat effect during the coagulation of silicic acid; but his coagulation was slow, the time being at least 30 minutes, and he used dilute solutions. Graham[2] however, had reported about twenty years before that a rise of 1.1°C occurred during the setting of a 5% jelly. It does not appear possible to calculate the heat of formation from Graham's data. On the ordinary interpretations of 5%, however, the value of heat of setting would appear to lie between 1100 cal. and 2000 cal. per gram. mol, of H_2SiO_3.

Wiedemann and Lüdeking[3] attempted to determine the heat of setting of solutions of colloids by means of a calorimeter of about 18 cc. capacity. They accelerated the setting of a mixture of solutions of water glass and hydrochloric acid by means of ammonia. Their results appear consistent, but their values of $C = 12.2$ and 11.2 cal. are difficult to correlate to our present heats of reaction.

Experimental

We have determined the time of set for various mixtures of solutions of six different brands of sodium silicate with solutions of acetic acid at several different fixed temperatures. The silicate samples were supplied by the Philadelphia Quartz Company. The acetic acid from which the solutions were made was glacial acetic acid, C.P., J. T. Baker. All water used was freshly distilled water which was boiled in lots of 3 to 4 liters to expel all gases, especially carbon dioxide. After being boiled vigorously, it was cooled quickly in snow and was kept, as were all solutions, in tightly stoppered glass bottles.

The strength of all solutions was determined by titration. Silicate solutions were titrated for their alkali content with standard sulfuric acid, using methyl orange. The acetic acid solutions were titrated with standard sodium hydroxide, using phenolphthalein. The silica content was determined for the silicate solutions from the alkali content and the known soda-silica ratio supplied by the maker. We have checked this gravimetrically in one case. The silicate solutions were not filtered. Very little suspended matter was visible. A very slight sediment was noticeable after several weeks, although at the time the samples were used practically no deposit was visible.

Runs were made by mixing accurately measured volumes of the standardized dilute silicate solution, the standardized dilute acetic acid solution and distilled water. The solutions and the water had been standing for hours in tightly stoppered containers in an accurately controlled water thermostat. Two 100 cc. Pyrex Griffin beakers, carefully cleaned and dried, had stood for several minutes in the thermostat immersed to within 1 cm. of the top.

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[1] J. Thomsen: "Thermochemische Untersuchungen," 1, 211 (1882).

[2] T. Graham: J. Chem. Soc., 17, 318 (1864).

[3] E. Wiedemann and C. Lüdeking: Ann. Physik, (3) 25, 145 (1885).

They had been covered with watch glasses. The measured volume of dilute solution was placed in one, and the measured volume of dilute acetic acid in the other. The water was added to the acid. At a given time the silicate was quickly poured into the acetic acid with stirring. To avoid the loss of the silicate solution which adheres to the beaker, the same beaker had had the same amount of silicate poured from it a few minutes before. We found this method necessary and accurate. The possible error in the volume of the silicate solution was found to be negligible. This rapid mixing avoided errors in the timing, especially for short runs.

The beaker containing the resulting mixture was covered with a watch glass and placed on a tray in the thermostat, immersed in the water so that the level of water on the outside was higher than that of the solution inside. The beakers with watch glass covers just failed to float. The volume in the beaker was always 80 cc., except in the case of the 0° thermostat, where a different procedure proved necessary.

The contents of a number of beakers in the thermostat were watched until the peculiar opalescent appearance preceding setting was observed. The stirring rod test for setting was then applied. This has been described in the preceding paper. It is carried out as follows. A stirring rod 10 cm. in length and made of glass 3 mm. in diameter is drawn out to a short stubby point, the tapered portion being about 5 mm. long. The point is fire polished. The rod is thrust into the gel at an angle of about 20° to the vertical. The gel is considered set when the rod fails to fall over. An operator with a little experience can obtain check determination differing by less than 2% of the time easily and regularly. Two different operators can check each other. A deliberate attempt to mutilate the surface and body of the gel will not produce errors greater than 3%. The beakers are not removed from the bath during testing.

Four thermostats were used. In the 0° thermostat, the mixtures for which the time of set was to be determined were contained in 200 cc. Erlenmeyer flasks. These were corked and 100 cc. beakers were inverted over the cork to prevent water leaking inside. They were buried in damp fine snow. The snow was frequently replenished from above. The excess water produced was withdrawn from below. Tests showed that the contents of the flasks remained within .1° of 0° C. A longer rod of the same diameter was used to determine the time of set. This method proved much simpler for the operator at 0° C. than the method of keeping the mixed solutions, 80 cc. in volume, in 100 cc. beakers as was done at other temperatures. The method of burying the 160 cc. mixtures in flasks in the snow was not adopted, however, until careful tests showed that the same results were obtained with the easier method than with the method of beakers at the same temperature. The method of burying the flasks guaranteed much closer thermal control.

The three other thermostats were made out of metal tubs about 20 inches in diameter and 12 inches deep. The 26° bath had no external insulation but those at 40° and 56° were insulated by a layer of dry sawdust between the tub and a much larger tub. Each was stirred by a brass paddle stirrer. The temperatures of the 26°, 40° and 56° baths were controlled by toluene mercury regulators.

The 26° bath had a 100 watt intermittent heater controlled through a relay by the regulator. The 40° bath had a Cenco 125 watt continuous heater of the knife type and a 125 watt intermittent heater controlled by the regulator and a relay. To reduce arcing at the relay contacts a 15 watt carbon lamp was connected across the relay contacts. The 125 watt heater was, therefore, controlled by the regulator in that the relay simply shunted from time to time, as necessary, the 15 watt lamp in series. Using this scheme, no arcing even with 250 watt heaters has been observed and the telephone relays, Western Electric E 493, have worked satisfactorily. The 56° bath had one 250 watt continuous heater and a 250 watt heater controlled as in the case of the 40° bath. We have not found temperature variation as large as .1°C during any of our runs.

Timing was accomplished by means of a stopwatch or a good ordinary watch for the longer runs. The temperature of the thermostat was checked frequently. The watch glasses fitted tightly and, apparently, during the setting, a negligible amount of water or acetic acid was lost through evaporation. Containers in which gel had set were washed carefully with dilute sodium hydroxide and thoroughly with water, although tests had shown no measurable effect on the time of set through the presence of particles of a previously set gel.

In all of the runs reported here, we have kept the silica concentration constant. Because of the different soda-silica ratios of the samples, this has meant a different sodium hydroxide concentration with different samples. For any one brand of silicate, however, the sodium hydroxide concentration was constant, as was, of course, the silica concentration. Six different concentrations of acetic acid were used.

The results obtained are given in the following tables. Trouble was experienced in the case of the "B.W." brand of water glass. Here the high soda concentration necessitated the highest concentration of acetic acid. It was found that when the silicate was poured into the acetic acid-water mixture the result curdled somewhat except at 0°. This caused an error which is readily observed in the tables.

In the results which follow the average of the time for at least two satisfactory runs is given for each mixture at each temperature. Ordinarily three check runs were made. An immense amount of work was required. Each table gives the soda-silica ratio, the concentration in the resulting mixture, expressed in gram mols per liter and the time of set in minutes for four different temperatures expressed in degrees Centigrade. It should be noted that the soda-silica ratio as given is a weight ratio. The mol. ratio is 1.032 times the weight ratio; for example the weight ratio of the C brand is given by the maker as 1:2.00, giving 1:2.06 for the mol ratio.

Tables showing Time of Set for Various Mixtures

TABLE I

"S" brand Water Glass

Ratio $Na_2O:SiO_2 = 1:3.86$

Concentrations				Time of Set—Minutes			
Mixture	NaOH	SiO_2	CH_3COOH	0.0°	26.2°	40.7°	55.8°
0	.323	.644	.500	1308.	89.	24.0	7.0
1	"	"	.625	2001.	134.	39.5	11.0
2	"	"	.750	2715.	177.	53.3	14.0
3	"	"	.875	3242.	224.	66.0	18.0
4	"	"	1.000	3807.	265.	74.0	21.8
5	"	"	1.125	4502.	308.	86.0	25.0

TABLE II

"N" brand Water Glass

Ratio $Na_2O:SiO_2 = 1:3.22$

Concentrations				Time of Set—Minutes			
Mixture	NaOH	SiO_2	CH_3COOH	0.0°	28.0°	40.6°	55.8°
0	.388	.646	.625	1440.	87.	26.5	8.4
1	"	"	.750	1990.	121.	39.8	11.1
2	"	"	.875	2787.	160.	53.0	16.4
3	"	"	1.000	3550.	196.	62.5	20.5
4	"	"	1.125	3891.	218.	74.0	23.2
5	"	"	1.250	4700.	260.	84.0	26.8

TABLE III

"K" brand Water Glass

Ratio $Na_2O:SiO_2 = 1:2.84$

Concentrations				Time of Set—Minutes			
Mixture	NaOH	SiO_2	CH_3COOH	0.0°	27.4°	40.4°	56.2°
0	.440	.646	.625	1080.	66.0	19.7	5.9
1	"	"	.750	1648.	97.0	29.2	9.1
2	"	"	.875	2214.	133.0	41.3	11.8
3	"	"	1.000	2789.	166.0	53.0	15.0
4	"	"	1.125	3108.	201.0	63.0	18.0
5	"	"	1.250	3518.	233.0	68.7	19.4

TABLE IV

"U" brand Water Glass

Ratio $Na_2O:SiO_2 = 1:2.44$

Concentrations				Time of Set—Minutes			
Mixture	NaOH	SiO_2	CH_3COOH	0.0°	25.9°	40.4°	55.8°
0	.508	.640	.750	1568.	105.5	26.2	8.3
1	"	"	.875	2118.	145.0	38.7	11.2
2	"	"	1.000	2720.	189.0	50.5	14.4
3	"	"	1.125	3264.	228.0	60.5	18.3
4	"	"	1.250	3585.	265.0	70.5	20.7
5	"	"	1.375	4092.	292.0	81.7	24.4

TABLE V

'C" brand Water Glass

Ratio $Na_2O:SiO_2$ = 1:2.00

	Concentrations			Time of Set—Minutes			
Mixture	NaOH	SiO_2	CH_3COOH	0.0°	25.9°	40.4°	55.8°
0	.623	.642	.750	560.	38.0	10.3	3.1
1	”	”	.875	1063.	73.7	20.9	5.6
2	”	”	1.000	1568.	108.0	29.8	8.5
3	”	”	1.125	1972.	142.0	38.2	10.6
4	”	”	1.250	2375.	165.0	48.0	13.2
5	”	”	1.375	3113.	199.0	55.5	16.1

TABLE VI

"B.W." brand Water Glass

Ratio $Na_2O:SiO_2$ = 1:1.58

	Concentrations			Time of Set—Minutes			
Mixture	NaOH	SiO_2	CH_3COOH	0.0°	26.3°	40.3°	55.8°
0	.791	.645	.938	255.	20.9	5.0	1.8
1	”	”	1.091	730.	52.0	13.6	3.9
2	”	”	1.250	1076.	76.5	20.4	6.4
3	”	”	1.408	1340.	100.0	28.5	8.1
4	”	”	1.561	1570.	123.0	32.6	9.8
5	”	”	1.720	1900.	142.0	40.0	11.4

For each brand of silicate the logarithm of the time of set given in Tables I to VI for each of the six mixtures was obtained. This was plotted as ordinate against the reciprocal of the absolute temperature as abscissa. A typical set of curves for the "C" brand is shown in Fig. 1. From the curves for the six mixtures of each brand of silicate, the slope was obtained. The curves were found to be linear. These values are tabulated in the following table:

TABLE VII

Values for the Slope of the Curves for Log Time of Set against Reciprocal Absolute Temperature

Mixture	Brand "S"	"N"	"K"	"U"	"C"	"B.W."
			(Values in degrees)			
0	3668.	3640.	3638.	3662.	3660.	3512.
1	3632.	3625.	3690.	3675.	3644.	3616.
2	3673.	3600.	3607.	3666.	3648.	3582.
3	3667.	3618.	3625.	3666.	3635.	3593.
4	3628.	3581.	3620.	3600.	3628.	3584.
5	3601.	3569.	3608.	3572.	3628.	3600.

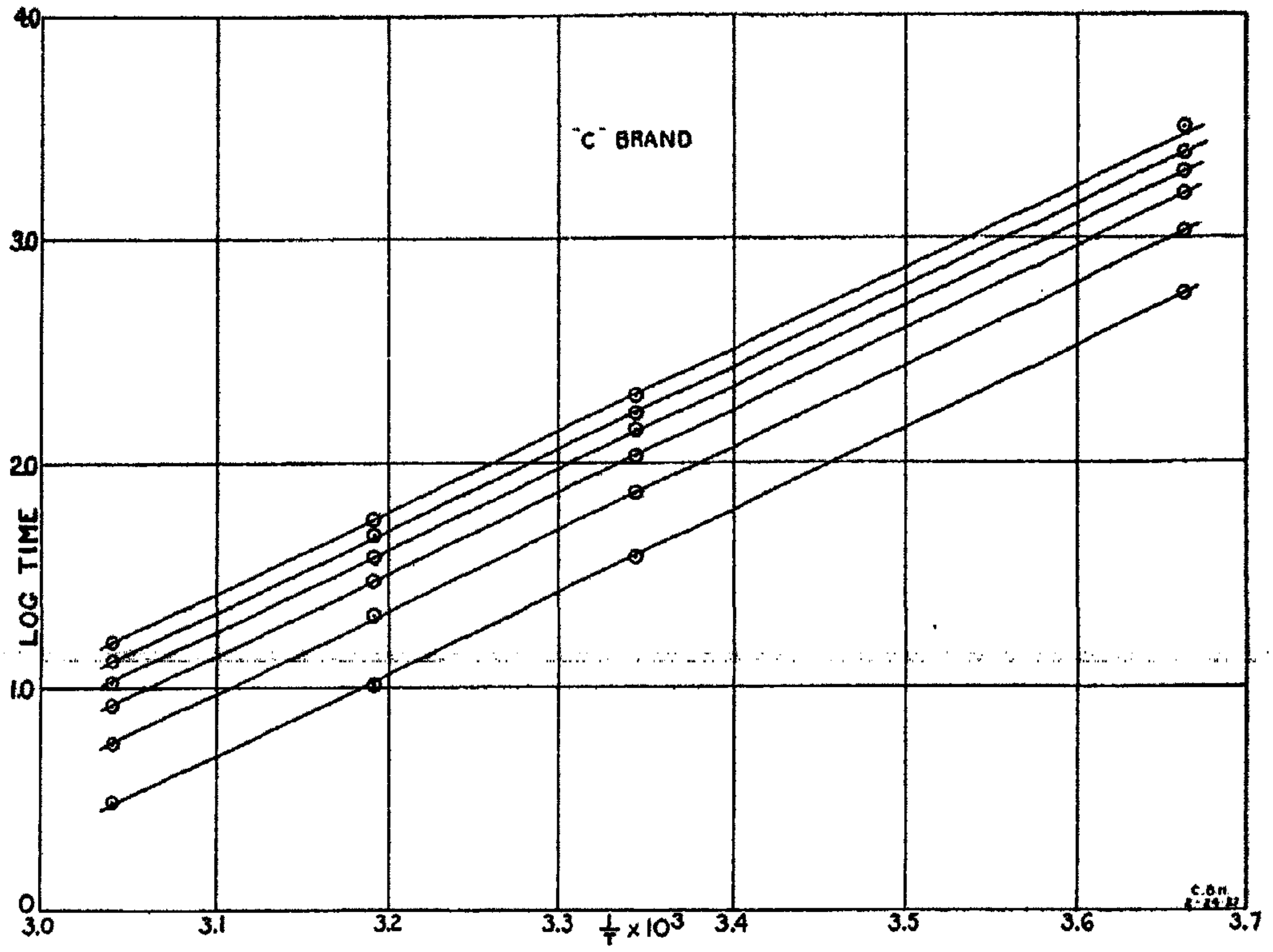

FIG. 1
Effect of Temperature on Time of Set.

The values are seen to show good agreement except for the "B.W." brand. The mixtures for this silicate, except those at 0°, showed curdling, as has been mentioned. Their lack of agreement is, therefore, to be expected. The curdling was more pronounced, the higher the temperature. It seems reasonable to assume that where curdling occurred, the concentration of reacting substances in the solution would be decreased. This would result in a slower reaction and a larger value of log time of set at higher temperatures. This would flatten the log t′ against 1/T curves and would give smaller values for the slope. This agrees with the results in Table VII for the "B.W." brand.

Interpretation of Results

As one of us has suggested in a previous paper,[1] we may make certain assumptions in our interpretation of these results. These assumptions are not unreasonable, and they lead to interesting results. They are:

1. That we are dealing with a process which follows the laws of ordinary chemical reactions so far as its velocity is concerned.

2. That Arrhenius' equation may be applied to our results.

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[1] C. B. Hurd and H. A. Letteron: J. Phys. Chem., 36, 604 (1932).

3. That for a given run the time of set measures the time when a certain fixed proportion of the silica, in whatever form, has reacted.

These assumptions are discussed in the paper to which reference has been made. If we develop our ordinary equations for the velocity of a chemical reaction where

x = amount changed in time, t
a = original concentration
n = order of reaction

we shall obtain the following familiar equations:

$$\frac{dx}{dt} = k(a-x)^n \tag{1}$$

$$\frac{dx}{(a-x)^n} = kdt \tag{2}$$

gives

$$\frac{1}{n-1}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right] = kt \tag{3}$$

It is easily shown for any fractional change of the concentration a, that the time, t′ is given by the relation

$$t' = \frac{c'}{ka^{n-1}} \tag{4}$$

where c′ = constant depending upon fraction x/a and on n.

We may now write Arrhenius' equation

$$\frac{d \ln k}{dT} = \frac{Q}{RT^2} \quad \text{or} \quad \frac{d \ln k}{d\, 1/T} = -\frac{Q}{R} \tag{5}$$

From (4) we obtain

$$\ln t' = \ln c' - \ln k - (n-1) \ln a \tag{6}$$

If now we maintain a and x/a constant, we may obtain from (5) and (6)

$$\ln t' = +\frac{Q}{RT} - (n-1) \ln a + c'' \tag{7}$$

From our values of Table VII, obtained as the slope of the curves for log t′ against 1/T illustrated by Fig. 1, we may obtain values for the heat of activation, Q, for the setting process for gels from the six brands of water glass. They are obtained by multiplying the values given in Table VII by 2.303 R, since by equation (7)

$$\frac{d \ln t'}{d\, 1/T} = \frac{Q}{R}.$$ Table VIII gives the results.

TABLE VIII

Values of the "Heat of Activation" for the Setting of Silicic Acid Gels

	"S"	"N"	"K"	"U"	"C"	"B.W."
0	16795	16667	16657	16767	16757	16080
1	16630	16595	16895	16826	16684	16555
2	16815	16483	16515	16786	16702	16401
3	16790	16952	16595	16786	16643	16451
4	16612	16395	16575	16483	16612	16410
5	16505	16342	16520	16350	16612	16482
mean	16691	16572	16626	16666	16668	16397

These figures show remarkable agreement. An estimate of the possible error from the accuracy of the timing and temperature measurements, considering that in all cases the logarithm of time plotted was the mean of at least two separate determinations, gives as the maximum probable error in the value of the "heat of activation" less than 2%.

It is noticeable, however, that the six values for each brand, going downward in each vertical column in Table VIII, show a drift toward lower values. That is, a general decrease in the heat of activation is shown for each brand as the acidity of the mixtures increases. This decrease is not large, but since it occurs in each of the five columns, it is apparently not the result of error. We should note at this point, of course, that it is more difficult to thermostat a 250 cc. Erlenmeyer flask and its contents for three days at 0° than it is to keep the contents of a beaker at 26° for three hours, but errors in the ice bath readings alone could not alter the slope of the curves. They are the result of points obtained from data at all four temperatures.

Formulation of a Theory. It is difficult to formulate a theory which shall give a clear picture of the process of setting of a silicic acid gel and which shall, of course, be subject to verification or rejection on the basis of experimental results. As has been pointed out in the preceding paper, the lack of sufficient quantitative data constitutes a real difficulty. From a study of existing data, however, and a consideration of certain of our own experimental results, a part of which are as yet unpublished, we are prepared to suggest the following theory for examination.

When a solution of sodium silicate and a dilute acid are mixed, a practically instantaneous reaction occurs, forming silicic acid and the sodium salt of the acid used, the latter, of course, mainly in the ionized form. The silicic acid particles slowly coalesce to form a structural framework for the gel. Beyond a certain stage, this process proceeds rapidly. The mechanism of linkage appears to be that of the splitting out of water from two hydroxyl groups of neighboring molecules of silicic acid. This agglomeration continues until the whole mass is filled with a fibrillar framework.

There is, in the literature, sufficient evidence to convince us that the exclusion of the solid-solution theory supported by Katz[1] and the emulsion

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[1] Katz: Kolloidchem. Beihefte, 9, 1 (1918).

theory, supported by Wo. Ostwald[1] is justified. Certain work under investigation in this laboratory, on the electrical conductivity of mixtures of sodium silicate and acetic acid during the process of setting, cause us to favor the fibrillar or brush-heap theory rather than the cellular theory.

It is impossible to give any definite reference for the genesis of the idea of the splitting out of water molecules from hydroxyl groups of neighboring molecules of silicic acid. It is a common idea to be found in both organic and inorganic chemistry. Compare the discussion on the polysilicic acids in Mellor.[2] The formation of higher silicic acids, in connection with silicic acid gels has been mentioned by Jordis[3] while the idea of chains held together by chemical forces in the silicic acid gel was stated by Gaunt and Usher.[4] They have even postulated a long, highly hydrated chain to give the ratio of metasilicic acid. The linkage is through oxygen atoms.

A similar idea in the organic field has been suggested by Kienle[5] in a theory for the formation of artificial resins. It should be noted that in this case the condensation takes place between hydroxyl groups on molecules of different substances, such as glycerine and phthalic acid.

We had believed, when starting this research, that a difference might be found in the time of set and in the effect of temperature on the time of set if the composition of the original sodium silicate could be varied considerably. This we have done, varying the $Na_2O:SiO_2$ ratio from 1:3.86 in the "S" brand which gives a mol ratio of 1:3.99 or essentially 1:4., down to a mol ratio of 1:1.63 for the "B.W." brand. If the process of gel formation requires the formation of chains of partially dehydrated silicic acid, formed by the splitting out of molecules of water from neighboring hydroxyl groups, it is evident that in a solution in which the process has already partially occurred, such as a solution containing trisilicic acid, the gel formation should occur more rapidly than in a solution containing ortho or metasilicic acid. It is conceivable though not necessarily probable, that the effect of temperature on the rate of reaction should be different.

It is, of course, not at all certain that we have in the solution of the "S" brand, let us say, any different form of silicic acid than we have in the solution of any of the others, although one might expect to find sodium salts of the higher silicic acids in those samples of silicate where the ratio of the number of mols of silica to one of soda is high, such as the "S" brand with the mol ratio $Na_2O:SiO_2$ of 1:3.99.

It has been shown in various studies of aqueous solutions of sodium silicates, such as the work of Kahlenberg and Lincoln[6] on the lowering of the freezing point and the electrical conductivity of solutions of sodium meta-

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[1] Wo. Ostwald: "Theoretical and Applied Colloid Chemistry," translated by Fischer, 103 (1917).

[2] J. W. Mellor: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 6, 308 (1925).

[3] E. Jordis: Z. anorg. Chem., 44, 200 (1905).

[4] Gaunt and Usher: Trans. Faraday Soc., 24, 32 (1928).

[5] R. Kienle: Ind. Eng. Chem., 22, 590 (1930).

[6] L. Kahlenberg and A. T. Lincoln: J. Phys. Chem., 2, 77 (1898).

silicate, $Na_2SiO_3 \cdot 9H_2O$, that the experimental evidence shows the influence of 2 Na and 2 OH ions but shows no evidence of a SiO_3 ion. This hydrolysis had been mentioned previously by Kohlrausch. On the other hand, Harman[1] presents evidence to show the existence of the SiO_3 anion in solutions of silicates of low soda-silica ratio, such as 1:1, but he states that in solutions of high ratio such as 1:3 or 1:4 the simple SiO_3 ion is not present, but there are present either aggregations of simple silicate ions with or without colloidal silica or definite complex silicate ions.

We feel, therefore, unable to state with certainty that we are starting our reaction with silicic acid in different form, from the "S" brand down to the "C" brand. Our results show, however, that the effect of temperature on the time of set is the same, from the "S" to the "C" ratios in acid solutions, as is shown by the values given in Table VIII.

It would be very interesting to discover whether the actual time of set is affected by the original soda-silica ratio, in two solutions having the same final sodium hydroxide, silica and acetic acid concentrations, one of which was produced by adding acetic acid to a low soda-silica ratio silicate such as the "C" brand with its ratio $Na_2O:SiO_2$ = 1:2.06 mol ratio while the other was made by adding sodium acetate and acetic acid to a solution of a silicate such as the "S" brand with a soda-silica ratio 1:4, mol ratio. We cannot answer this question from the results given in this paper, but the results of a series of determinations of this type at present under way in this laboratory should answer the question as to whether the original condition of the silica affects the time of set.

A comparison of the values of the "heat of activation," mentioned in this paper, the average being Q = 16,640 calories with the average value obtained in the previous paper by Hurd and Letteron, Q = 16,940 calories, confirms the results given in that paper with much greater accuracy.

Summary

The time of set of various mixtures of solutions of six different commercial sodium silicates with acetic acid at four different temperatures have been determined. The soda-silica ratios range from 1:4.0 to 1:1.63 mol ratio. The temperatures were approximately 0°, 26°, 40° and 56°C.

The effect of temperature on time of set was found to be the same, regardless of the soda-silica ratio. A value was obtained for a quantity analogous to Arrhenius' heat of activation for a homogeneous chemical reaction. The average value of 16,640 calories was obtained. The data given here confirm the former results, obtained by Hurd and Letteron, on various mixtures of one sample of sodium silicate with acetic acid.

A theory for the mechanism of formation of a silicic acid gel has been suggested.

The theory has been considered from the point of view of the effect of the temperature on the time of set.

Schenectady, N.Y.

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[1] R. Harman: J. Phys. Chem., **29**, 1155 (1925); and more especially **30**, 359 (1926).

PHOTOCHEMICAL REDUCTION OF CARBON DIOXIDE IN AQUEOUS SOLUTION

BY M. QURESHI AND S. S. MOHAMMAD

Since the advent of the formaldehyde theory of photosynthesis, suggested by M. Berthelot in 1860 and formulated clearly by Baeyer in 1870, a number of attempts have been made by different workers to reduce carbon dioxide with the help of light-energy in the laboratory. The ordinary 'dark' reaction, involving the reduction of carbonic acid to formic acid by means of nascent hydrogen in the presence of alkalies, discovered by Kolbe and Schmidt[1] and confirmed by Malay[2] and Ballo,[3] was shown by Lieben[4] to be unaffected by light. Fenton[5] was able to accomplish the reduction of CO_2 in aqueous solution direct to formaldehyde without the intermediate formation of formic acid, by means of metallic magnesium. There is nothing in the literature, as far as the writers are aware, to prove that this reaction is influenced by light.[6] Losanitsch and Jovitschitsch,[7] and Löb[8] tried the effect of silent electric discharge, which may be regarded as equivalent to that of the short wave ultra-violet light, on the system, CO_2 + water vapour, and found formic acid and formaldehyde, among the products of the reaction.

D. Berthelot and Gaudechon,[9] using ultra-violet light from a quartz mercury lamp, succeeded in obtaining formaldehyde from mixtures of carbon dioxide and hydrogen, and CO and hydrogen, but failed to obtain formaldehyde from CO_2 and water. Stoklasa and Zdobnicky[10] found that CO_2 was reduced to formic acid by nascent hydrogen in the presence of potassium hydroxide. When ultra-violet light was used and other conditions remained the same, formaldehyde and sugar were formed. No formaldehyde was obtained by the action of ultra-violet on CO_2 and water, unless nascent hydrogen and potassium hydroxide were also present. Contrary to this, Usher and Priestley[11] and Baly, Heilbron and Barker[12] claimed to have got formaldehyde by exposing aqueous solutions of CO_2 to ultra-violet light. Spoehr,[13] Baur and

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[1] Ann., 119, 251.

[2] Ann., 135, 118.

[3] Ber., 6 (1884).

[4] Monatshefte, 1895-1897.

[5] J. Chem. Soc., 1907, 687.

[6] Quantitative experiments carried out in this laboratory show that the reaction is not influenced by light. Dhar has, however, recently reported to the contrary in 'Nature' of Feb. 6, 1932.

[7] Ber., 30, 135 (1897).

[8] Z. Elektrochemie, 1906, 1174.

[9] Compt. rend., 150, 1690 (1910).

[10] Biochem. Z., 30, 432 (1911).

[11] Proc. Roy. Soc., 84B, 101 (1911).

[12] J. Chem. Soc., 119, 1025 (1921).

[13] J. Am. Chem. Soc., 45, 1184 (1923).

Rebmann,[1] Baur and Büchi,[2] and Porter and Ramsperger[3] on repeating the work of the above-mentioned authors failed to obtain any trace of formaldehyde or sugars. The work of Porter and Ramsperger proved the importance of exercising extreme care in avoiding contamination of materials with organic matter in experiments of this nature. Positive tests for formaldehyde were invariably obtained whenever CO_2 came in contact with wax or grease; whereas negative tests were obtained when the joints were replaced by quartz-to-glass seals. Baly and collaborators[4] in a later paper claimed to have obtained complex compounds of the nature of carbohydrates by exposing aqueous solutions of CO_2, in which white insoluble powders, capable of adsorbing carbonic acid were suspended, to the action of ultra-violet light. Aluminium powder, barium sulphate, freshly precipitated aluminium hydroxide and the basic carbonates of aluminium, magnesium and zinc were employed. Mezzadroli and co-workers[5] obtained formaldehyde and small quantities of sugar by exposing solutions of bicarbonates of different metals to ultra-violet light.

Attempts were also made by many workers to reduce CO_2 in the visible light or sunlight in the presence of various inorganic and organic catalysts. Moore and Webster[6] claimed to have effected the synthesis of formaldehyde from CO_2 and water in sunlight by employing various inorganic catalysts such as uranyl salts, colloidal ferric hydroxide, etc. Baly and Heilbron[7] also obtained formaldehyde by exposing solutions of CO_2 to visible light in the presence of chlorophyll, malachite green, and methyl orange. Spoehr, Baur and Rebmann and Baur and Büchi, in the works already cited, failed to confirm the results of the above-mentioned authors. The whole subject of photosynthesis in vitro received a fresh stimulus through the publication of a series of papers by Baly and his collaborators,[8] in which the authors claimed to have obtained carbohydrates through the reduction of carbonic acid adsorbed on the surface of coloured powders in the visible light. The powders employed were freshly prepared pure basic carbonates of nickel, and cobalt. On passing CO_2 through conductivity water containing the above powders in suspension, and exposing it to the light of an ordinary tungsten lamp or a 100 watts half-watt lamp, deductable quantities of organic matter, were obtained within two hours. The photosynthesis of organic matter ceased after two hours, owing to the poisoning of the surface of the catalyst, and greater intensity of illumination led to the decomposition of carbohydrates already formed. In later experiments, nickel carbonate, prepared electrolytically and activated by exposure to white light for six hours, was used.[9] Recently Baly[10] has described

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[1] Helv. Chim. Acta, **5**, 828 (1922).
[2] Helv. Chim. Acta, **6**, 959 (1923).
[3] J. Am. Chem. Soc., **47**, 79 (1925).
[4] Proc. Roy. Soc., **116A**, 197 (1927).
[5] Atti Accad. Lincei, (6) **6**, 160 (1927).
[6] Proc. Roy. Soc., **87B**, 163 (1913).
[7] J. Soc. Chem. Ind., **40**, 377R (1921).
[8] Proc. Roy. Soc., **116A**, *212, 219 (1927)*.
[9] Proc. Roy. Soc., **122A**, 393 (1929).
[10] Trans. Faraday Soc., **27**, 545 (1931).

another series of experiments, in which nickel carbonate, ferric oxide, and chromium oxide, supported on aluminated Kieselguhr, were found to be efficient in the photosynthesis of carbohydrates. It is claimed that with such supported catalysts, 0.0025 grms of organic matter can be synthesized per one gram of the powder used in two hours. Bell,[1] on repeating the work of Baly and collaborators, fails to obtain any indication of photosynthesis.

Dhar and Sanyal,[2] employing direct sunlight, claimed to have obtained formaldehyde from aqueous solutions of CO_2 alone and in the presence of inorganic and organic 'photo-catalysts,' such as ferric chloride, colloidal ferric hydroxide, copper sulphate uranyl nitrate, chromium sulphate, methylene blue and methyl orange. This was, however, contradicted by Burk,[3] who failed to obtained a a positive test for formaldehyde, by making use of pure reagents and concentrated sunlight. In view of the objections raised by Burk, G. Rao and Dhar[4] repeated the experiments of Dhar and Sanyal, with some additions, and still obtained positive tests for formaldehyde and in some cases for carbohydrates. Recently, Atma Ram and Dhar[5] have published another paper, dealing with the same subject in which a great variety of coloured catalysts including those already used, has been employed. It is claimed that aqueous solutions of sodium bicarbonate mixed with some of these coloured catalysts and exposed to direct sunlight in sealed glass bulbs for many hours give positive tests for formaldehyde and carbohydrates.

The above review of the literature on the subject of photosynthesis in vitro, while showing the contradictory nature of results obtained by various workers in this important field of research, indicates the necessity of repeating the work already done and exploring fresh avenues of attack on the problem. The following is the first instalment of the work that is being conducted in this laboratory in this connection.

Experimental

The experiments detailed below were performed with three different sources of light, namely quartz mercury vapour lamp, direct sunlight, and tungsten filament lamps. All the chemicals employed were either Kahlbaum's special reagents or Merck's extra pure chemicals. In certain doubtful cases, they were prepared freshly in the laboratory or purified by recrystallisation. In many cases, two control experiments, one with simple water to guard against the contamination of CO_2 and another without CO_2 to test the action of light on the substance employed as a catalyst were performed. The water used for the preparation of solutions and for the purposes of tests was twice-distilled conductivity water. The carbon dioxide gas, employed in these experiments, was obtained by the action of pure hydrochloric acid on marble and passed through four wash bottles, containing chromic acid, sulphuric acid, and conductivity water, before use. When grease is not employed on the

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[1] Trans. Faraday Soc., 27, 771 (1931).

[2] J. Phys. Chem., 29, 926 (1925).

[3] J. Phys. Chem., 31, 1338 (1927).

[4] J. Phys. Chem., 35, 1418 (1931).

[5] J. Phys. Chem., 36, 567 (1932).

joints of the apparatus, simple washing of the gas with conductivity water is quite enough. The tests employed were as follows: Schryver's test for formaldehyde; Schiff's reagents (modified by Denige) for aldehydes in general; Tollens' reagent, reduction of mercuric acid and permanganate of potash for formic acid; Molisch test for carbohydrates; Fehling's solution for reducing sugars and formaldehyde; Benedict's solution for reducing sugars only. Since a large portion of these experiments depend for their reliability on the purity of materials used and the care taken in the application of Schryver's test, it was thought necessary to find out by preliminary examination, the degree of sensitiveness and the optimum conditions for the successful application of the test. Examination with known solutions of formaldehyde of varying strength showed that this test is capable of detecting easily one part formaldehyde in 10^6 to 10^7 parts water. Even at this low concentration a clear pink colour develops within one second of the addition of the reagents, provided (1) the reagents are freshly prepared and (2) the amount of hydrochloric acid added is not below a certain limit. If the reagents are not freshly prepared the time required for the development of the colour increases. The amount of hydrochloric acid most suitable for the immediate development of the colour was found by taking 10 cc. of a solution of formaldehyde (1 in 10^6) and noting the time required for the appearance of pink colour after adding 2 cc of a 1% freshly prepared solution of phenylhydrazine hydrochloride, 1 cc of a 5% freshly prepared solution of potassium ferricyanide and varying amounts of hydrochloric acid (sp. gr. 1.126). The results tabulated in Table I show that the time decreases with increasing amount of hydrochloric acid, reaches a minimum with 3 cc of the acid, and then becomes constant with further increase in the amount of the acid.

TABLE I

Amount of HCl. (sp. gr. 1,126) added to 10 cc of the solution	Time required for the appearance of the pink coloration
1. 2 drops of HCl.	8 seconds
2. 4 " " "	5 "
3. 0.5 cc " "	3 "
4. 1.0 " " "	2.5 "
5. 2.0 " " "	1.5 "
6. 2.5 " " "	1.2 "
7. 3.0 " " "	within one second
8. 3.5 " " "	" " "
9. 4.0 " " "	" " "
10. 5.0 " " "	" " "

The pink colour changes into muddy red and then into purple after a few hours. It may be pointed out that simple conductivity water also develops a slight purple colour after 24 hours.

(a) *Experiments in Ultra-Violet Light.*

(1) A medium-sized flask of fused transparent quartz, containing conductivity water was placed at a distance of 6 inches from a quartz mercury vapour lamp of horizontal type, burning at 230 volts, 3.5 amps, and a fairly rapid stream of CO_2 was passed through it. The lamp was provided with a reflector at its back. The gas after bubbling through the illuminated water passed on to another flask, containing conductivity water, which was shielded from light. No positive test for formaldehyde or sugar was obtained with any of the two solutions after exposures extending from 2 to 24 hours.

(2) A vertical quartz mercury lamp of the immersion type (110 volts, 3.5 amps), manufactured by Hanovia Company was surrounded by a quartz jacket, through which water was kept running. The lamp, together with the jacket, was placed in a quartz beaker containing conductivity water, the latter being surrounded by a cylindrical vessel of copper, nickel-plated from inside. The lamp was started and kept running for periods of time varying from one to 24 hours, while a continuous stream of CO_2 was passing through the conductivity water. As before, no formaldehyde or carbohydrates could be detected. Experiments were repeated with barium sulphate and aluminium bicarbonate, suspended in conductivity water, but without success.

(3) Next monochromatic ultra-violet light was tried. The mercury lines 254 and 313 mμ were isolated by the following filters and filter combinations.

254 mμ	Chlorine gas at 1 atm. pressure in a vessel of fused transparent silica with plane paralleled sides—thickness 4 cm.
313 mμ	(1) Potassium chromate 0.2034 grm per litre (2) p-nitroso-dimethylaniline 0.014 grm per litre in two separate quartz cells 0.5 cm. each.

Carbon dioxide was passed through conductivity water placed in a small quartz flask placed immediately behind the filters. Exposures up to 32 hours failed to reveal any trace of formaldehyde.

(b) *Experiments in Sunlight.*

Two series of experiments were performed in direct sunlight; and in view of the repeated claims made by Dhar and and collaborators,[1] many inorganic and organic catalysts employed by these authors, were used. In the first series of experiments, a fairly rapid stream of CO was passed through the solutions or suspensions, contained in flasks of pyrex placed in direct sunlight. In another closed flask, containing the same amount of materials and exposed for the same length of time, side by side with the first, no CO was passed. At the end of each experiment solutions were filtered and distilled under reduced pressure. The distillate was tested for formaldehyde, while the residue in the flask, after being evaporated to dryness and extracted with pure methyl alcohol, was

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[1] Dhar and collaborators: J. Phys. Chem., **29**, 926 (1925); **35**, 1418 (1931); **36**, 567 (1932).

examined for the carbohydrates. When formaldehyde was detected, it was estimated colorimetrically with the help of a colorimeter of a Duboscq type, made by the Klett Manufacturing Company. The results are tabulated in Table II.

TABLE II

	System exposed	Time of exposure	Formaldehyde or carbohydrate detected	Estimated amount
1.	Conductivity Water + CO_2	4,6,12	none	
2.	Conductivity Water + CO_2 + Copper Sulphate	4,6	"	
3.	Conductivity Water + CO_2 + Ferric Chloride	4,6	"	
4.	Conductivity Water + CO_2 + Basic Nickel Carbonate	2,4,6	"	
5.	Conductivity Water + CO_2 + Basic Cobalt Carbonate	2,4,6	"	
6.	Conductivity Water + CO_2 + Chromium Sulphate	4,6	"	
7.	Conductivity Water + CO_2 + Manganous Chloride	4,6	"	
8.	Conductivity Water + CO_2 + Methyl Orange	4	Formaldehyde	0.0002%
9.	Conductivity Water + Methyl Orange	4	"	nearly the same
10.	Conductivity Water + CO_2 + Malachite Green	4	"	0.00012%
11.	Conductivity Water + Malachite Green	4	"	nearly the same
12.	Conductivity Water + CO_2 + Colloidal Chlorophyll	6	"	0.0001%
13.	Conductivity Water + Colloidal Chlorophyll	6	"	nearly the same

In the second series of experiments, 100 cc of solutions were sealed in bulbs blown from ordinary glass and exposed to direct sunlight, usually between 10 in the morning and 4 in the afternoon. Tests were carried out as described above. The results are given in Table III.

TABLE III

	System exposed	Time in hours	Formaldehyde or Carbohydrate	Estimated amount %
1.	Conductivity water saturated with CO_2	65	none	
2.	5% Solution of sodium hydroxide saturated with CO_2	50	"	
3.	5% Solution of NaOH	50	"	
4.	5% Solution of sodium bicarbonate (Merck's)	50	Formaldehyde	0.0002
5.	5% Solution of sodium bicarbonate prepared in the laboratory	"	none	
6.	3% Sodium bicarbonate (Merck) 1 gm basic $NiCO_3$	"	Formaldehyde	0.00018
7.	Conductivity water (freshly boiled) + basic $NiCO_3$ (1 grm) sealed after evacuation	65	none	
8.	Water + $NiCO_3$ + Impurities	55	Formaldehyde	0.0002
9.	Conductivity water (freshly boiled) + copper acetate (1 grm) sealed after evacuation	55	Formaldehyde	0.0005
10.	Colloidal Chlorophyll (0.0048 grm per 100 cc) sealed after evacuation	19 completely decolorized	"	0.0001

(c) *Experiments in the Light of a Tungsten Filament Lamp.*

These experiments were performed with finely powdered basic carbonates of nickel and cobalt purified according to the method described by Baly and collaborators in one of their papers, on "the photosynthesis of naturally occurring compounds."[1] The carbonates after being washed free from alkali were dried at 100° and activated by exposure to the light of a quartz mercury lamp for 30 minutes. Ten grams of these powders were suspended in 250 cc of conductivity water in a pyrex flask through which was maintained a continuous stream of CO_2. The flask was placed at a distance of 9 inches from a 500 watt tungsten filament lamp. After two hours exposure the contents of the flask were filtered and distilled under reduced pressure. The distillate was tested for formaldehyde while the residue in the flask, after being evaporated to dryness and extracted with pure methyl alcohol, was tested for carbohydrates. Experiments were repeated with increasing distances from the light source but no organic matter of the nature of carbohydrates was detected in the residue obtained after the evaporation of alcoholic extracts in a platinum

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[1] Baly and collaborators: loc. cit.

dish. Molisch test for carbohydrate in the residue as such and Benedict's test after hydrolyzing the residue with hydrochloric acid gave negative results. The exact weights of the residue obtained in the main and control experiments are shown in the following table. There is practically no difference between the amounts of residue in the photosynthesis experiments and the blank ones.

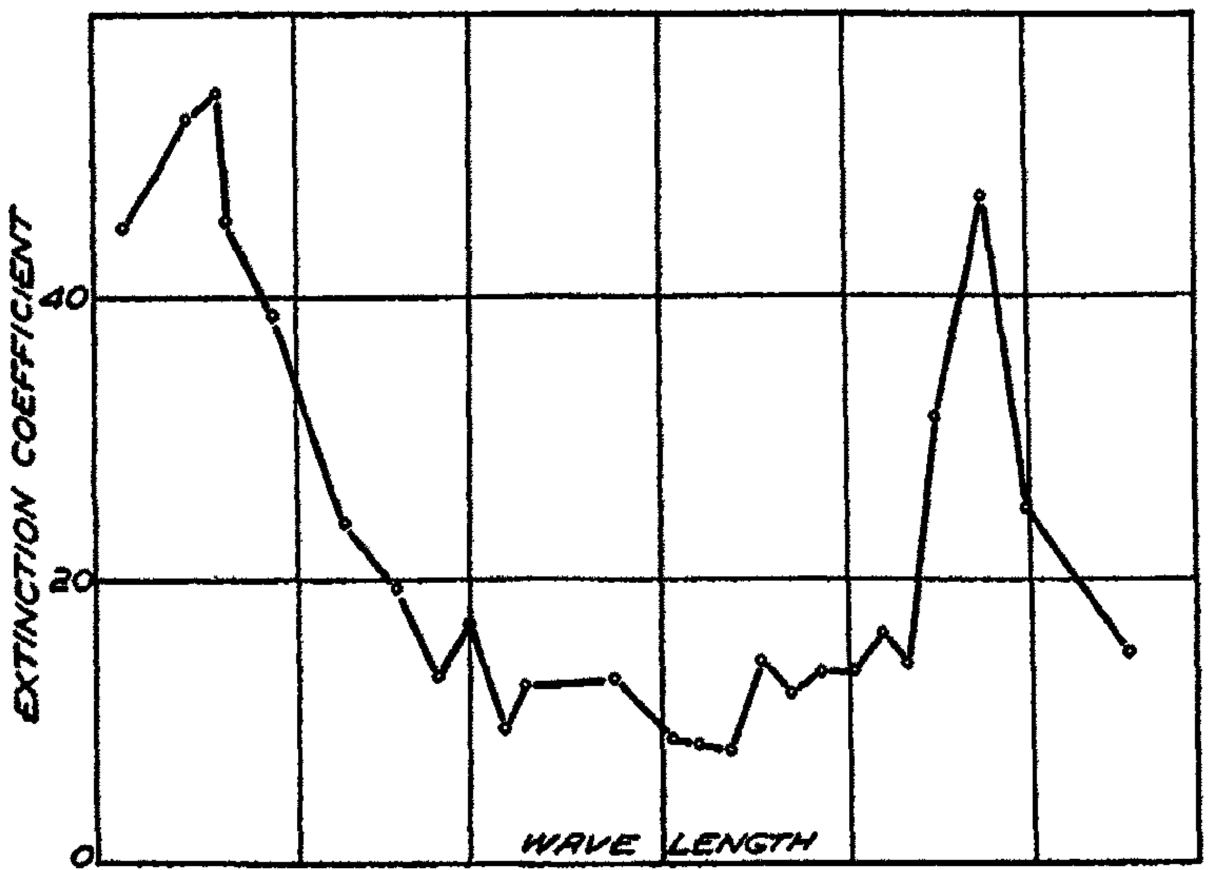
TABLE IV

Experiment	Total residue in grms.	Residue from Methyl Alcohol	Net residue in grms.
1. 10 grms of $NiCO_3$ in 250 cc of conductivity water, agitated in the dark for two hrs.	0.0070	0.0006	0.0064
2. 10 grms of $NiCO_3$ in 250 cc of water – CO_2 passed for 2 hours in the dark	0.0084	0.0006	0.0078
3. 10 grms of $NiCO_3$ in 250 cc of water, simply exposed for 2 hrs.	0.0076	0.0006	0.0070
4. 10 grms of $NiCO_3$ in 250 cc of water – CO_2 passed in the exposed solution for 2 hrs.	0.0086	0.0006	0.0080

Further experiments with electrolytically prepared nickel carbonate and supported catalysts, described by Baly and his collaborators in their recent publication are being carried out, and will be reported in due course.

(d) *Chlorophyll.*

Reference to the work of those investigators who have used chlorophyll as a 'sensitizer' in their experiments on photosynthesis shows that in many cases little or no mention is made of the state of purity of the preparations used. By the word 'chlorophyll' one can mean anything from a mixture of all the plant pigments to a definite chemical compound known as chlorophyll a or b. In the experiments mentioned above, specially pure chlorophyll (a) was always employed. It was prepared from the dried leaves of a kind of Indian nettle which grows wild in this part of the country by following in every detail the method employed by Willstätter and Stoll in their well-known work and described by them in "Untersuchungen über die Assimilation der Kohlensaure," Berlin, 1918. 100 grms of the dried materials yielded 0.273 grams of the pure pigment. The extinction coefficients of its solution in pure acetone for lights of different wave-lengths were determined by a spectrophotometer of of König and Martens type, made by Schmidt and Häensch (Berlin), using a pointolite lamp as a source of light. The results of these photometric measurements, given below, indicate two regions of highest absorption in the blue-violet and the red portion of the spectrum, at wave-lengths 432 and 641 mμ, respectively. In addition to the above, there are four adsorption maxima at 497, 537, 578 and 613 mμ. The region of least absorption lies in the yellow and green at 569 – 552 and 512 – 507 mμ. These results are also shown graphically in the form of an absorption-curve, Fig. 1.



ABSORPTION CURVE OF CHLOROPHYLL a

FIG. I

TABLE V

Concentration—0.00486 per cent.
Thicknesses—2.5, 5.5, 12.5 cms.

No.	Wave-length	Extinction coefficient	No.	Wave-length	Extinction coefficient
1.	682.4 mμ	14.8	14.	537.2 mμ	12.95
2.	653.6 "	25.3	15.	512.2 "	12.44
3.	641.6 "	47.2	16.	507.2 "	9.38
4.	628.8 "	31.57	17.	497.2 "	16.86
5.	620.4 "	14.10	18.	489.0 "	13.25
6.	612.6 "	16.20	19.	478.8 "	19.40
7.	605.0 "	13.70	20.	465.8 "	23.50
8.	595.6 "	13.58	21.	447.6 "	38.87
9.	586.8 "	11.95	22.	434.4 "	47.10
10.	578.4 "	14.30	23.	432.8 "	54.20
11.	569.7 "	7.85	24.	423.6 "	52.85
12.	560.8 "	8.50	25.	407.2 "	45.10
13.	552.6 "	8.80			

In order to prepare a colloidal solution of chlorophyll a, the following procedure, recommended by Willstätter and Stoll, was adopted:—

100 cc of a solution of chlorophyll a in acetone were poured into a beaker of one litre capacity. 400 cc of conductivity water, after being boiled and suddenly cooled to 30° by immersion in a freezing mixture, were poured at once into the chlorophyll solution and the beaker was constantly shaken until the solution turned green. This solution was now distilled under reduced pressure

at 30° – 35°, the receiver being placed in a mixture of salt and ice. As the distillation proceeded, more conductivity water was added from time to time by means of a thistle funnel, reaching to the bottom of the distilling flask. Within 3 to 4 hours, the whole of the acetone in the original solution was displaced by water. The distillation was continued until the distillate failed to give any test for acetone. The colloidal solution so prepared was coloured pure green and did not show any fluorescence.

Discussion

The results of our experiments on the action of heterogeneous and monochromatic ultra-violet light on carbonic acid in aqueous solution conclusively prove the incapacity of these radiations to bring about the required activation of carbonic acid. The positive tests for formaldehyde or sugars obtained by other investigators, were probably due either to the contamination of the materials used or to the lack of sufficient precautions in the application of the tests. Theoretical considerations too, rule out the possibility of obtaining positive results with the wave-length 313 mμ. According to the thermochemical equation,

$$6\ CO_2 + 6\ H_2O = C_6H_{12}O_6 + 6O_2 - 674000\ \text{cal.}$$

nearly 112,300 cals are required for the decomposition of one gram-molecule of carbonic acid.

This quantity of energy according to the quantum theory of photo-chemical action, must be present in N light quanta i.e.

$$112{,}300\ \text{cals} = N\ h\ \nu$$

putting the values of N (6.062×10^{23}) and the Planck constant h (6.547×10^{-27} ergs) the value of ν is found to be 1.18×10^{15} which corresponds to a wave-length of 255 mμ. This means that radiations of wave-lengths greater than 255 mμ do not contain sufficient amount of energy to decompose carbonic acid molecule in one step into formaldehyde or sugar. We have tried the effect of radiations of wave-length 254 mμ without any positive result. The next experiments should be tried with radiations of 200 mμ which according to Baly[1] are capable of reducing carbonic acid to formaldehyde.

Attempts to achieve photosynthesis in the visible light fall into two groups. To the first group belong the experiments in which organic and inorganic substances have been employed as sensitizers or "photo-catalysts." The results of our experiments in this connection as detailed in Tables II and III stand in clear contradiction to those of G. Rao, A. Ram and Dhar.[2] Where formaldehyde has been detected in the exposed solutions containing CO_2, it has been found in an almost equal amount in a blank experiment performed under identical conditions but without CO_2. There is hardly any room left for doubt as to the source of small quantities of formaldehyde obtained in the experiments of the authors, quoted above. It is most probably derived either from impurities present in the preparations used or from the photo-decomposition

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[1] Baly: J. Chem. Soc., **119**, 1025 (1921).

[2] J. Phys. Chem., **35**, 1418 (1931); **36**, 567 (1932).

of the materials themselves. Merck's chemicals are generally despatched in glass containers having a coating of wax on the corks or stoppers. Special care has to be exercised in the opening of these containers, as even a small quantity of wax or cork material finding its way into the contents, can render them quite unsuitable for a work of this nature. As an instance of this error, reference may be made to the experiments of the present writers with solutions of sodium bicarbonate, mentioned in Table III. While positive tests were often obtained by the use of Merck's extra pure chemical, not a trace of formaldehyde was to be found when sodium bicarbonate prepared in the laboratory with all the necessary precautions, was employed. Further, especially purified nickel carbonate gave negative results, when illuminated in the presence of CO_2, but the addition of a very small trace of grease led to a positive test for formaldehyde.

The danger of using organic substances such as chlorophyll, malachite green, methyl orange, and copper acetate, in experiments on photosynthesis in 'vitro,' is so obvious that one need not discuss it in any detail. Suffice it to say that all the four substances mentioned above, and a number of other organic compounds, give rise to formaldehyde under more or less strong illumination. A colloidal solution of chlorophyll a, prepared by the present writers by the method described above, gives positive indication of the formation of formaldehyde, both on illumination with CO_2 and without it. The same is the case with malachite green, methyl orange and copper acetate, the latter substance yielding comparatively large amounts of formaldehyde (see Table III).

In view of the above it is, therefore, not at all surprising that Atma Ram and Dhar should have obtained positive tests in their experiments referred to above, in which a current of CO_2 was passed in beakers containing chlorophyll, malachite green and copper acetate, suspended or dissolved in conductivity water and exposed to direct sunlight. No mention is made in the paper of Atma Ram and Dhar, of any blank experiment performed with the object of testing the action of light on these substances in the absence of CO_2 with the exception of a brief remark in the case of chlorophyll suspensions to the effect that formaldehyde was obtained in greater amount than when chlorophyll alone was exposed and distilled. The only reference to such control experiment is to be found in a previous paper by G. Rao and Dhar,[1] in which it is stated that comparative experiments were performed with chlorophyll and aniline dyes and in every case greater yields of formaldehyde were obtained in the presence of CO_2, than without it. From this it is concluded that CO_2 is reduced to formaldehyde in the presence of these dyes. In view of the fact that it is extremely difficult if not impossible, to perform experiments in the sunlight under exactly identical conditions the above conclusion is hardly justified. The passage of CO_2 with the consequent stirring of the mixture produces a difference in the conditions of the two experiments, which can lead to erroneous results. The experiments performed by the present writers show

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[1] G. Rao and Dhar: J. Phys. Chem., 35, 1418 (1931).

that the amounts of formaldehyde produced in the two cases, are the same within the experimental error.

The second group of experiments on 'photosynthesis in vitro' include those attempts in which coloured powders, capable of adsorbing carbonic acid on their surface, such as basic carbonates of nickel and cobalt have been employed. These experiments form a category by themselves because it is believed that in the presence of these surfaces, a molecule of carbonic acid is activated doubly; first through adsorption on the surface and secondly, through the absorption of the radiant energy. There are, no doubt, some good reasons in favor of this mode of approach to the problem and it receives a further support from the fact that photosynthesis in vivo is, to all appearance, a heterogeneous action taking place on the surface of the chloroplast in the leaves. But the present writers have so far failed to obtain any indication of photosynthesis by the use of these powders. It must, however, be admitted that the investigations of Baly and his collaborators open out vast possibilities of further research in this important line, which need be explored with increasing patience and skill. Further investigations on this line are being carried out in this laboratory, and will be reported in due course.

Summary

1. Experiments on the photochemical reduction of CO_2 in aqueous solution have been carried out in the ultraviolet, sunlight, and the light of tungsten filament lamps.

2. The results of experiments with heterogeneous and monochromatic ultra-violet light indicate that the light of wave-length 254 $m\mu$ is incapable of bringing about the required activation of carbonic acid.

3. Experiments, performed in direct sunlight with various inorganic and organic photosensitizers, suspended or dissolved in aqueous solutions of CO_2, give no indication of the reduction of CO_2 under these conditions, thus contradicting the claims put forward by Dhar and collaborators.

4. The experiments of Baly and collaborators have been repeated, using specially purified and activated basic nickel carbonate, with negative results.

5. Chlorophyll (a) was prepared in a pure condition from the dried leaves of an Indian nettle, in accordance with the method of Willstätter and Stoll, and its extinction coefficients for light of different wave-lengths determined with the help of a spectro-photometer of König and Martens type.

The colloidal solution of chlorophyll (a), and the ordinary solutions of pure malachite green, methyl orange and copper acetate after exposure to sunlight in sealed bulbs from which CO_2 was excluded, were found to contain formaldehyde.

7. The results have been compared with those of other workers and possible causes of the discrepancies pointed out.

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India, April 20, 1932.

STUDIES ON THE MECHANISM OF IONIC EXCHANGE IN COLLOIDAL ALUMINUM SILICATES*

BY HANS JENNY

Introduction

In 1819 the Italian chemist Gazzari[46] made the interesting observation that clay decolorizes liquid manure and retains soluble substances which in turn can be released to growing plants. Gazzari's work is perhaps the first study on exchange adsorption or ionic exchange which at present holds such a prominent place in general colloid chemistry. However, it was really the classical work of Thomas Way[52] on "The power of soils to absorb manure" which, in 1850, stirred the agricultural chemists and divided them into two hostile camps in regard to the nature of these processes. So revolutionary were Way's discoveries from the viewpoint of soil fertility that he himself came to the conclusion: "It cannot be regarded in any other light than as a direct impress of the wonderful hand of providence."

Way was the originator of the following instructive experiment: If a solution of KCl percolates through a column of soil, differential adsorption takes place. Only the positive part of the salt (K) is retained, while the negative (Cl) remains in the soil solution. In the place of the adsorbed potassium another element, mostly Ca, appears in the liquid phase.

This replacement is "wonderful" indeed, since the valuable element K, indispensable for plant growth, is retained by the soil and prevented from leaching at the cost of the common element Ca. For 80 years this experiment has remained the corner stone of all investigations on base exchange in soils. It has been confirmed again and again in various modifications. There is no general agreement, however, as to the mechanism of the phenomenon. Way was inclined to believe that the process was a chemical one, although he was aware of certain abnormal, non-chemical characteristics such as speed of reaction, influence of temperature, existence of lyotropic series and others. Liebig,[31] not knowing the law of mass action, vehemently opposed Way and advanced a physical explanation of adsorption. Since that time the disputation about the chemical or physical nature of base exchange in soils has not come to rest. The situation is quite similar to the one existing in the chemistry of proteins and in the explanation of adsorption in general colloid chemistry.

In studying the voluminous literature on ionic exchange one gains the impression that apparently the diversity of opinion is partly due to psychological prestige reasons, since the experimental material presented is in most cases not adequate to substantiate the conclusions drawn. Most of the workers picked up a random sample of soil and conducted experiments without

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* Contribution from the Department of Soils, Missouri Agricultural Experiment Station, Columbia, Mo. Journal Series No. 334.

knowing exactly what they were working with. Natural soils are too complicated and represent systems too variable to yield precise information about the mechanism of ionic exchange. Fortunately there are two promising ways to avoid this uncertainty of the nature of the adsorbent. One is the study of ionic exchange with artificial clays (zeolites, permutits); the other is the isolation of the colloidal fraction from soil and its subsequent purification by methods which do not affect the nature of the colloid. A systematic study with such artificial and purified colloids in which both the nature of the colloidal complex and the properties of the participating ions are considered should reveal a qualitative and quantitative insight into the mechanism of ionic exchange. Such was the aim of the investigation herewith reported.

Practical Significance of Ionic Exchange.

Aside from theoretical interest, ionic exchange is of far-reaching importance in soil studies and in many industrial problems. The fixation of fertilizers added to the soil is still the classical problem of applied ionic exchange. The ions adsorbed in soils can be easily utilized by plants; in the process of the liberation of nutrients by living organisms ionic exchange undoubtedly plays a very significant rôle.

It is being realized more and more that there is a relation between ionic exchange and soil formation. The first step in the weathering of aluminum silicates is an ionic exchange in which the hydrogen ions of water and carbonic acid replace the cations on the surface of the crystal lattice of the minerals. The differential leaching of K, Na, Ca, Mg, from soils is easily understood on the basis of the behavior of cations in the exchange adsorption.[25] Gedroiz[20] has even gone so far as to propose a scheme of soil classification which is based on the nature of the adsorbed ions on the colloidal soil complex. The great problem of the reclamation of alkali soils is now more fully understood. The important investigations of Gedroiz,[20] Sigmond,[47] Kelley,[27] Burgess[12] and others have shown that ultimately it is a base exchange reaction on a very huge scale.

Physical, as well as chemical, properties of soils are closely associated with exchange adsorption. Wiegner[59] and his pupils have been able to show that coagulation, dispersion, viscosity, hydration and structure of colloidal clays are greatly affected by the nature of the adsorbed ions. These observations have been confirmed by Baver[1] and others.

A direct consequence of base exchange studies with clays has been the invention of water softening[35] by the zeolite or permutit process, in which Ca-ions of the water are exchanged against Na-ions of the aluminum silicate. In sugar factories the principle of base exchange has become a vital factor in the development of refining methods. There are yet many possibilities for the application of base exchange in industry, such as in the tanning of leather, stabilization of emulsions and suspensions in general, manufacturing of milk products and others.

The Nature of the Colloidal Complex.

Colloidal clays found in natural soils exhibit crystalline properties. On the basis of Debye-Scherrer diagrams the presence of montmorillonite, beidellite, halloysite and bauxite in soils has been definitely established.[22,28] Fortunately, the recent work of Bragg[10] and Pauling[43] permits a deeper insight into the nature of these colloidal complexes. According to these investigators silicates are made up of ions which act as impenetrable spheres with characteristic diameters. On account of their abundance and large size the oxygen ions (r = 1.32Å) play an important rôle in the structure of aluminum silicates. The small but highly charged Si^{++++}(r = 0.39Å) and Al^{+++}(r = 0.57Å) ions are surrounded by four or six oxygen ions forming tetrahedrons or octahedrons which are considered the "building stones" of aluminum silicates. The remaining electric valence forces of the O^{--} ions are saturated by cations (K^+, Ca^{++}) which are packed in the interstices of the oxygen polyhedrons. The crystal is held together by the electrostatic forces existing between cations and anions. The packing of the building stones can be close or open. St. Naray-Szabo[57] expresses the density of the packing quantitatively by the "volume" occupied by one oxygen ion. From the viewpoint of ionic exchange it is very significant to note that mainly such crystallized aluminum silicates as have an open packing are distinctly capable of base exchange and adsorption. In the following selected list (Table I) the correlation between density of packing and ionic exchange capacity is indicated:

TABLE I

Packing of Oxygen Ions and Intensity of Ionic Exchange

Mineral	Formula	Volume per oxygen ion Å³	Ionic exchange
Corundum	Al_2O_3	14.0	Very little or none
Quartz	SiO_2	18.7	Little
Muscovite	$K(Al_2,Mg_3)(AlSi_3O_{10})(OH)_2$	19.2	Distinct
Nosean	$Na_6Al_6(SiO_4)_6.2Na_2SO_4$	23.1	Pronounced
Ultramarine	" " " "	23.1	Very pronounced

Pronounced ionic exchange is observed mainly in the natural and artificial zeolites which have such big interstices that large ions such as K^+ and Ba^{++}, as well as H_2O molecules can move freely in the interior of the crystals. Crystals with close packing exchange only at their outer surfaces. Their ability to adsorb ions depends, therefore, on the size of the colloidal particles. Thus, Kelley[28] was able to increase the exchange capacity of bentonite clays by mere grinding in a ball mill. On the other hand, Wiegner[55] demonstrated that in case of permutit gels (related to ultramarine in the above table) the degree of dispersion is without material effect upon ionic exchange. The importance of crystal structure in relation to ionic exchange is illustrated convincingly in Figs. 1 to 3. Al_2O_3 and SiO_2 simply do not permit ions to enter the crystals on account of the architectural arrangement of the oxygen ions. In the case of ultramarine the pattern of alternating aluminum and silicon tetrahedra furnishes large cavities consisting of a cubical space with an edge of 3.7Å and six crosswise arranged prolongations in which there is superfluous space for "wandering" constituents.[23]

On the basis of these modern pictures of aluminum silicates ionic exchange can be much better visualized than has been hitherto possible. The electronegatively charged framework of O^{--} and possibly OH^- ions acts as the attractive wall (inner layer of the Helmholtz double layer) for the adsorption of cations. The structural arrangement of the O^{--} ions remains undisturbed as long as the positive and negative electrical charges are balanced. The forces of attraction are mainly electrostatic in nature (except perhaps of H^+) and are greater the closer the cations can approach the oxygen ions. It is to be expected, therefore, that ions of different size and electric charge act differently both in their adsorption and release. The search for such relationships between ionic exchange and properties of the ions was one of the main objects of this investigation.

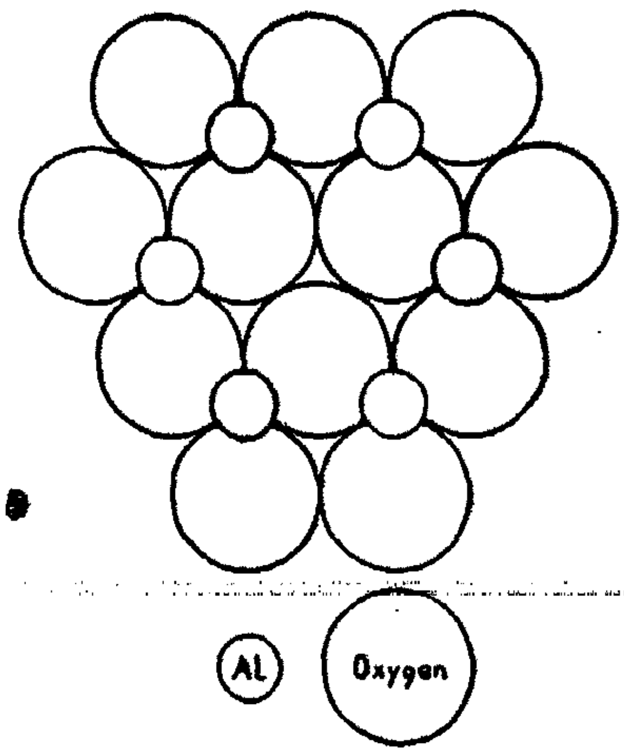

Fig. 1
Structure of aluminum oxide(Al_2O_3). Close packed system (Bragg[10]).

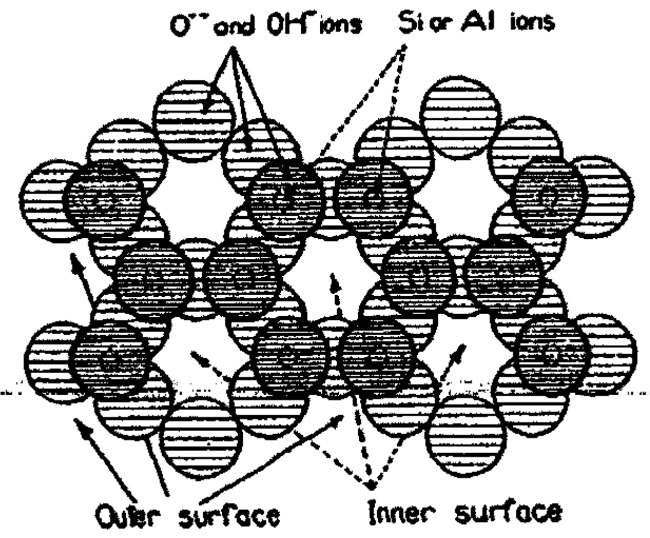

Fig. 2
Arrangement of oxygen ions in an open packed system (St. Naray-Szabo[37]).

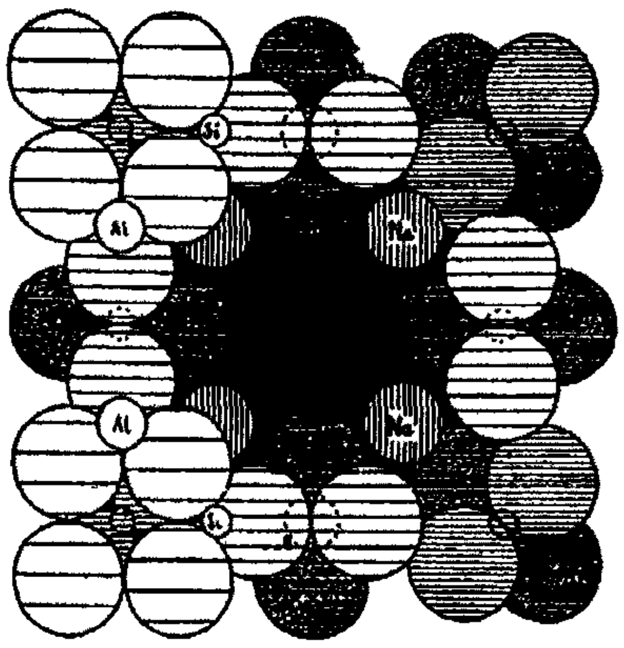

Fig. 3
Structure of ultramarine (Jaeger[23]). The large circles represent oxygen ions. Note the big cavity in the interior of the cell containing exchangeable Na ions.

Presentation of Experimental Material*

In these investigations ionic exchange studies were made on both artificial and natural colloidal aluminum silicates. *Artificial aluminum silicates:* Ordinary permutits furnished by J. D. Riedel in Berlin and Folin-permutit obtained from Arthur H. Thomas Company were converted into pure

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* Credit for part of the experimental work is due to E. R. Shade and W. H. Allison.

Table II

System: *NH_4 — permutit (Riedel) + monovalent cations.* 1 g. permutit containing 4.15 millequivalents exchangeable NH_4; volume 100 cc.; time of reaction 8-10 days; room temperature. y% = NH_4 exchanged in percentage of total exchangeable NH_4. a = milliequivalents of salt added.

NH_4-permutit (Riedel) + LiCl		NH_4-permutit (Riedel) + NaCl		NH_4-permutit (Riedel) + KCl		NH_4-permutit (Riedel) + RbCl		NH_4-permutit (Riedel) + CsCl		NH_4-permutit (Riedel) + HCl	
y%	a	y%	a	y%	a	y%	a	y%	a	y%	a
19.75	5.42	28.11	2.00	33.98	2.01	38.95	1.95	30.96	2.01	47.95	2.93
29.64	13.55	34.70	5.00	52.53	5.03	58.31	4.90	62.65	5.02	82.65	7.33
33.01	27.10	45.06	10.00	66.26	10.06	71.08	9.79	73.73	10.05	92.30	14.65
42.65	67.75	66.50	50.00	79.04	25.15	86.75	24.48	93.97	25.31	100.00	36.62
52.77	135.50	76.39	100.00	87.47	50.30	—	—	—	—	—	—
—	—	—	—	90.84	100.60	—	—	—	—	—	—

Table III

System: *NH_4 — permutit (Folin)[1] + monovalent cations.* 0.629 g. NH_4 — permutit containing 2.07 milliequivalents exchangeable NH_4; volume 250 cc.; time of reaction one week; room temperature. y% = NH_4 exchanged in percentage of total exchangeable NH_4. a = milliequivalents of salt added.

NH_4-permutit (Folin) + LiCl			NH_4-permutit (Folin) + NaCl			NH_4-permutit (Folin) + KCl			NH_4-permutit (Folin) + HCl		
y%	a	pH of supernatant liquid	y%	a	pH of supernatant liquid	y%	a	pH of supernatant liquid	y%	a	pH of supernatant liquid
8.53	1.171	7.13	24.04	1.000	6.91	31.56	1.004	7.50	40.60	0.963	6.55
19.28	2.928	7.15	38.55	2.500	—	50.38	2.509	6.95	83.90	2.407	—
25.08	5.856	7.15	53.04	5.000	7.15	69.66	5.018	6.82	97.10	4.814	3.61
35.18	14.640	7.08	60.60	12.499	6.89	83.96	12.545	7.26	98.75	12.035	2.37

[1] This NH_4-permutit contains small amounts of exchangeable H-ions.

Table IV

System: *$NH_4 - H -$ Putnam clay + monovalent cations.* 6.909 g. colloid containing 2.070 milliequivalents exchangeable NH_4; volume 500 cc.. time of reaction 10 days, room temperature, y% = NH_4 exchanged in percentage of total exchangeable NH_4. a = milliequivalents of salt added.

NH_4 – H – Putnam clay + LiCl				NH_4 – H – Putnam clay + NaCl				NH_4 – H – Putnam clay + KCl				NH_4 – H – Putnam clay + HCl			
y%	a	pH of sol	pH of supernatant liquid	y%	a	pH of sol	pH of supernatant liquid	y%	a	pH of sol	pH of supernatant liquid	y%	a	pH of sol	pH of supernatant liquid
34.40	1.171	5.20	5.72	27.62	1.078	5.24	5.76	37.72	1.004	5.16	6.00	52.18	0.963	4.70	5.20
40.72	2.928	5.20	5.15	39.45	2.695	5.24	5.22	57.95	2.509	4.90	5.26	87.32	2.407	3.53	3.41
50.38	5.856	4.95	4.76	50.50	5.389	4.81	5.27	70.23	5.018	4.62	4.36	90.30	4.814	2.76	2.70
63.81	14.640	4.62	4.74	62.85	13.473	4.78	4.80	78.92	12.545	4.24	4.25	93.92	12.035	2.13	2.12
72.80	29.280	4.44	4.55	73.28	26.945	4.49	4.49	91.28	25.090	4.10	4.02	95.50	24.070	1.69	1.70

Table V

System: *$NH_4 -$ Putnam clay + monovalent cations.* 4.955 g. colloid containing 4.15 milliequivalents NH_4; volume 500 cc., time of reaction 7 days, room temperature; pH of sol = 8.56. y% = NH_4 exchanged in percentage of total exchangeable NH_4. a = milliequivalents of salt added.

NH_4 – Putnam clay + LiCl				NH_4 – Putnam clay + NaCl				NH_4 – Putnam clay + KCl			
y%	a	pH of sol	pH of supernatant liquid	y%	a	pH of sol	pH of supernatant liquid	y%	a	pH of sol	pH of supernatant liquid
37.78	2.654	7.7	7.7	33.73	2.000	7.3	8.2	50.94	1.945	8.3	7.8
44.07	6.636	7.1	7.9	43.74	5.000	7.0	8.1	74.12	4.862	7.9	7.6
50.85	13.272	7.1	7.4	49.14	10.000	8.0	7.8	85.77	9.723	8.1	7.7
64.94	33.180	6.9	7.6	61.65	24.997	8.0	8.0	96.77	24.308	7.9	7.4
69.26	66.360	6.7	7.7	67.06	49.995	7.0	7.6	99.20	48.615	7.7	7.7

TABLE VI

System: *NH_4 — H—Putnam Soil + monovalent cations.* 10 g. of soil containing 2.279 milliequivalents exchangeable NH_4; volume 250 cc., time of reaction one week, room temperature. y% = NH_4 exchanged in percentage of total exchangeable NH_4. a = milliequivalents of salt added.

NH_4 – H – Putnam soil + LiCl			NH_4 – H – Putnam soil + NaCl			NH_4 – H – Putnam soil + KCl			NH_4 – H – Putnam soil + HCl		
y%	a	pH of sol	y%	a	pH of sol	y%	a	pH of sol	y%	a	pH of sol
25.81	1.171	5.60	25.81	1.000	5.44	34.41	0.972	5.34	37.26	0.963	4.15
37.26	2.928	5.24	37.26	2.450	5.20	37.35	2.431	4.84	65.95	2.407	3.02
45.86	5.856	5.10	43.01	5.000	5.00	68.82	4.862	4.78	82.86	4.814	2.22
54.48	14.640	4.74	48.74	12.499	4.70	77.42	12.154	4.55	91.75	12.035	—

TABLE VII

System: *NH_4 — H—bentonite + monovalent cations.* 2.850 g. colloid containing 2.195 milliequivalents exchangeable NH_4; volume 500 cc., time of reaction one week; temperature 28°C. y% = NH_4 exchanged in percentage of total exchangeable NH_4. a = milliequivalents of salt added.

NH_4 – H – bentonite + LiCl			NH_4 – H – bentonite + NaCl			NH_4 – H – bentonite + KCl			NH_4 – H – bentonite + HCl		
y%	a	pH of sol	y%	a	pH of sol	y%	a	pH of sol	y%	a	pH of sol
56.47	1.171	6.02	45.15	1.000	5.32	48.36	0.988	6.10	47.72	0.963	4.55
65.62	2.928	6.30	53.85	2.500	6.18	54.02	2.470	5.75	69.25	2.407	2.80
76.08	5.856	5.92	59.68	5.000	5.93	67.55	4.940	5.95	87.20	4.814	2.29
85.55	14.640	5.42	76.70	12.499	5.60	91.25	12.349	5.44	99.70	12.035	1.80
96.18	29.280	5.55	87.75	24.998	5.08	101.20	24.699	5.05	101.40	24.070	1.50

Li-Na-K-NH$_4$-permutits by leaching with chlorides for several months as previously described.[24] H-permutit was prepared by electrodialysis in a Bradfield three compartment cell.[6]

Natural aluminum silicates: Adopting the method of Bradfield,[4] soil collected from the B-horizon of the Putnam silt loam was churned and after standing for several days was run through a supercentrifuge in order to isolate the colloidal particles. According to the data of Baver[1] these are of the dimensions of 100-150 mμ (ϕ). Electrodialysis in Bradfield cells converted the clays, which originally contained various exchangeable cations, into pure hydrogen systems. Pure basic clays were then obtained by adding the proper amounts of LiOH, NaOH, KOH, or NH$_4$OH to the H-clays. Corresponding samples of bentonite clays from Wyoming were prepared in the same way. The amount of base added was equal to the saturation capacity of the clays which was determined by titration curves according to Bradfield[7] and by replacement of H$^+$ by KCl. Both methods gave very similar results.

The *exchange experiments* were conducted as follows: stock solutions of clay sols (3-5%) were transferred into volumetric flasks (250, 500 cc.), and redistilled, carbon dioxide-free water was added nearly up to the graduation mark. These colloid-water systems were kept for a week in a constant temperature room in order to permit the colloidal particles to reach the hydration

Table VIII

System: *NH$_4$-bentonite + monovalent cations.* 1.770 g. colloid containing 1.980 milliequivalents NH$_4$; volume 500 cc., time of reaction 10 days, room temperature; pH of sol = 8.56, y% = NH$_4$ exchanged in percentage of total NH$_4$. a = milliequivalents salt added.

NH$_4$-bentonite +LiCl			NH$_4$-bentonite +NaCl			NH$_4$-bentonite +KCl		
y%	a	pH of sol	y%	a	pH of sol	y%	a	pH of sol
69.75	3.56	—	70.25	5.04	8.15	78.34	5.02	8.14
81.37	8.89	—	80.86	12.59	8.05	84.90	12.55	8.20

Table IX

System: *H-permutit + monovalent cations.* 2.500 g. permutit containing 1.743 milliequivalents exchangeable H$^+$; volume 125 cc., time of reaction one week, temperature 26°C. y% = H$^+$ exchanged in percentage of total exchangeable H. a = milliequivalents of salt added.

H-permutit + LiCl			H-permutit + NaCl			H-permutit + KCl		
y%	a	pH of supernatant liquid	y%	a	pH of supernatant liquid	y%	a	pH of supernatant liquid
1.13	2.135	5.00	2.69	2.014	4.75	7.92	2.008	—
1.41	5.338	4.91	3.20	5.035	4.70	11.01	5.020	—
2.54	10.677	4.88	4.52	10.070	4.64	15.55	10.040	—
3.11	21.354	4.86	6.51	20.140	4.52	20.88	20.080	—

TABLE X

System: *H-Putnam clay + monovalent cations.* 3.330 g. H-colloid containing 1.881 milliequivalents exchangeable H^+; volume 250 cc.; time of reaction one week, temperature 28°C. y% = H^+ exchanged in percentage of total exchangeable H. a = milliequivalents of salt added.

H − Putnam clay + LiCl				H − Putnam clay + NaCl				H − Putnam Clay + KCl			
y%	a	pH of sol	pH of super-natant liquid	y%	a	pH of sol	pH of super-natant liquid	y%	a	pH of sol	pH of super-natant liquid
7.34	2.135	3.90	4.00	6.54	2.014	3.92	3.92	15.71	2.008	3.72	3.67
11.01	5.338	3.80	3.92	11.01	5.035	3.80	3.81	27.22	5.020	3.59	3.64
15.74	10.677	3.74	3.82	15.73	10.070	3.73	3.75	41.35	10.040	3.57	3.62
25.36	21.354	3.70	3.74	26.70	20.140	3.69	3.70	59.70	20.080	3.54	3.59
32.75	32.031	3.69	3.72	35.08	30.210	3.65	3.66	73.30	30.120	3.57	3.56

TABLE XI

System: *H-bentonite + monovalent cations.* 2.210 g. H-colloid containing 1.872 milliequivalents exchangeable H; volume 250 cc.; time of reaction one week; temperature 28°C. y% = H exchanged in percentage of total exchangeable H. a = milliequivalents of salt added.

H − bentonite + LiCl				H − bentonite + NaCl				H − bentonite + KCl			
y%	a	pH of sol	pH of super-natant liquid	y%	a	pH of sol	pH of super-natant liquid	y%	a	pH of sol	pH of super-natant liquid
12.32	0.712	3.20	3.18	15.81	2.014	3.05	2.67	15.16	0.972	3.13	3.34
17.58	1.778	3.02	3.04	17.58	2.500	2.98	3.10	19.47	2.008	2.85	2.90
18.43	2.135	2.90	3.10	20.78	5.035	2.80	3.00	24.60	4.860	—	2.84
23.13	5.338	2.85	2.97	26.28	10.070	2.77	2.93	32.63	10.040	2.72	2.84
27.09	10.677	2.76	2.94	29.68	12.500	—	—	35.20	12.150	2.75	2.71
32.10	17.780	2.70	2.86	34.20	20.140	2.65	3.02	45.60	24.300	2.71	2.60
32.60	21.354	2.76	2.98	37.60	25.000	—	—	46.89	20.080	2.74	2.85
39.75	32.031	2.87	3.18	43.65	30.210	2.72	—	62.60	30.120	2.76	2.90

TABLE XII

System: *H-Sharkey clay + monovalent cations.* 2.366 g. H-colloid containing 1.908 milliequivalents exchangeable H; volume 250 cc.; time of reaction 10 days; room temperature. y% = H exchanged in percentage of total exchangeable H. a = milliequivalents of salt added.

H – Sharkey clay + LiCl				H – Sharkey clay + NaCl				H – Sharkey clay + KCl			
y%	a	pH of sol	pH of supernatant liquid	y%	a	pH of sol	pH of supernatant liquid	y%	a	pH of sol	pH of supernatant liquid
11.32	2.848	—	3.55	10.80	2.014	3.63	3.56	15.52	2.008	3.46	3.49
14.98	5.694	—	3.50	15.52	5.036	3.50	3.50	23.28	5.020	3.30	3.35
18.03	9.966	—	3.53	18.56	10.070	3.63	3.50	34.58	10.400	3.30	3.30
25.78	21.354	—	3.42	27.26	20.140	3.37	3.49	50.62	20.072	3.29	3.49

TABLE XIII

System: *Li, Na, K-Putnam clay + HCl (old sols).* 1.420 g colloid containing 0.8075 milliequivalents exchangeable bases, volume 250 cc., time of reaction one week, temperature 28°C. y% = base exchanged in per cent, as determined by HCl adsorption. a = milliequivalents of HCl added.

Li – Putnam clay + HCl		Na – Putnam clay + HCl		K – Putnam clay + HCl	
y%	a	y%	a	y%	a
45.88	0.3774	45.73	0.3774	42.80	0.3774
78.70	0.8075	80.30	0.8075	69.55	0.8075
84.82	1.496	86.03	1.496	80.43	1.496

TABLE XIV

System: Li, Na, K, H-Putnam clay + *NH_4Cl (young, 4 day old sols)*. 7.5 g. Putnam clay containing 4.50 milliequivalents exchangeable cations; volume 500 cc.; time of reaction one week; temperature 25-28°C. y% = percentage of adsorbed ions released as determined by NH_4 – determination of the supernatant liquid before and after exchange reaction. a = milliequivalents NH_4Cl added.

Li – Putnam clay – NH_4Cl				Na – Putnam clay – NH_4Cl				K – Putnam clay + NH_4Cl				H – Putnam clay + NH_4Cl			
y%	a	pH of sol	pH of supernatant liquid	y%	a	pH of sol	pH of supernatant liquid	y%	a	pH of sol	pH of supernatant liquid	y%	a	pH of sol	pH of supernatant liquid
41.12	2.25	6.75	6.90	40.23	2.25	6.96	7.00	30.22	2.25	6.82	7.20	5.34	2.25	3.65	3.67
57.08	4.50	6.75	7.01	58.90	4.50	6.80	6.90	42.03	4.50	6.75	6.90	9.12	4.50	3.63	3.60
66.28	9.00	6.46	6.92	68.02	9.00	6.52	6.40	52.45	9.00	6.55	6.70	11.33	9.00	3.58	3.56
68.22	18.00	6.22	6.75	65.60	18.00	6.22	6.33	59.40	18.00	6.31	6.26	8.45	18.00	3.54	3.61
62.24	36.00	6.10	6.25	62.25	36.00	6.10	6.10	36.92	36.00	6.02	6.09	21.93	36.00	3.54	3.51

TABLE XV

System: Li, Na, K, H-bentonites + *NH_4Cl (young, 4 day old sols)*. 5 g. bentonite clay containing 4.50 milliequivalents exchangeable cations; volume 500 cc.; time of reaction one week; temperature 25-28°C. y% = percentage of adsorbed ions released as determined by NH_4 – determination of the supernatant liquid before and after exchange reaction. a = milliequivalents NH_4Cl added.

Li – bentonite + NH_4Cl				Na – bentonite + NH_4Cl				K – bentonite + NH_4Cl				H – bentonite + NH_4Cl			
y%	a	pH of sol	pH of supernatant liquid	y%	a	pH of sol	pH of supernatant liquid	y%	a	pH of sol	pH of supernatant liquid	y%	a	pH of sol	pH of supernatant liquid
37.12	2.25	6.64	7.32	31.91	2.25	6.60	6.80	26.65	2.25	6.50	7.03	11.05	2.25	2.94	3.08
46.52	4.50	6.50	7.03	49.95	4.50	6.32	6.86	43.75	4.50	6.35	7.01	14.45	4.50	2.86	3.00
68.42	9.00	6.31	7.15	70.87	9.00	6.12	6.72	61.73	9.00	6.16	6.89	20.48	9.00	2.80	2.94
78.85	18.00	5.91	6.66	78.67	18.00	5.92	6.60	69.84	18.00	6.16	6.83	38.13	18.00	2.78	2.89

equilibrium. This precaution is necessary since it had been found that by diluting concentrated clay sols the hydration of the colloidal particles may become so strong as to bring about apparent negative adsorption. After equilibrium had been reached, neutral salt solutions (0.1-1.0 normal) were added and the flasks filled with water up to the graduation mark. After a week's standing at constant temperature (within ± 1°C) during which time the flasks were shaken daily, the colloidal particles were separated from the liquid by centrifuging or ultrafiltration.

The amount of ions exchanged was either found by direct determination (in release of ions) or by difference (in adsorption of ions). NH_4 was determined by distillation (occasionally also Nessleration); K was analyzed by the chloroplatinic method; and H was determined by titration using cresolphthalein as an indicator. Since the supernatant liquid of the H-systems treated with chlorides always contained Al^{+++}, titration of H^+ had to be made in the presence of $AlCl_3$. Extensive titration with mixtures of HCl, $AlCl_3$ and LiCl, NaCl, KCl showed that the endpoint is reached at pH 9.2 which is in good agreement with the data reported by Britton.[11] All experiments reported were entirely repeated at least twice.

TABLE XVI

System: Li, Na, K-bentonite + HCl (old sols)

0.950 g. colloid containing 0.8075 milliequivalents exchangeable bases, volume 250 cc., time of reaction one week, temperature 28°C. y% = bases exchanged in per cent, as determined by HCl adsorption.

a = milliequivalents of HCl added.

Li-bentonite + HCl		Na-bentonite + HCl		K-bentonite + HCl	
y%	a	y%	a	y%	a
43.85	0.404	42.65	0.404	39.96	0.404
59.83	0.808	60.40	0.808	50.36	0.808
70.58	1.615	69.10	1.615	59.41	1.615

TABLE XVII

Release of adsorbed Li, Na, and K, ions against HCl (Young sols)

Fifty cc. of electrodialyzed H-bentonite (1.11 g. colloid) and 30.82 cc. of H-Putnam clay (1.65 g. colloid) were each diluted with 180 cc. H_2O. After 24 hours 0.936 milliequivalents of LiOH, NaOH, KOH, respectively, were added and the resulting *salt clays* were shaken daily for a week; 0.936 milliequivalents of HCl were then added and all systems were brought to a volume of 250 cc. After 9 days the sols were centrifuged and the HCl remaining in the clear supernatant liquid was determined by titration. The following results were obtained:

Li-bentonite + HCl = 77.90% exchanged (symmetry value)
Na-bentonite + HCl = 76.41% " " "
K-bentonite + HCl = 74.12% " " "
Li-Putnam clay + HCl = 84.48% " " "
Na-Putnam clay + HCl = 86.10% " " "
K-Putnam clay + HCl = 80.90% " " "

TABLE XVIII

Release of adsorbed Li, Na, K from permutits by HCl
1 g. permutit in 100 cc. volume; time of reaction one week; room temperature

Nature of permutit	Milliequivalents of exchangeable bases in 1 g. permutit	Milliequivalents HCl added	Percent exchanged (Symmetry value)
Li-permutit I	1.78	1.78	82.05%
Na-permutit I	2.34	2.34	77.40%
K-permutit I	1.64	1.64	73.20%
Na-permutit II	2.72	2.72	89.98%
K-permutit II	2.72	2.72	85.45%

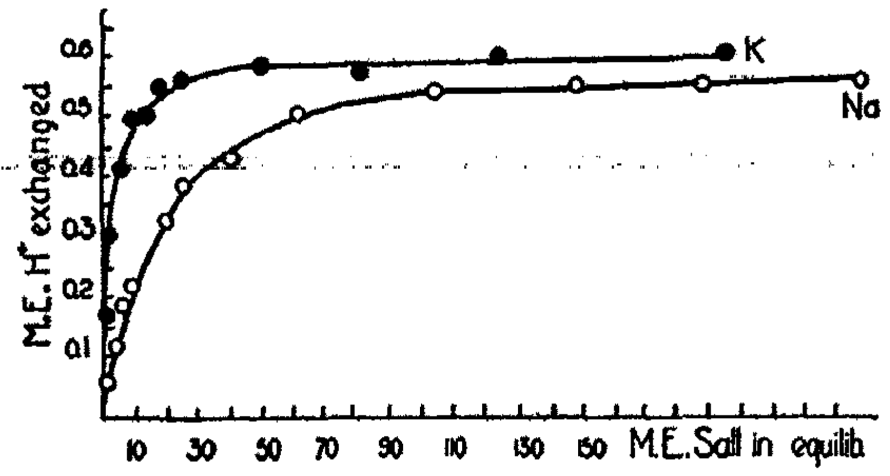


FIG. 4
Adsorption of cations by H-Putnam clay. (1 gr clay plus increasing amounts of NaCl, KCl.)

Mathematical Formulation of the Process of Ionic Exchange

The magnitude of ionic exchange is among other things a function of the amount of the salt added. Most investigators have been working with moderate concentrations only, omitting very dilute or highly concentrated systems. The neglect of including wide concentration ranges has been in many instances the direct cause of fruitless disputations as to the chemical or physical nature of the exchange process. There is no question that in all systems studied ionic exchange reaches a distinct maximum at which further additions of neutral salts remain ineffective in releasing adsorbed ions (See Fig. 4). The maximum (flat branch of the curve), however, does not necessarily correspond to the total exchange capacity of the colloid. Removal of released ions and repeated additions of electrolyte will in many cases liberate additional amounts of adsorbed ions until the absolute exchange maximum is reached.

For permutits the maximum exchange capacity lies between 400-500 milliequivalents of cations per 100 g. colloid, depending upon the preparation of the material. In many cases the cation-aluminum ratio in permutits is one. Natural clays contain considerable inert material and have much lower exchange capacities. The values found by the author are 85-100 milliequivalents of base for bentonites and 55-70 for Putnam clays as determined by continuous leaching with neutral salts, or potentiometric titration of H-systems with $Ca(OH)_2$ up to pH 7.

It is always necessary to state the methods used in determining the total ionic exchange capacity of a colloid, since not all methods give concordant results. There is considerable controversy among soil scientists as to the "correct" method of measuring the exchange capacity.

A considerable number of equations have been used to describe the functional relationships in ionic exchange reactions. Some of these are entirely empirical; others are supported by more or less convincing theoretical reasoning (Ganssen, Wolf, Freundlich, Rothmund and Kornfeld, Schmidt, Arrhenius, Wiegner, Vageler). The following three widely used formulae will be considered:
Ganssen's equation:*[19] On the basis of the law of mass action Ganssen derived the following formula:

$$K = \frac{x^2}{(m \cdot n - x)(g - x)}$$

where K = equilibrium constant,
m = exchange complex (permutit) in g,
n = total amount of exchangeable bases in the exchange complex,
g = total amount of salt in solution,
x = amount adsorbed.

Wiegner's equations:[55,57] Wiegner, who approached base exchange from the colloid-chemical viewpoint, found that Freundlich's parabolic isotherm was able to describe satisfactorily the exchange reactions:

$$x/m = k \cdot c^{1/p}$$

where x/m = adsorbed amount per g. of adsorbing substance,
c = concentration of added salt after equilibrium has been reached,
k, p = constants.

Later Wiegner[24] modified the equation in order to express the fact that ionic exchange is independent of dilution:

$$\frac{x}{m} = k\left(\frac{c}{a - c}\right)^{1/p}$$

where a = concentration of salt added at the beginning of the reaction.
Vageler's equation:[50] Recently Vageler has suggested a new equation which expresses the observation that under higher concentrations the ionic exchange reaches a maximum:

$$y = \frac{x \cdot S}{x + C}$$

y = amount adsorbed per g. adsorbing substance,
x = amount of salt in equivalents added per g. adsorbent,
S = maximum exchange capacity (saturation capacity),
C = half value, that is the conc. of x at which 50% of S is exchanged.

---

* H. W. Kerr's[29] "new" theory and equation of base exchange are identical with the work of Ganssen, published twenty years ago.

This hyperbolic equation is identical in form with the well-known adsorption isotherm of Langmuir. The latter corresponds in a way to the law of mass action of surface reactions (Pauli).[40]

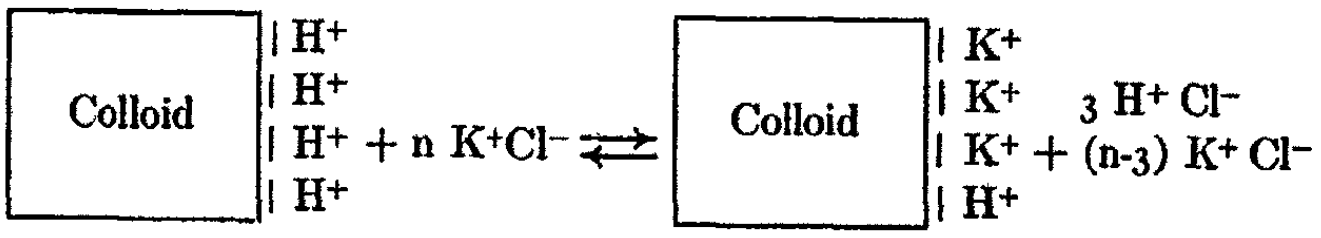
In the present study all three types of equations have been used to describe the experimental data, but no equation has proved entirely satisfactory. It depends on how wide a range in concentration is investigated and what ions are included. In dilute to moderate concentrations of ions with low atomic weights the Freundlich-Wiegner equation is very valuable, but at higher concentrations, especially for larger ions, (including H) the formula fails. Here the Vageler-Langmuir equation proves to be more satisfactory. No equation is able to characterize, for instance, the finer differences existing between closely related ions, such as Na and Li in the case of exchange with H-clay. An equation which embraces the behavior of several cations at various concentrations would have to contain more parameters than just one or two. This, of course, would render the physical interpretation of the constants difficult.

In order to numerically characterize the individual behavior of various ions a single magnitude would be extremely desirable. For this purpose a single point on the exchange curve must be used, since no satisfactory formula having but one parameter exists. The numerical magnitude selected in this study is called *"symmetry value."* It expresses the intensity of ionic exchange in percentage when the number of ions added to the system is made equal to the total number of exchangeable ions on the colloidal complex. For example, 100 grams of colloidal clay containing 60 milliequivalents of exchangeable NH_4 are mixed with a solution of NaCl having 60 milliequivalents of Na. Ionic exchange takes place and the Na ions replace 20 milliequivalents of NH_4 ions. The symmetry value is then $20/60 \cdot 100 = 33.33\%$. It is of interest to note that this symmetry value is in many cases approximately identical with the magnitude of the constant k in the Freundlich-Wiegner adsorption isotherm.

It might be worth while in this connection to point out a principal difficulty in the formulation of equations for base exchange reactions. Investigators who approach ionic exchange reactions on colloidal clays from the classical chemical standpoint often express the concentration of exchangeable cations as equivalents per total volume of the sol, as for instance, "one milliequivalent of hydrogen ions in 1000 cc. clay-suspension" (pH 3). In formulating equations for such "solutions" the exchangeable ions are treated as if they were uniformly distributed in the entire volume of the sol. But such is certainly not the case. The cations do not move at liberty in the solution. They are assembled on the surface of the suspended colloidal particles and are much closer together than the common concentration expression (pH 3 in the above case) indicates. In other words, the exchange reactions on the micelle occur in *concentrated* rather than in dilute solutions even if only one single colloidal particle were suspended in a liter of water. Attempts to measure the order of magnitude of ion concentrations on permutit surfaces lead to values $>1-2$ normal. Under such circumstances the laws of classical chemistry which apply only to dilute solutions cannot be expected to yield good quantitative results. The "constants" in the equations may not be constants. The formulae will have to be modified. Inter-ionic effects and polarization phenomena must be taken into consideration and individual ionic properties such as charge, radius and electric field strength will certainly play an important rôle. It will be shown in the following discussion that a mere application of the laws of dilute solutions can embrace but a small part of the multitude of reactions encountered in ionic exchange.

The Avidity of the Colloidal Complex as a Factor in Ionic Exchange

If natural clays and artificial aluminum silicates are subjected to electrodialysis they take up exchangeable hydrogen ions. The H-systems are usually called H-clay, H-permutit, etc. The pH of such systems depends upon the concentration of the solid phase present as shown by many investigators, notably by Bradfield.[5] Wiegner[58] and Pallmann[38] have recently investigated in great detail this phenomenon and distinguish in such systems two types of hydrogen ions, "free ions," which are in true solution (very small in number), and "swarm ions," which are on the surface of the colloidal particles moving and sedimenting with them. From a theoretical standpoint it is of great interest to note that the adsorbed H-ions also affect the H_2-electrode as well as invert sucrose. Upon addition of a neutral salt ionic exchange occurs, the cation of the salt taking the place of the hydrogen ion on the colloid. The H-ions enter the intermicellar liquid and can be determined (by titration) after separation of the solid from the liquid phase by centrifuging or ultrafiltration. Using Zsigmondy's notation, the reaction can be written as follows:



$$\boxed{\text{Colloid}}\begin{array}{l}|\,H^+\\|\,H^+\\|\,H^+\\|\,H^+\end{array} + n\,K^+Cl^- \rightleftarrows \boxed{\text{Colloid}}\begin{array}{l}|\,K^+\\|\,K^+\\|\,K^+\\|\,H^+\end{array}\begin{array}{l}3\,H^+Cl^-\\+\,(n\text{-}3)\,K^+Cl^-\end{array}$$

The nature of the inner layer (negative sign) is not indicated in the above equation. It is assumed that it consists mainly of negatively charged O^{--} and OH^- ions.

Colloidal clays show great differences in the amount of hydrogen ions released. This is well illustrated in Fig. 5, which shows the amount of H^+ released from five grams of H-colloid upon addition of various amounts of KCl. The number of hydrogen ions freed depends, of course, upon the number of exchangeable H-ions adsorbed per unit colloid (capacity factor) and *also upon the strength with which they are tied up to the negative places on the colloidal micelle* (intensity factor). The affinity between the positive outer (H^+) and negative inner layer (O^{--}, OH^-, in Helmholtz's double layer) need not be constant for all colloidal aluminum silicates, since it obviously depends on the lattice arrangement of the negative ions in the colloidal complex. The ease of replacement of hydrogen ions which shall be called *avidity* (Truog)[49] varies considerably in different soils as pointed out by Parker.[39]

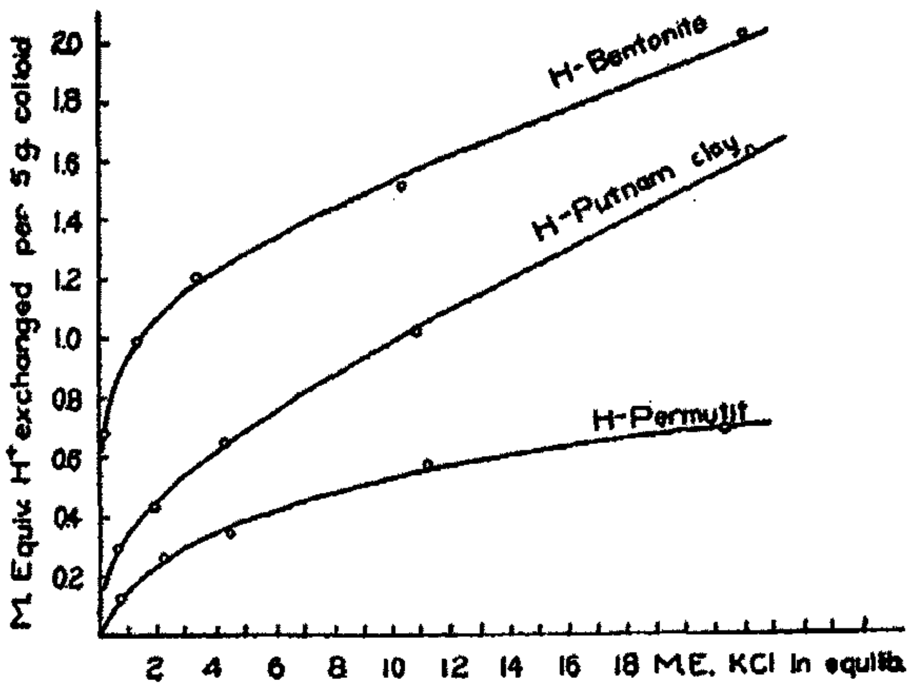


Fig. 5
Release of adsorbed hydrogen ions by KCl from various colloidal aluminum silicates.

In Table XIX the magnitude of avidity for three different aluminum silicates is expressed in various numerical terms. Irrespective of the formula or mode of presentation used to characterize the intensity of the ionic exchange, it is clearly seen that all values increase from left to right. H-permutit has the smallest avidity and H-bentonite the greatest. According to Vageler's C-value 23.31 milliequivalents of KCl must be added to replace 50 per cent of the adsorbed H^+ from permutit, while only 6.87 milliequivalents are necessary to replace 50 per cent in the case of H-bentonite. If one adds the same amounts of K^+ ions as there are exchangeable H^+ ions on the colloids, only 8 per cent of the H^+ ions are replaced from the permutit, while 18.4 per cent are released from the bentonite (symmetry value). In other words, *the H-ions are held more tightly on permutits than on bentonites. Putnam clay occupies an intermediate position.*

Table XIX

Avidity of Various Aluminum Silicates in the Exchange of H^+ against KCl

Numerical characterization	H-Permutit	H-Putnam clay	H-Bentonite
Constant k (Freundlich's isotherm)	5.94	12.05	15.22
Symmetry value	8.0%	15.0%	18.4%
Constant C (Vageler-Langmuir equation)	23.31	10.74	6.87
Apparent dissociation constant p K	7.28	5.97	5.67
Increase in avidity	——————→		

In the same table figures are given for the "apparent dissociation constant." It has been calculated according to Bradfield,[8] who accepts the viewpoints of Loew, Ramann, Truog and others, and who considers clays as colloidal acids. He characterizes the nature of the mineral soil acids with the apparent dissociation constants based on the following equation:

$$pH = pK + \log \frac{[\text{salt}]}{[\text{acid}]}$$

Experimentally pK is determined by adding just enough base to the H-clay to neutralize one-half of the exchangeable H^+ ions. The resulting pH value corresponds to pK.

Naturally the dissociation constant and the avidity index must stand in close relation to each other since both are expressions for the affinity between the H-ion and the clay "anion." It is evident from Table XIX that on the basis of pK, H-permutit is a weaker acid than either H-Putnam clay or H-bentonite.

Table XX

Effect of Base and Time of Reaction on the Magnitude of the Apparent Dissociation Constant of Colloidal "Clay Acids"
(Based on pH measurements of sols)
"normality" = 0.0028 N

Base used for neutralization	Time of reaction	Permutit* $\times 10^{-7}$	Putnam clay $\times 10^{-7}$	Bentonite clay $\times 10^{-7}$
LiOH	4 days	0.141	5.02	8.91
	46 days	0.355	14.46	28.19
NaOH	4 days	0.224	5.62	12.60
	46 days	0.692	11.75	30.91
KOH	4 days	0.525	10.72	21.38
	46 days	1.203	30.20	70.80

* H-Permutit was ground in a mortar until it formed a relatively stable suspension.

Unfortunately the dissociation constant of colloidal clay acids is not of such great value as the dissociation constant of true weak acids. The trouble is that pK does not prove to be a constant; it varies enormously with the experimental methods used as seen in Table XX. From data of Baver[1] it can be calculated that the dissociation constant for a 0.016 "normal" clay acid suspension varies 1900 per cent according to the base applied (LiOH, $Ca(OH)_2$). It is also certain that pK varies with dilution, and furthermore it has a very great time factor. For these reasons the term "avidity index" instead of "dissociation constant" is used in order to avoid an impression of accuracy and consistency that does not exist.

The qualitative similarity between the avidity index and the dissociation constant leads to important suggestions regarding the release and adsorption of ions by colloidal aluminum silicates of various avidities, which demonstrates the heuristic value of the clay acid-viewpoint in ionic exchange.

a) *Release of H-ions.*

Under comparable conditions *weak clay acids release less H^+ than strong* clay acids.* This statement follows directly from the empirical definition of avidity. It has been tested by adding different salts to the H-colloids. Table XXI shows the relationship expressed in terms of symmetry values.

TABLE XXI

Release of H^+ from Electrodialyzed Colloidal Aluminum Silicates
(Symmetry values)

Substance added	H-Permutit	H-Putnam clay	H-Bentonite
$AgNO_3$	6.78%	7.91%	13.78%
KNO_3	—	11.30%	19.92%
KCl	8.0 %	13.0 %	18.4 %
NaCl	2.7 %	6.2 %	14.6 %
LiCl	1.0 %	6.7 %	18.0 %

It is evident that for all of the five different cations and two different anions used, more H-ions are replaced from the bentonite (stronger acid) than from the permutit (weaker acid). This shows that the differences in affinity existing between the various aluminum silicates and H-ions are independent of the salts used in the exchange experiments in this investigation.

On the basis of stoichiometrical replacement the corollary follows that a *"strong"* clay acid H-system adsorbs more cations than a weak clay acid.* This statement is of particular importance from the viewpoint of fertilizer applications to soils of humid regions which possess considerable amounts of exchangeable H-ions in their colloidal complexes.

b) *Adsorption of H-ions.*

Under comparable conditions weak clay acids adsorb more H-ions than "strong" clay acids. In other words, if HCl is added to basic clays, K-clays for instance, the aluminum silicate of lowest avidity will adsorb the most H-ions. In Table XXII the effect is shown quantitatively on the basis of symmetry values.

TABLE XXII

Adsorption of H^+ from HCl by Various Aluminum Silicates
(Symmetry values)
(From Tables III, IV, VII, XIII, XVI, XVIII)

System	Percentage of H adsorbed
NH_4-permutit	83.58%
NH_4-Putnam clay	74.82%
NH_4-bentonite clay	60.90%
K-permutit	85.45%
K-Putnam clay	69.55%
K-bentonite clay	50.36%

---

* "Strong" in a relative meaning, as contrasted with "weak."

In every case permutit takes up the most H-ions and bentonite the least. If HCl is replaced by weak acids such as acetic acid, the effect still holds for Putnam clay and bentonite but is less conspicuous for permutits.

If the ionic exchange is stoichiometric the corollary follows that *adsorbed monovalent cations are more easily replaced* (by H^+) *from a weak clay acid than from a strong one.*

From the clay acid standpoint the entire problem of ionic exchange corresponds to the phenomenon of distribution of a base between two acids. If both acids are weak and their dissociation constants known, ionic exchange might be predicted quantitatively, as has been attempted by Bradfield. Since in this study only neutral salts of strong acids are brought into contact with clays the application of the above principle is excluded.

Summary of Discussion of Avidity of Soil Colloids.

1) Various colloidal aluminum silicates have different affinities for hydrogen ions. Bentonite has a high avidity, permutit a low one. Putnam clay takes an intermediate position.

2) From the clay-acid viewpoint, the avidity index can be related to the apparent dissociation constant of the clay acids. Putnam clay is a weaker acid than bentonite, while permutit is weaker than Putnam clay.

3) The following relations existing between ionic exchange and strength of clay acids have been suggested:

a) The weaker the clay acid the less H-ions will be released upon addition of a neutral salt.

b) The weaker the clay acid the less cations will be adsorbed by H-systems.

c) The weaker the clay acid the more H-ions will be adsorbed by basic systems.

d) The weaker the clay acid the easier are adsorbed cations replaced by H-ions.

Lyotropic Series and Exchange-Adsorption

The adsorption of monovalent cations by NH_4- and H-colloids exhibits characteristic differences in the three types of aluminum silicates investigated. The various silicates will be discussed separately.

a) *Permutit systems (artificial zeolites).*

Fig. 6 and Tables II, III and IX, show that the intensity of ionic exchange is different for all cations studied. The individual behavior of the various ions is regularly manifested throughout the range of concentration used and can be expressed by various numerical values as indicated in Table XXIII.

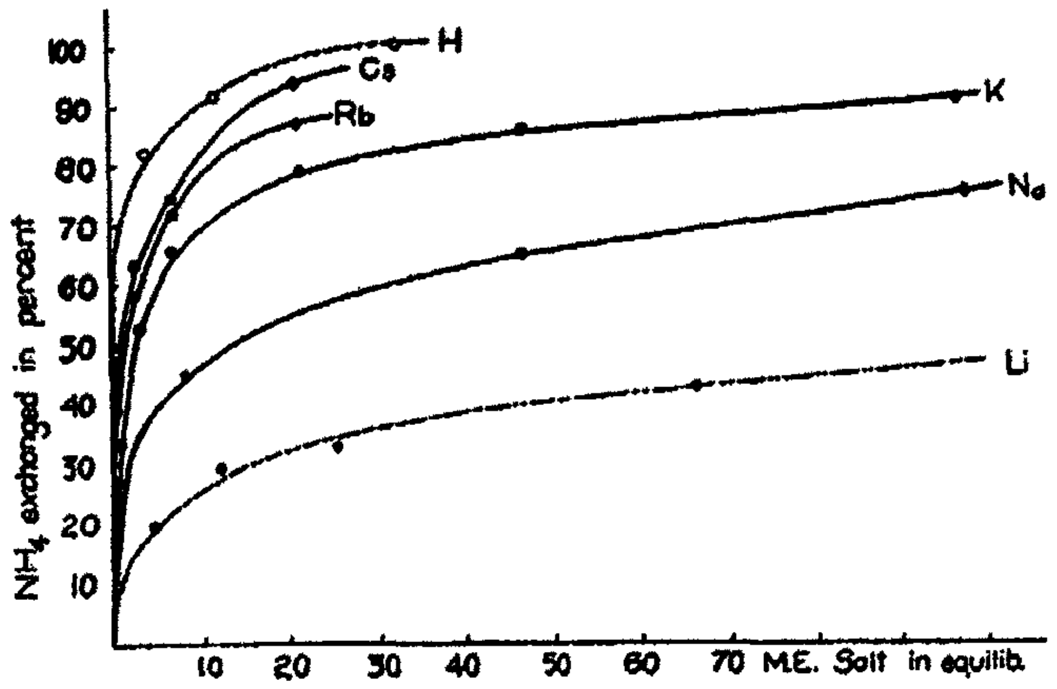


FIG. 6
Adsorption of cations by NH_4-permutit.
(From Table II)

TABLE XXIII

Lyotropic Series as characterized by Various Numerical Values
(*NH_4-permutit + monovalent chlorides*, equilibrium concentrations)

Salt added	Symmetry value	Wiegner-Freundlich isotherm		Vageler-Langmuir isotherm		Ganssen equation
		1/p	k (1/p=0.57)	S	C (S = 4.15)	K
LiCl	16.5%	0.392	15.21	2.30	61.56	0.029
NaCl	32.5%	0.296	29.46	3.45	14.53	0.209
KCl	48.0%	0.226	45.07	3.88	6.46	0.715
RbCl	54.5%	0.226	56.75	4.07	2.09	1.947
CsCl	56.5%	0.296	57.98	4.31	1.44	2.421

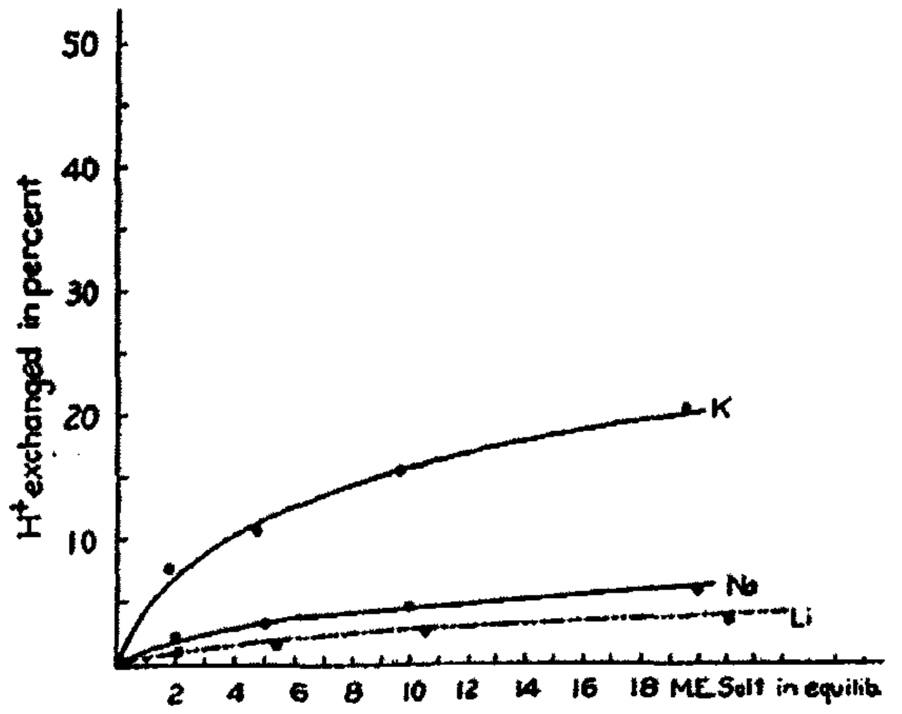


FIG. 7
Adsorption of cations from chlorides by H-permutit.
(From Table IX)

The magnitudes of all constants in the various equations clearly express a systematic trend in regard to the cation used. Whether the formula is based on strictly chemical principles (law of mass action) or whether it designates physical adsorption, the lyotropic series is always manifested. The above type of comparison is valid for all systems studied. For the sake of simplicity and uniformity the symmetry value will be mainly used for the quantitative characterization of the exchange intensity of the various cations.

The lyotropic series is independent of concentration and is noticeable in pure NH_4-systems, in pure H-systems (Fig 7) or in mixtures of NH_4-H-systems, as illustrated in Table XXIV.

Table XXIV

Adsorption of Monovalent Cations by Various Permutit Systems (Symmetry Values)

System	Li %	Na %	K %	Rb %	Cs %	H %
NH_4-permutit (Table II)	16.5	32.5	48.0	54.5	56.5	—
NH_4-H-permutit (Table III)	16.0	33.5	44.0	—	—	83.6
pH range	7.0–7.1	6.9–7.1	6.8–7.5	—	—	2.4–6.5
H-permutit (Table IX)	1.0	2.7	8.0	—	—	—
pH range	4.9–5.0	4.75	4.60	—	—	—.

Although H-permutit adsorbs fewer cations than NH_4-permutit, the lyotropic series is noticeable in every case, both under alkaline and acid conditions. For all permutit systems the lyotropic series assumes the following form in regard to adsorption:

$$\mathrm{Li} < \mathrm{Na} < \mathrm{K} < \mathrm{Rb} < \mathrm{Cs} < \mathrm{H}$$

Li is least adsorbed and H is best adsorbed. The differences are very great, amounting to 240 per cent between Li and Cs in NH_4-permutit and 700 per cent between Li and K in H-permutit.

b) *Putnam clay-systems.*

Tables IV, V, VI and X and Figs. 8, 9 and 10 give information as to the existence of the lyotropic series in the natural soil colloid, Putnam clay. Again pure NH_4-and H- and combined NH_4-H-clay systems were studied. A glance at the various graphs reveals at once that the lyotropic series is clearly manifested, but at the same time one may notice a significant difference in the case of Li and Na. Both curves are closely associated. In dilute concentrations Li is slightly better adsorbed than Na, while at higher concentration it is somewhat less attracted. Table XXV expresses the adsorption intensity on the basis of symmetry values.

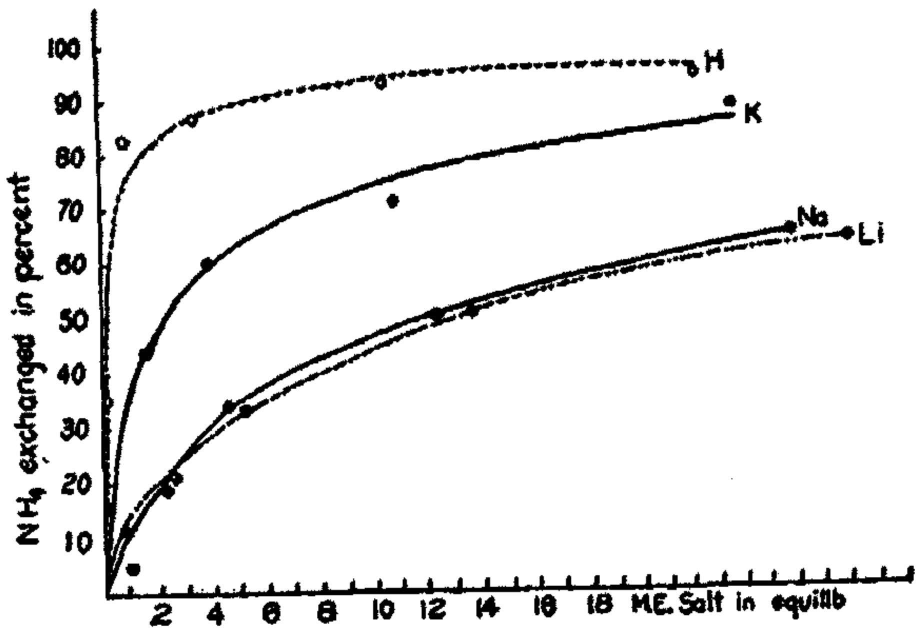


FIG. 8
Adsorption of cations by NH_4-H-Putnam clay.
(From Table IV)

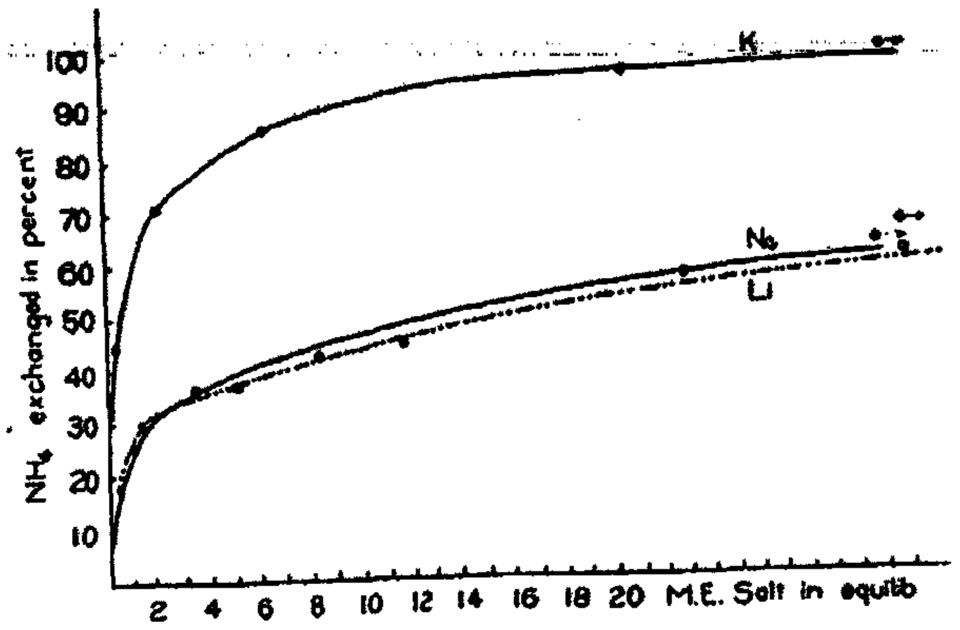


FIG. 9
Adsorption of cations by NH_4-Putnam clay.
(From Table V)

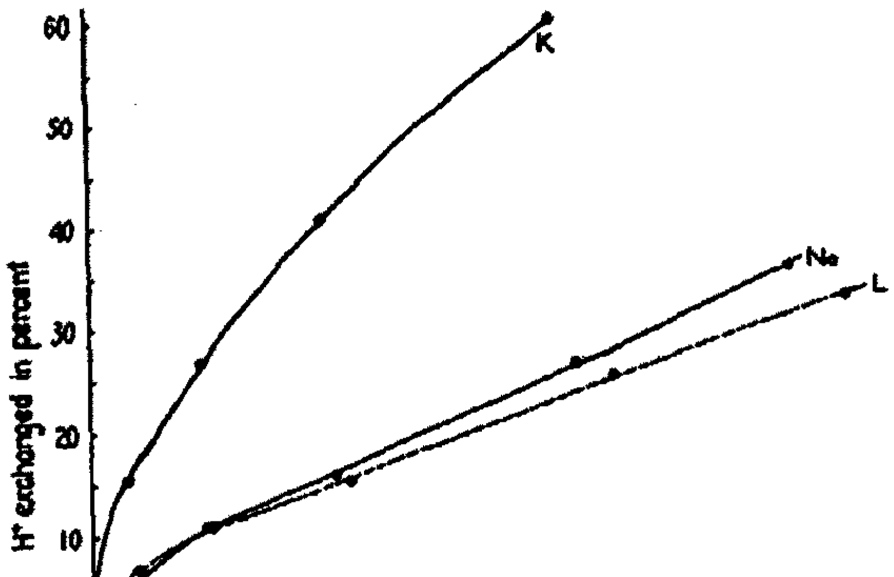


FIG. 10
Adsorption of cations by H-Putnam clay.
(From Table X)

Table XXV

Adsorption of Monovalent Cations by Various Putnam Clay Colloids (Symmetry Values)

System	Li	Na	K	H
NH_4-Putnam clay (Table V)	31.5%	32.8%	63.7%	—
pH of sol at equilibrium	7.24	7.04	8.00	—
NH_4-H-Putnam clay (Table IV)	37.5%	35.7%	54.0%	83.0%
pH of sol at equilibrium	5.26	5.23	5.05	4.15
NH_4-H-surface soil (Table VI)	33.2%	35.8%	55.0%	63.8%
pH at equilibrium	5.31	5.22	4.88	3.10
H-Putnam clay (Table X)	6.7%	6.2%	13.0%	—
pH at equilibrium: sol	3.91	3.93	3.72	
Intermicellar liquid	4.05	3.93	3.67	
H-Sharkey clay (Table XII)	9.0%	10.4%	15.2%	

For all five systems the symmetry values express quantitatively the adsorption similarity of Li and Na. In natural clays and soils the lyotropic series is also independent of the nature of the adsorbed ion, concentration of salt added and acidity or alkalinity of the system. In fact, every cation brings the sol to a pH value characteristic for the added ion. The order of the ions in the lyotropic series must be written as follows:

$$Li = Na < K < H$$

Experiments conducted with colloidal clay extracted from a river bottom soil known as Sharkey clay yielded a similar series as shown in Table XXV.

c) *Bentonite clay systems.*

Tables VII, VIII, XI and Figs. 11 and 12 give information about cation adsorption in natural bentonite clays from Wyoming. Certain peculiarities are striking. In all systems the curves are closer together than either in Putnam clays or permutits. Such is especially the case for the NH_4-H-bentonite series. The Li-curve is especially interesting. In dilute concentrations Li is better adsorbed than Na, it approaches the intake of K and even exceeds it in the case of NH_4-H-bentonite. In higher concentrations the behavior of the cation is more similar to the Putnam clay systems, especially in the case of H-bentonite. None of the formulae proposed is able to describe satisfactorily the irregularities within the family of the curves. Characterization of the adsorption intensity by symmetry values gives the following data (Table XXVI).

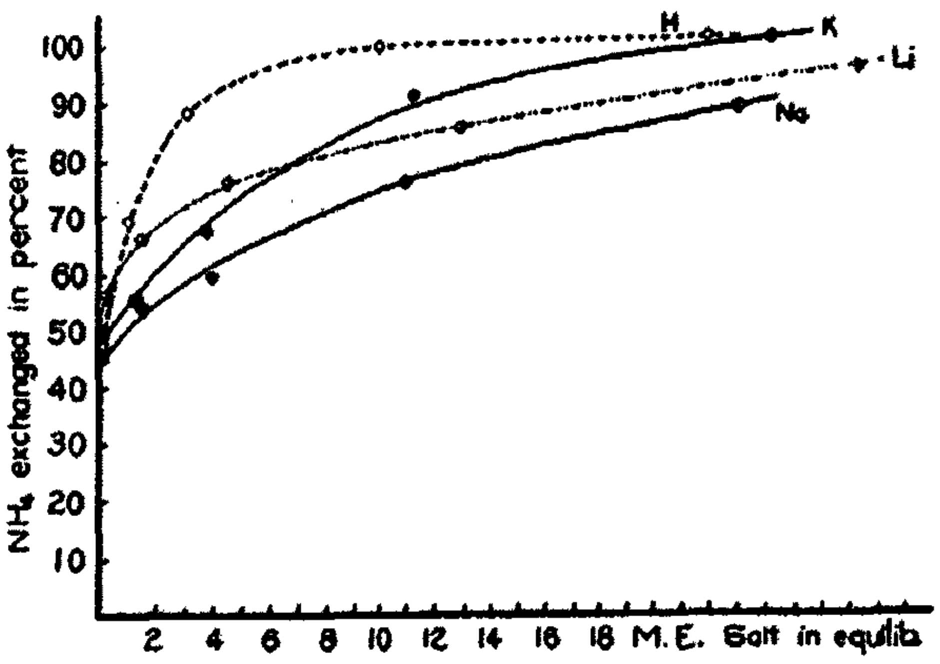


FIG. 11
Adsorption of cations by NH$_4$-H-Bentonite.
(From Table VII)

TABLE XXVI

Adsorption of Monovalent Cations by Bentonite Clay Systems
(Symmetry Values)
(From Tables VII, XI)

System	Li	Na	K	H
NH$_4$-H-bentonite clay	60.5%	50.6%	53.0%	60.90%
pH of sol at equilibrium	6.12	5.82	5.89	4.30
H-bentonite clay	18.0%	14.6%	18.4%	—
pH of sol at equilibrium	2.98	3.06	2.87	

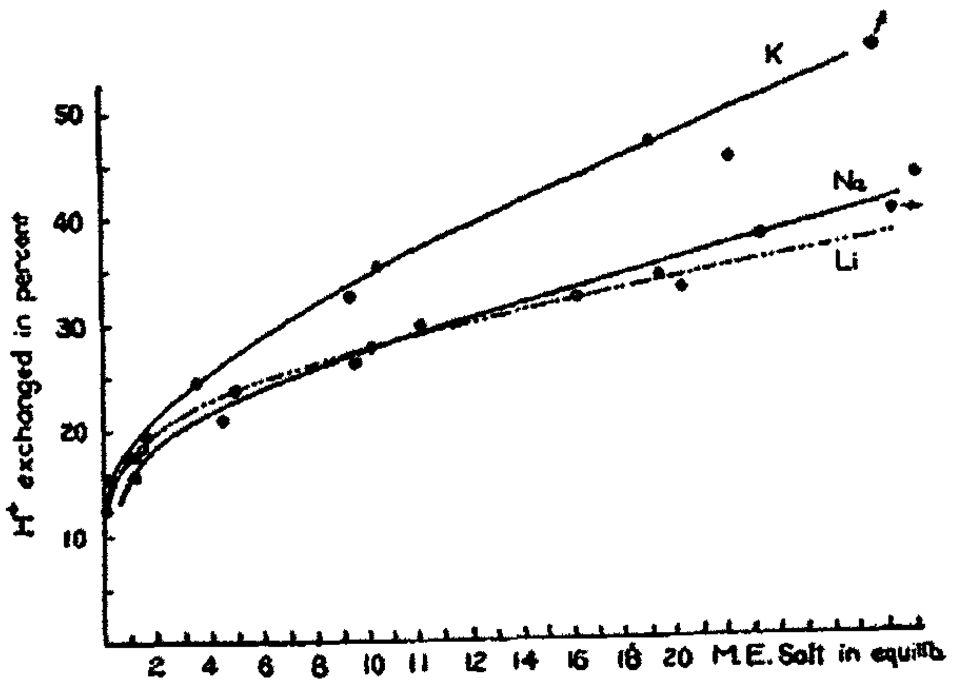


FIG. 12
Adsorption of cations by H-Bentonite.
(From Table XI)

Although the absolute intensity of exchange is different in the two systems, the abnormal position of Li is clearly manifested. The symmetry value of Li is close to that of K and even exceeds it in the NH_4-H-system. Two experiments conducted at alkaline reactions (pH of NH_4-sol = 8.5) gave very similar results. Comparisons on the basis of Vageler's C-value, calculated for comparable concentrations (5-12 milliequivalents of salt) are shown in Table XXVII.

TABLE XXVII

Adsorption of Li, Na, K by NH_4- and NH_4-H-bentonite Colloids
(Vageler's C-values)
(From Tables VII, VIII)

System	Li	Na	K
NH_4-bentonite clay, alkaline reaction	2.30	2.78	1.65
NH_4-H-bentonite clay, acid reaction (Same system as in Table XXVI)	1.77	3.59	1.25

The numbers indicate the milliequivalents of salt that must be added in order to replace 50 per cent of the exchangeable NH_4. Again Li approaches the effectiveness of Na and K.

For dilute concentrations and on the basis of symmetry values the lyotropic series assumes the following form:

NH_4-H-bentonites: $Na < K \leqq Li < H$
H-bentonites: $Na < Li = K$

Generally speaking all curves lie closer to the H-curve than in the case of the previous systems.

d) *Summary of the adsorption of monovalent cations.*

1) The lyotropic series representing the individual behavior of cations is manifest in all systems studied.

2) The presence of the series is independent of the strength of clay acid, acidity or alkalinity of the system, concentration range, temperature, time of reaction, size of colloidal particle, etc.

3) The various colloids exhibit characteristic differences in the position of the elements in the series. In dilute to moderate concentrations the order in the NH_4-systems is as follows:

permutits: $Li < Na < K < Rb < Cs < H$
Putnam clays: $Li = Na < K < H$
bentonite clays: $Na < K \leqq Li < H$

Lithium is the most affected ion. It gradually shifts from the lowest position in permutits to nearly the highest in bentonites. At very high concentrations the lyotropic series becomes less accentuated.

Release of Ions and Lyotropic Series

In the discussion on adsorption the fact has been stressed that the various cations exhibit characteristic individualities in regard to their adsorbability. It would be of great interest to learn whether the adsorbed ions retain their individuality after they have "settled down" on the surface of the colloidal particles. There are various methods which would permit more or less satisfactory answers to this question, for instance, the study of hydration of clays, viscosity, cataphoresis and so forth. In this paper, interest will be concentrated around the *outgo* or release of adsorbed cations and its relation to the lyotropic series. In order to obtain quantitative information it is necessary to prepare under strictly comparable conditions, a series of clays which contain but one kind of exchangeable cation, for example Li or Na or K. This was done by leaching clays with neutral salts or by adding hydroxides to H-clays.

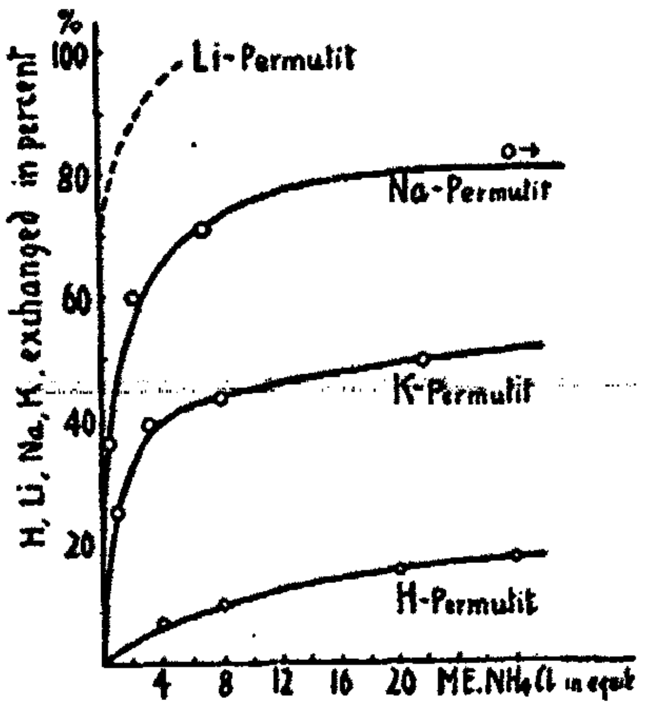


Fig. 13

[Release of adsorbed Li, Na, K, and H from permutits by NH_4Cl.

a) *Release of adsorbed ions from permutit systems.*

The outgo of adsorbed ions was studied by treating Li, Na, K, NH_4, and H-permutits with various amounts of NH_4Cl or HCl. Fig. 13 and Table XXVIII, which express the intensity of exchange in terms of symmetry values, illustrate quantitatively that the cations behave individually in their outgo as well as in their intake.

Table XXVIII

Release of Adsorbed Ions from Permutits. (Symmetry Values)
(From Table XVIII and Jenny[24])

System	Release against NH_4^+	Release against H^+	
		System I	System II
Li-permutit	70%	82.05%	—
Na-permutit	55.0%	77.40%	89.98%
K-permutit	37.5%	73.20%	85.45%
H-permutit	5.46%	—	—

Although the absolute values differ in the two columns because the H-ion is a much more energetic replacing agent than the NH_4-ion, it is clearly seen that in both cases Li is much easier released than either Na or K. The release of adsorbed cations is just in the reverse order to their adsorbability, and the lyotropic series can be written as follows:

Release: Li > Na > K > H

The outgo of the various cations was determined by analyzing the replacing NH_4Cl and HCl solutions before and after the experiment.

b) *Release of adsorbed ions from Putnam clay systems.*

The "basic clays" were prepared by adding just enough hydroxide to electrodialyzed clays to neutralize quantitatively all exchangeable H-ions. The number of exchangeable H-ions on the colloid was determined by continuous leaching with KCl and titration of the resulting HCl as described in a previous chapter. Figs. 14 and 15, and Table XXIX express the relationship between outgo of bases and intake of NH_4 and H quantitatively.

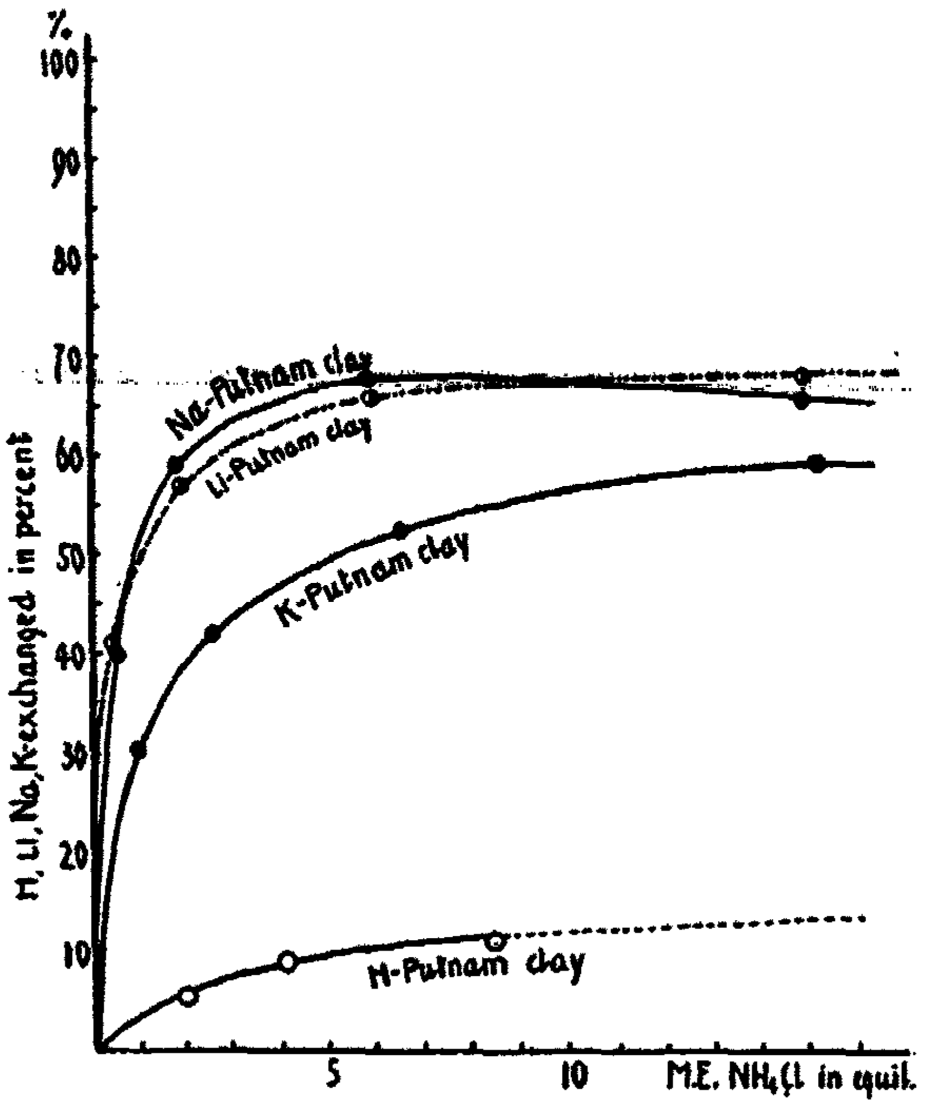


FIG. 14
Release of adsorbed Li, Na, K, and H from Putnam clays by NH_4Cl.
(From Table XIV)

TABLE XXIX

Release of adsorbed cations from Putnam clays
(Symmetry Values)

System	Released against NH_4Cl from Table XIV	Released against HCl (old sol) from Table XIII	Released against HCl (young sol) from Table XVII
Li-Putnam clay	57.08%	78.70%	84.48%
Na-Putnam clay	58.90%	80.30%	86.10%
K-Putnam clay	42.03%	69.55%	80.90%
H-Putnam clay	6.90%	—	—

Generally speaking, the picture is the same as that for permutits. Again HCl displaces much larger amounts of adsorbed cations than NH_4Cl, but in both sets of experiments the order of release of adsorbed ions is consistent. The lyotropic series reads as follows:

$$\text{Release: Li} = \text{Na} > \text{K} > \text{H}$$

Li and Na are close together, the former being held slightly tighter than the latter in moderate concentrations. Remembering the order of the lyotropic series found for the adsorption of cations by Putnam clay, it is evident that the outgo is just the reverse of the intake.

Table XXIX also indicates the presence of a *hysteresis* phenomenon. Freshly prepared, young (one week old) basic clays have higher symmetry values than older sols in which HCl was added six months after the Li-, Na-, K-clays had been prepared. In young sols the ions apparently are less firmly bound by the colloid than in older sols. In other words, it seems that ageing renders the liberation of adsorbed ions more difficult.

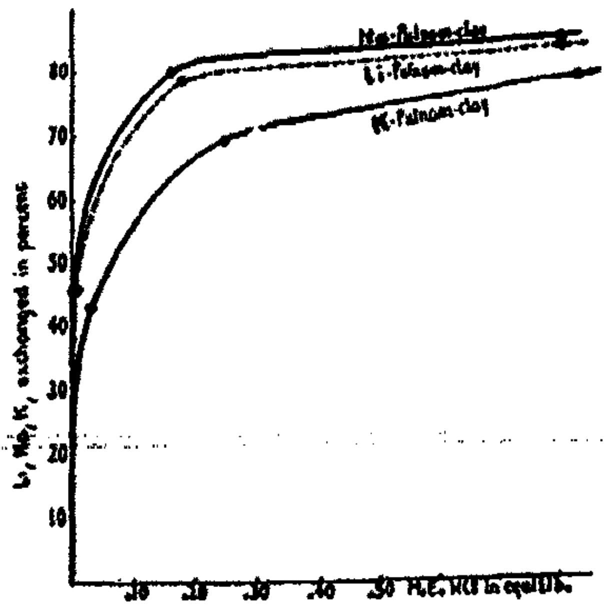


FIG. 15
Release of Li, Na, and K against HCl from Putnam clay. (From Table XIII)

c) *Release of adsorbed ions from bentonite clays.*

The bentonite "basic clays" were prepared similarly to the Putnam clays. The results of the two systems are exactly comparable since the transformation of the H-systems into salt systems and the subsequent ionic exchange experiments were always run in parallel. This is of importance because of possible disturbances due to the observed hysteresis phenomenon. Figs. 16 and 17 and Table XXX explain the release of Li, Na, K, NH_4 and H against NH_4Cl and HCl.

TABLE XXX

Release of Adsorbed Ions from Bentonite Clays
(Symmetry Values)

System	Release against NH_4^+	Release against H^+	
		(old sol)	(young sol)
	From Table XV	From Table XVI	From Table XVII
Li-bentonite clay	46.52%	59.83%	77.90%
Na-bentonite clay	49.59%	60.40%	76.41%
K-bentonite clay	43.75%	50.36%	74.12%
H-bentonite clay	14.45%	—	—

The data for the bentonite clays confirm the observations made in the other systems. Again H^+ replaces more cations than NH_4^+, but the lyotropic series remains consistent. The ageing effect is also noticeable, the availability of Li, for instance, decreased 23 per cent in six months.

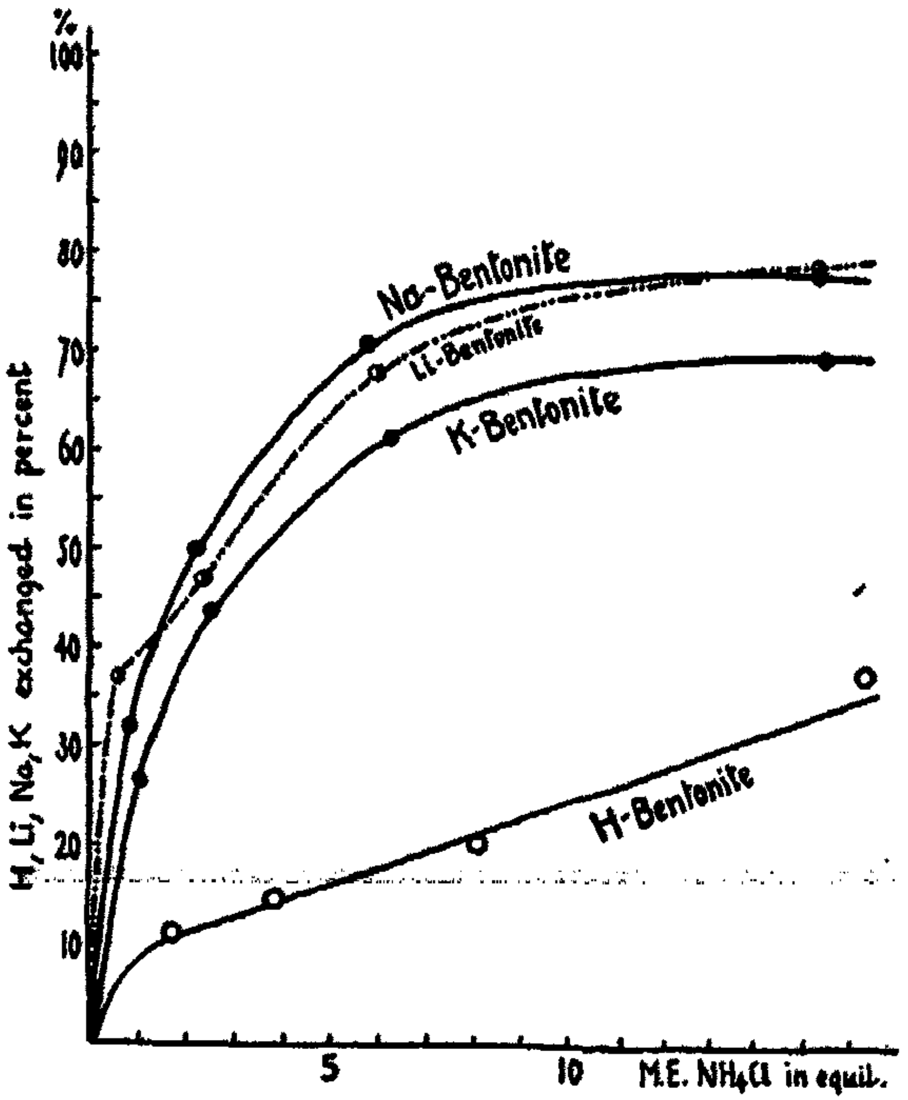


Fig. 16
Release of adsorbed Li, Na, K, and H from Bentonites by NH_4Cl.
(From Table XV)

The order of the elements in the lyotropic series reads as follows:

$$\text{Release: Li} \overset{\geq}{\underset{<}{=}} \text{Na} > \text{K} > \text{H}$$

There exists a slight difference between the intake and outgo of cations in bentonite systems. According to symmetry values Li stands closer to K in the adsorption series, while in release it acts more like Na. However, a glance at the adsorption curves in Fig. 11 shows that in higher concentrations Li behaves in the intake more like Na than K. As pointed out in the chapter on mathematical formulation it is very difficult to characterize the irregular behavior of the Li ion in bentonite systems with a single value. Generally speaking, the lyotropic series is somewhat less marked in bentonite than either in Putnam clay of permutit. It is of considerable interest to note that in dilute NH_4Cl concentration the adsorbed ions Li, Na, K are more strongly held on Putnam clay particles (weaker clay acid) than on the bentonite colloid, while under high NH_4Cl concentrations the reverse is true.

d) *Summary on release of monovalent cations.*

1) The adsorbed ions retain their individuality in their release from the colloid.

2) Generally speaking, the order of the ions in the lyotropic series during release is the reverse of the order during adsorption.

The Explanation of the Lyotropic Series encountered in Ionic Exchange

After it has been established that the cations behave individually during ionic exchange, both in intake and outgo, it would be of interest to learn more about the underlying causes of the lyotropic series observed. Can the constants of the equations or the symmetry values be correlated with ionic properties and is it possible to throw some light on the shifting of the ions within the Hofmeister series? Not only would a satisfactory answer be significant for clay studies, but also from the viewpoint of general colloid chemistry, since the lyotropic series and their irregularities have been observed in numerous other colloidal systems.

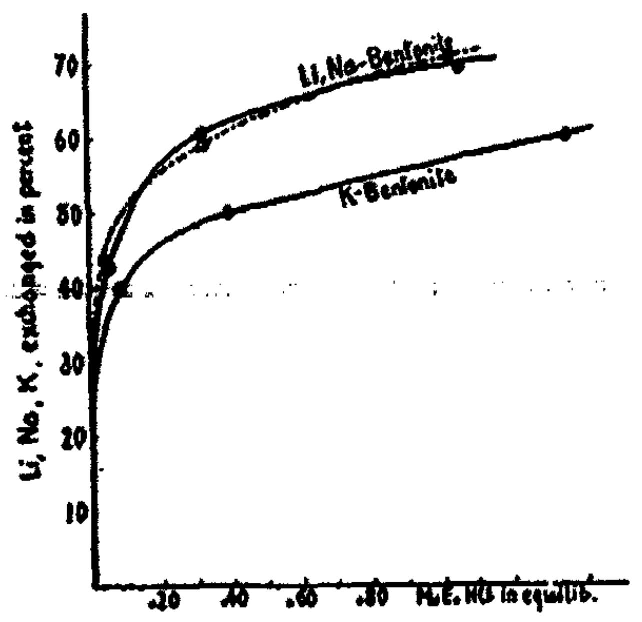


FIG. 17
Release of Li, Na, and K against HCl from Bentonite. (From Table XVI)

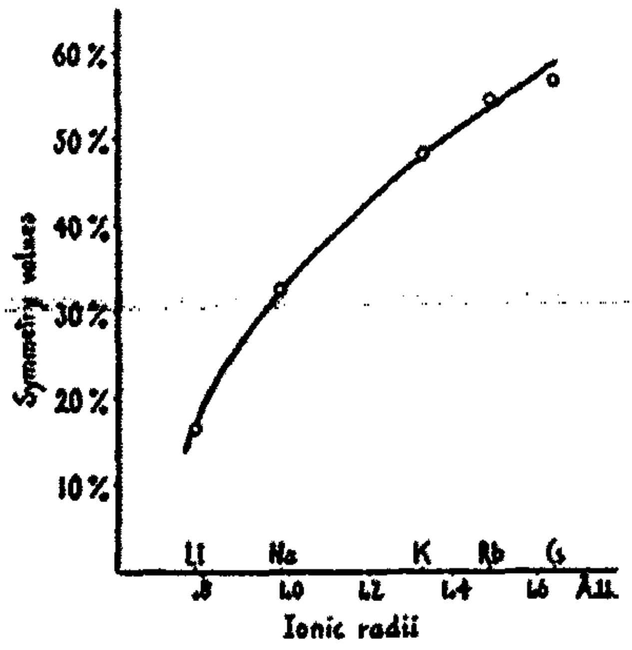


FIG. 18
Adsorption of cations by NH_4-permutit in relation to ionic radii.

a) *The normal series in NH_4-permutit-systems.*

The intake of cations by NH_4-permutit proceeds according to the following series:

$$Li < Na < K < Rb < Cs$$

In order to be able to visualize the ionic exchange these symbols of cations must be replaced by measurable properties of the ions. A glance at the periodic system reveals that the ions in the lyotropic series are arranged according to their atomic weights. From the viewpoint of surface mechanics, however, atomic weight is less instructive than other properties, such as electric charge and size of ions, since these permit calculations of attraction and space relationships. Since all cations investigated in this study are of identical charge, the ionic exchange intensities, expressed as symmetry values, can be directly related to the size of the ions. This has been done in Fig. 18. It is clearly seen that the *symmetry values are greater the larger the radius of the cation.* The relation is not quite linear. The resulting curve is slightly convex showing that a straight line relation is found (except for Cs) if the symmetry values are plotted against the logarithms of the ionic radii. Apparently there exists a distinct *space relationship* in ionic exchange reactions. The colloid particle seems to prefer ions of large size. From the viewpoint of *energy relationships* the size of ions and their charge must be combined. In calculations of molecular energy and crystal lattice energy the electrostatic potential of the ions plays a very important rôle. Since the crystal structure of the colloidal exchange complex does not alter during ionic exchange, as revealed independently by microscopical and by X-ray analyses, the electric field of the active places on the crystal-surface remains constant; it is permissible, therefore, to relate the intensity of ionic exchange expressed as symmetry values directly to the potential of the exchanging cation. Fig. 19 illustrates that adsorption *is better the smaller the electrostatic potential of the cation.* Very similar curves are obtained if the constants of the Wiegner-Freundlich isotherm are correlated with radii and potential.*

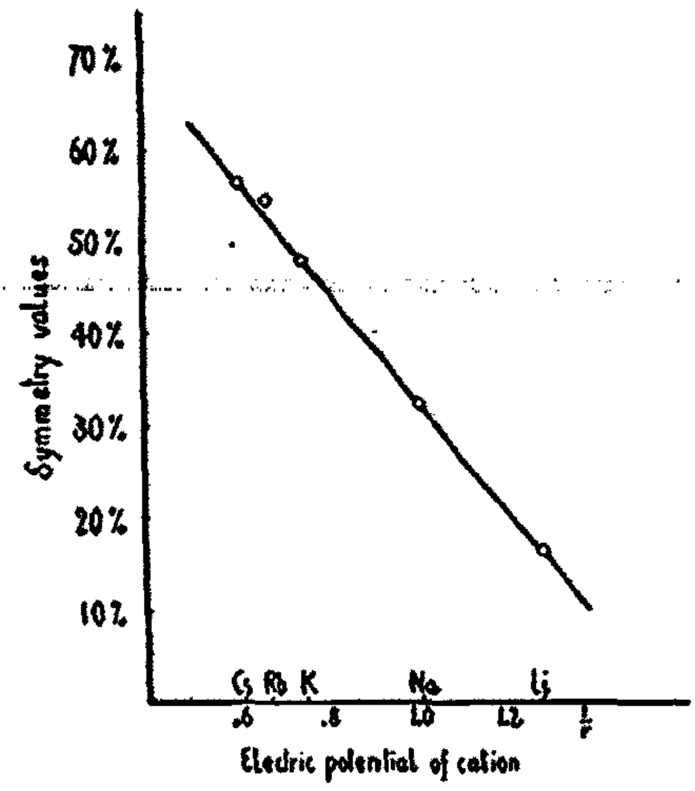


Fig. 19
Adsorption of cations by NH_4-permutit in relation to electric potential.

These findings are not only interesting but also puzzling. They are interesting because the observed relationships give the lyotropic series in ionic exchange a physical meaning which can be expressed numerically. On the other hand, the results are puzzling because they are directly opposite to what one would expect from analogies of attraction and energy relations in crystal lattices. According to Born,[3] Kossel,[31] Goldschmidt[21] and others,[41] the attraction between anions and cations in ionic crystals, obeys *Coulomb's law* which demands that for cations of equal charge a small ion (Li) be attracted with greater force and held more tightly than a large ion (K,Cs). Symmetry values should decrease with increasing ionic radii and increase with electric potential. Strangely enough, they exhibit a reverse relationship.

The colloidal aluminum silicates belong to the polar ionic crystal compounds as pointed out in the chapter on the nature of the colloidal complex.

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* In previous work[34] it was found that the constants k of the Wiegner-Freundlich equation are directly proportional to the true ionic volume of the exchanging cations. Although this result is highly significant from the standpoint of the energy of hydration, it should be pointed out that this relation had been obtained on the basis of the old ionic radii of Bragg, which, according to Wasastjerna, are somewhat too great.

The electrostatic bond conception can, therefore, be applied to the ionic exchange reactions in permutits. The active places of attraction for the cations are O^{--} ions and probably also OH^- ions on the surface of the colloidal particle. These two anions differ mainly in their strength of attraction for cations. The sizes are almost alike, but on account of the double electric charge the oxygen anions are more powerful "adsorbents." They form the negative inner layer of the Helmholtz double layer. A force of attraction (and, of course, also Born's repulsion) exists between an isolated surface anion and the adsorbed cation which is equal to $\frac{e_a \cdot e_c}{(r_a + r_c)^2}$ where e_a, e_c are the charges and r_a, r_c are the radii of the cation and anions respectively. The energy liberated at equilibrium is expressed as $\frac{e^2}{r_a + r_c}$ if cation and anion are monovalent. The energy of formation of such an ionic molecule is a measure of the stability of the compound. It is evident from the radius sum in the denominator that *attraction and stability are greater the smaller the radii of the ions.* For a constant anion the molecular energy varies for different cations as follows:

$$Li > Na > K > Rb > Cs$$

If the ions are deformable the above energy equation must contain an additional term which expresses the energy gained due to the electric polarization effect. For ions within a polar crystal the polarization effect is small and the crystal energy can be calculated on the basis of mere Coulomb attraction, if the so-called Madelung constant for the lattice is known. Adsorption compounds on the surface of crystals and colloidal complexes such as the aluminum silicate particles take an intermediate position between single ionic molecules and large lattice molecules. The surface ions are not symmetrically surrounded by electric charges of opposite sign. The coordination number of surface ions is likely to be less than that of interior ions and consequently the ionic radii will become somewhat smaller. In attempting to calculate ionic exchange energies on colloidal aluminum silicates, it would be necessary to consider the polarization of the deformable surface oxygen anion in the presence of exchangeable cations. Such detailed calculations have not yet been made.

The results found in this investigation show *that in ionic exchange the cations apparently act contrary to Coulomb's law.* The small Li ion is least adsorbed and most easily released, while the large K ion is strongly attracted and difficultly replaced. The effect of the interionic distance is reversed.

In searching for a possible explanation of this phenomenon, the relation between symmetry values and ionic potential recalls the formula for the migration velocity of ions as based on Stokes law which also contains the expression e/r. The velocity of large ions is directly proportional to their potential, but for the monovalent cations Li to Cs the relation is a reverse one, as is the case for their adsorption by permutits. The large Cs and K ions migrate faster than the small Li and Na ions. In other words, there exists a striking similarity between adsorption and migration velocity of ions which can be formulated as follows: *the adsorption of monovalent cations is better the greater their mobility*, a conclusion which was postulated on theoretical reasoning by Mukherjee[38] several years ago.

It seems logical to attribute the order of the lyotropic series in adsorption and release in permutits to the same cause as that of the mobility of ions, namely, to the phenomenon of *hydration of ions*.

As soon as Arrhenius had postulated the theory of dissociation, the hypothesis that the ions interact with the surrounding water molecules was put forward by numerous eminent investigators (Arrhenius, Kohlrausch, Nernst, Drucker, Washburn). Recently the hydration of ions has been attacked by theoretical physicists (Fajans, Born, Debye, Webb, Lange) by the application of rigorous mathematical treatments. Their calculations are mainly based upon the following picture: The interaction of ions and water molecules is not a chemical, stoichiometrical one, but is essentially an electrostatic phenomenon. The electric field intensity ($e:r^2$) in the vicinity of an ion is very great, for instance, 180,000 volts per cm. at a distance of 10^{-7} cm. from the center of a sodium ion. Water molecules, which are permanent dipoles, become oriented and attracted, turning their negative side toward the cation. The number of polarized water molecules increases with the polarizing ability of the ion which is stronger the greater its charge and the smaller its radius. The small Li ion will, therefore, attract the most water molecules and the large Cs ion the least. Li will then be the largest ion and Cs the smallest. Hydration and mobility radii will, therefore, decrease according to the series:

Li, Na, K, Rb, Cs.

This is exactly the same order as the one found in adsorption by NH_4-permutits. The presence of water shells around ions also has been indicated by X-ray analyses of salt solutions.[44]

With the aid of the concept of hydration of ions, the mechanism of ionic exchange in permutits is easily visualized. The strongly hydrated, large and voluminous Li-ion cannot come very close to the negative oxygen ion of the crystal lattice, since there are one or two water molecules between the colloidal particle and the adsorbed cation. The forces of attraction are, therefore, weak because they vary inversely with the square of the distance between the electric charges (Coulomb's law). Adsorbed Li-ions are, therefore, easily replaced by less hydrated and consequently smaller ions, such as K, Rb, Cs, which are very strongly attracted by the negative places in the crystal lattice. They stick there tightly because the effective interionic distance is relatively small. Adsorbed slightly hydrated cations are replaced with difficulty particularly if the exchange is brought about by strongly hydrated ions such as Na and Li. On the basis of the hydration of ions the ionic exchange in permutits can be expected to take place as follows:

Adsorption: $Cs > Rb > K > Na > Li$
Release: $Li > Na > K > Rb > Cs$

which is exactly the lyotropic series observed.

The possible connection between ionic exchange in permutits and hydration of ions was first suggested by Wiegner.[56]

The observed contradiction between the electrostatic attraction of ions in crystals and in base exchange reactions on colloidal aluminum silicates is, therefore, only an apparent one. Coulomb's physical law can explain the behavior of the ions in both systems. The main difference is the following: in calculating the forces of attraction and the resulting energies according to the formulae given, the ionic radii of Goldschmidt and Pauling have to be used for crystals, while for ionic exchange reactions on the surface of the colloid the radii of the hydrated ions (electrodynamic radii) must be inserted. The latter vary much more than the former.

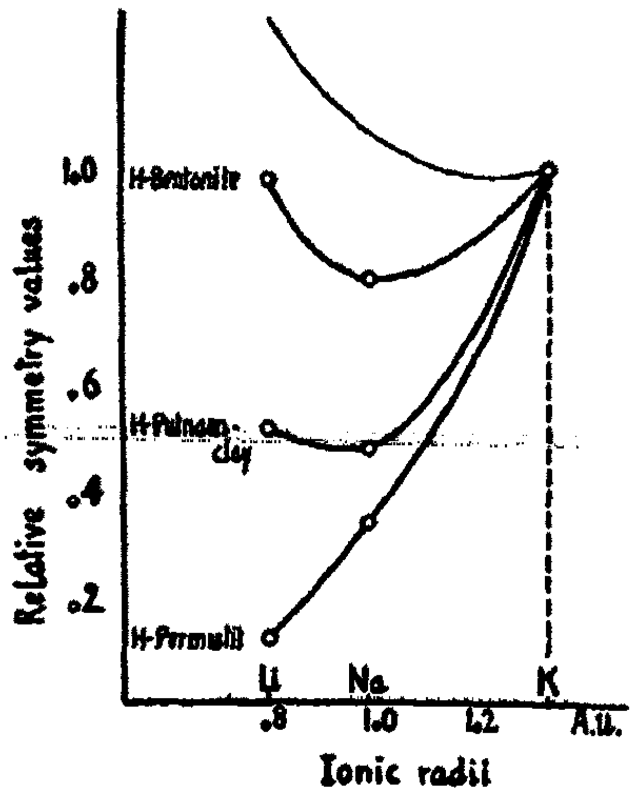

Fig. 20
Relative ionic exchange intensities as a function of ionic radii and nature of colloidal aluminum silicate.

b) *The disturbed lyotropic series in Putnam clay and bentonite systems.*

The normal lyotropic series encountered in NH_4-permutits is distinctly disturbed in Putnam clay and bentonite systems. In dilute and moderate concentrations the natural aluminum silicates adsorb relatively more Na and Li than K. For a quantitative comparison of the different lyotropic series it is best to reduce the symmetry values to *relative* exchange intensities. This has been done for the H-colloids in Fig. 20, by placing the symmetry value of K^+ equal to one. This procedure reveals at once a certain regularity in the disturbance of the various lyotropic series of the natural clay systems. It will be noticed that the H-permutit curve (lowest curve) exhibits a slightly concave bending. The bending is intensified in the H-Putnam clay curve and becomes most conspicuous in the H-bentonite system where a pronounced minimum is clearly noticeable. The impression is gained as if a pull is being exerted on the Li end of the curve in the direction of higher relative symmetry values. There exists a marked tendency to reverse the normal lyotropic series. A very similar picture can be obtained by plotting the relative symmetry values of the various Li-, Na-, K- and NH_4-systems. In NH_4-H-bentonite Li already lies higher than K. It could be easily conceived that there might exist a system in which the order of Li, Na, K is completely reversed as indicated by a thin line in Fig. 20. Temperature experiments demonstrate that the difference in exchange intensities between K and Na becomes smaller as the temperature increases. Indeed, Jaeger's experiments with Ag-ultramarines conducted at temperatures of 160°C, show that the lyotropic series is reversed. Jaeger[23] says, "The substitution of the Ag present, under equal conditions of temperature, concentration and time of heating (in sealed tubes) goes most rapidly and completely with Li and less rapidly with Na, K, Rb, Cs in decreasing ratio; the substitution of NH_4 is almost the same as that of K."

The observed irregularities in the lyotropic series of natural aluminum silicates can be interpreted as *various stages in the reversal of the normal hydration order of the exchanging cations.* This conclusion may also shed new light upon the behavior of ions in other colloidal systems where similar abnormalities are frequently encountered.

From the viewpoint of hydration of ions it is logical to connect the reversal of the lyotropic series with dehydration of ions. Obviously the most hydrated ion will be first affected by dehydration processes. This is demonstrated by the behavior of the Li-ion which is the first to begin shifting within the series. In bentonite and clay systems, for example, Li appears to be so strongly dehydrated that it becomes as active as Na. The fact that the cations may also act as dehydrated ions in ionic exchange was shown by Souviron[57] who studied adsorption in alcoholic solutions, and later by Ungerer who observed a dehydrating effect of the anion upon the cation.

c) *The effective size of ions in exchange reactions.*

The consideration of ionic radii sheds considerable light on the mechanism of ionic exchange. It becomes necessary, however, to attribute various sizes or spheres of influence to the same cation depending on the nature of the collidal system in which the reaction takes place. The following extreme cases are important:

a) crystal lattice radii (dehydrated ions).
b) hydrodynamic radii (hydrated ions).

Crystal lattice radii refer to completely dehydrated ions as found in crystals (NaCl, CaO, many silicates). The radii increase with atomic weight, from Li to Cs (see Table XXXI), and vary slightly with the coordination number.

TABLE XXXI

Ionic Radii (Spheres of Action) of Hydrated and Dehydrated Ions (Ångstrom units)

	Li^+	Na^+	K^+	NH_4^+	Rb^+	Cs^+
Crystal lattice radii	0.78	0.98	1.33	1.43	1.49	1.65
Hydrodynamic radii	10.03	7.90	5.32	5.37	5.09	5.05

The *hydrodynamic radii* represent the sizes of hydrated ions as found in solutions. They include the size of the ion proper and its water shell. These somewhat hypothetical radii vary considerably with concentration and are also affected by temperature. Table XXXI shows the hydrodynamic radii for ions in infinite dilution where hydration probably reaches a maximum. Although these radii are subject to revision they, nevertheless, demonstrate two significant things. First, the hydrodynamic radii are greater than the crystal lattice radii, and secondly the order of the element in the series is reversed. Crystal lattice ions increase from Li to Cs, while the hydrodynamic radii decrease. In colloidal systems containing kinetically mobile water molecules the effective size of a cation will have a value lying between the extremes listed in Table XXXI. For instance, Li may have an effective ionic radius greater, equal, or smaller than K, depending upon the conditions of hydration in the colloidal system. In permutits, at room temperature, fixation of cations takes place according to Coulomb's law on the basis of hydrodynamic radii, while in ultramarines at high temperature, ionic exchange proceeds according to crystal lattice radii. At present it is not yet possible to state a priori the nature of the effective sizes of ions in exchange reactions for any particular colloidal system.

The Peculiar Behavior of the Hydrogen Ion in Ionic Exchange

In the discussion of the mechanism of cation exchange the hydrogen ion was not mentioned. Owing to its great practical significance in the problem of soil acidity and on account of its peculiar behavior in adsorption and release, a separate consideration of the hydrogen ion becomes desirable.

In all systems investigated the hydrogen ion is unquestionably the best adsorbed ion. It is also most effective in replacing other cations from the surface of colloidal particles. Figs. 6, 8, 11 and the symmetry values in Tables XXIV–XXVI show that, independent of the avidity of the clay acid, the hydrogen ion curve is above the other curves, and that even in moderate concentrations it replaces almost completely all exchangeable monovalent cations. As to its release or exchangeability, the H-ion is most difficult to replace (Figs. 13, 14, 16); it sticks tenaciously to the colloidal particle. Unless the electrolyte added is able to bind the liberated H^+—as is the case with hydroxides—complete exchange with one salt treatment is hardly achievable.

This unique position of the H-ion in the lyotropic series was pointed out in earlier studies[24] and has since been confirmed by numerous investigators, especially by Kappen.[26] The results serve to bring out the omnipotence of the hydrogen ion in many important soil processes. It is the hydrogen ion that first replaces the cations in the crystal lattice of silicates thus initiating the chemical weathering process which ultimately leads to the formation of soil and soil colloids. It is the H-ion (excreted) also which enables plants and microbes to liberate adsorbed cations which are necessary for growth. On the other hand, since the hydrogen ion is the least affected ion in leaching processes of soils, it adheres so tenaciously to the soil colloids and accumulates in such vast amounts that it becomes a serious menace to the agriculture of humid regions. The American farmer annually applies thousands of tons of limestone to the soil in order to liberate and neutralize adsorbed hydrogen ions for the benefit of his crops.

From the viewpoint of the ionic exchange mechanism, the behavior of the H-ion is particularly interesting. The hydrogen ion consists of only a positive nucleus and is the smallest ion known. From analogy of Fig. 18 which shows that adsorption is directly proportional to size, the H-ion should be the least adsorbed cation. Contrary to this the H-ion is the most strongly adsorbed ion, exceeding the heavy elements Rb and Cs. On the basis of ionic size, H^+ acts even much more energetically than an H_3O-ion, which often is considered to be the adequate formula for the H-ion. The conditions are similar to those encountered in the migration velocity of ions where H exceeds by far any other cation.

The strong adsorption and difficult release of H-ions is perhaps better understood from a consideration of the forces of attraction. As mentioned before, the bonds existing between the oxygen ion frame and the adsorbed cations are considered to be of mere electrostatic nature (Coulomb attraction). There naturally exists for the adsorbed H-ions the tendency to form OH-ions and even H_2O molecules with O^{--} ions of the crystal lattice. The attraction between O^{--} and H^+ is very great. According to Debye[13] the two ions adhere so closely that the H-ion even plunges into the electron orbits of the oxygen ion. Fajans[17] emphasizes the great distortion of the oxygen ion due to the polarization of the H-ion. Pauling[43] approaches the "compound" from quantum mechanics and considers the bond to be of covalent type, the two ions sharing two electrons simultaneously. This latter covalent or homopolar bond represents true chemical linkage most closely.

It seems, therefore, possible to trace the action of the H-ion back to significant differences in the type of bonds between the cation and the anion. In the case of Li and Na where it is probable that at least one water molecule stands between the O^{--} and the cation the attraction is weak and of an electrostatic type, while in the case of H^+ the forces are strong and seem to be of a true chemical type. This difference may also explain why those investigators who work mainly with H-systems emphasize the chemical nature of "clay acids," while those who study ionic exchange with cations other than H^+ stress the electrostatic and physical aspect more strongly. In all cases, however, the ionic exchange has to be stoichiometrical in order to satisfy the requirements of electrical neutrality.

The Hydration of Colloidal Particles as affected by Ionic Exchange

Investigations on the water adsorption of soil colloids by various methods show decidedly that the hydration of the colloidal particles depends upon the nature of the adsorbed cation. According to previous studies[24] the water content of wet permutits varies as follows:

Li-permutit	Na-permutit	K-permutit	H-permutit
60.64% H_2O	57.50% H_2O	53.48% H_2O	71.60% H_2O

The water content of the permutit is greater the more hydrated the adsorbed cation. Curiously enough the H-permutit contains the most water, although the hydrogen ion behaves as a dehydrated ion during exchange. The pronounced hydration of the H-systems has been confirmed by other methods and investigators as seen from the following figures, based on molecular values:

Transformation of NH_4-permutit into H-permutit by leaching with dilute HCl (Jenny).[24]

	SiO_2	Al_2O_3	$(NH_4)_2O$	H_2O
NH_4-permutit	3.32	1	0.86	3.82
↓				
H-permutit	7.41	1	0	14.39

Transformation of Na-permutit into H-permutit by electrodialyses (Kappen).[26]

	SiO_2	Al_2O_3	Na_2O	H_2O
Na-permutit	3.20	1	1.00	4.66
↓				
H-Na-permutit	3.30	1	0.55	6.56

No one has attempted to explain this abnormality between slightly hydrated H-ions and strongly hydrated H-colloids, which—as Kappen points out—presents a serious handicap for a complete understanding of ionic exchange. However, on the basis of the work presented it seems possible to suggest a general mechanism for the hydration of soil colloids which explains—at least qualitatively—the relation between water adsorption and ionic exchange in macroscopic permutit grains.

Permutit gels contain large cavities (see Fig. 3), which are filled with adsorbed (wandering) ions and water molecules. For a given crystal lattice the number of water molecules which can be packed into one cavity apparently depends upon the number and size of the exchangeable ions within the cavity. *The smaller the number and the true* size of the adsorbed ions, the greater will be the number of water molecules in the system.* Upon this simple picture the following possibilities can be set forward:

1) *Monovalent systems:* Under ordinary experimental conditions ionic exchange in permutits is stoichiometrical. For every monovalent cation adsorbed one other monovalent cation is released. Obviously the number of water molecules within the cavities becomes dependent only upon the size of the adsorbed cation. The smaller the exchangeable cation in the the cavity, the greater the number of water molecules that can be packed into the system. The hydration of monovalent permutits should, therefore, vary according to the following series:

Li-permutit > Na-permutit > K-permutit, etc.

Experiments previously cited show that this series actually exists.

2) *Divalent systems:* For exchange with divalent cations the ionic replacement in permutits was also found to be stoichiometrical. For every divalent cation adsorbed, two monovalent cations are liberated. From the viewpoint of space relations a highly interesting situation arises. Although the entire

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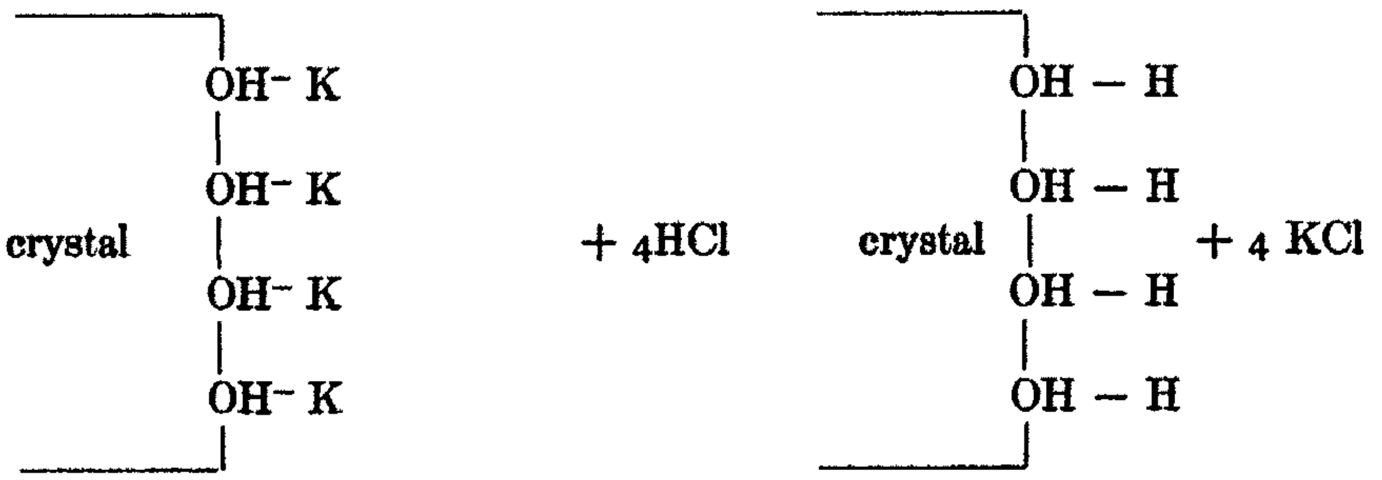
* Crystal lattice radii.

system remains electrically balanced, yet the place of one of the two cations remains unoccupied, since the divalent cation certainly is not split up into two parts. For instance, the volume of two Na-ions is 7.88 A^3, while the volume of one Ca-ion, which replaces two Na-ions, is only 4.99 A^3. The "empty" space can thus be filled with water molecules. This mechanism leads to the conclusion *that permutits with divalent cations are more hydrated than permutits with monovalent cations*, provided the ingoing and outgoing ions are of somewhat similar size, such as, for example, Li and Mg, Na and Ca, K and Ba. From analogy with monovalent systems it would be expected that within the divalent lyotropic series, the hydration decreases from Mg-permutit to Ba-permutit, according to the size of the divalent ions.

3) *The H-system:* Extending the ideas so far developed to H-systems, the conclusion follows at once that these should contain the most water of hydration. The H-ion is the smallest ion of all, it occupies very little space in the cavity which, therefore, can be filled with H_2O molecules nearly to the maximum of its water holding capacity. For instance, if a Na-permutit is converted into a H-permutit, the "cavity-water" should be increased at about the rate of one water molecule per Na-ion replaced. Data indicate, however, that the number of water molecules in H-systems is considerably greater than that provided by mere space relationships. The author believes that the additional water molecules represent *water of constitution* formed during the process of replacement. Remembering that aluminum silicates consist of a framework of oxygen, and possibly hydroxyl ions, it can be easily imagined that replacement of cations by H-ions creates "potential water molecules" which are liberated upon ignition of the new compound. Fig. 21 illustrates schematically this formation of crystal lattice water molecules as a consequence of replacement of cations by H-ions.



OH^- and $O^=$ ions on the surface of the crystal, as a part of the latter.

H_2O — molecules belonging to the crystal.

FIG. 21. Formation of crystal lattice water by adsorption of H^+.

Before the exchange the analyses of the water-free colloidal particle would yield $xSiO_2$, yAl_2O_3 and zK_2O, while after exchange H_2O would be found in place of K_2O.

The hydration of the H-system is thus considered to consist of at least two main parts. First, the ordinary water of hydration (water films around the colloidal particles and cavity water) and second, water of constitution. This water of constitution also explains why in many cases the H-systems exhibit a lower exchange capacity than the original zeolite complex, and furthermore it may account in part for the well known observation that ignition destroys the ionic exchange properties of the colloid.

Summarizing, it can be said that size consideration in ionic exchange can plausibly explain the observed relations between water adsorption of permutit *gels* and the nature of adsorbed ions (even including the abnormal H-system). For natural soil colloids (clay, bentonite-sols) complications may occur on account of differences in crystal structures and variations of size of colloidal particles due to ionic exchange and its consequent changes in the electrokinetic potential. In such systems the effect of the hydration of the ions in the outer surface and the polarization of water molecules due to the surface oxygen ions may overshadow to some extent the rôle played by the cavities.

General Summary

1) Ionic exchange (replacement of cations) has been studied in various artificial and natural aluminum silicates such as permutit, zeolite, Putnam clay and bentonite.

2) Electrodialyzed colloidal aluminum silicates contain exchangeable hydrogen ions and behave in many respects as colloidal acids. The strength of these acidoids varies as follows:

$$\text{permutit} < \text{Putnam clay} < \text{bentonite}$$

Permutit is the weakest acidoid.

3) In all exchange reactions very pronounced lyotropic series can be observed. The position of the various elements within the series varies according to the nature of the aluminum silicate. For the *adsorption* (intake) of monovalent cations the following relationships were found:

$$\text{Permutit: Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs} < \text{H}$$
$$\text{Putnam clay: Li} = \text{Na} < \text{K} < \text{H}$$
$$\text{Bentonite clay: Na} \leqq \text{Li} \leqq \text{K} < \text{H}$$

The *release* or outgo of adsorbed cations takes place in the reverse order of the intake.

4) The explanation of the individual behavior of the cations in the exchange process is based on Coulomb's law which expresses the magnitude of attraction existing between negative oxygen ions of the crystal lattice and adsorbed cations. Accepting the ideas of Wiegner, stress is laid on the radii of hydrated ions. It appears that these "hydrodynamic" radii vary according to the nature of the colloidal system.

5) The strong adsorption and difficult release of the hydrogen ion is easily understood by considering the strong chemical bonds existing between the adsorbed hydrogen ion and the oxygen and hydroxyl ions of the rigid crystal frame.

6) Ionic exchange affects the hydration of the colloidal particle. On the basis of space relationships it is suggested that clays with adsorbed divalent

cations should contain more water than clays having monovalent cations. H-systems are necessarily most hydrated.

References

[1] L. D. Baver: Missouri Agr. Exp. Sta. Research Bull., 129 (1929).
[2] M. Born: Z. Physik, 1, 221-249 (1920).
[3] M. Born: "Atomtheorie des festen Zustandes" (1923).
[4] R. Bradfield: Missouri Agri. Exp. Sta. Research Bull., 60 (1923).
[5] R. Bradfield: J. Phys. Chem., 28, 170-175 (1924).
[6] R. Bradfield: Ind. Eng. Chem., 20, 79 (1928).
[7] R. Bradfield: Proc. 1st Int. Congr. Soil Sc., 4, 858-868 (1928).
[8] R. Bradfield: J. Phys. Chem., 35, 360-373 (1931).
[9] W. L. Bragg and J. West: Proc. Roy. Soc., 114A, 450-473 (1927).
[10] W. L. Bragg: Trans. Faraday Soc., 25, 291-314 (1929).
[11] H. T. S. Britton: "Hydrogen Ions" (1929).
[12] P. S. Burgess and W. T. McGeorge: Arizona Agr. Exp. Sta. Tech. Bull., 15, 359-399 (1927).
[13] P. Debye: "Polar Molecules" (1929).
[14] C. Drucker: Z. Elektrochemie, 20, 79-81 (1914).
[15] P. Drude and W. Ernst: Z. physik. Chem., 15, 79-85 (1894).
[16] K. Fajans: Naturwissenschaften, 9, 1921.
[17] K. Fajans: Z. Elektrochemie, 34, 502-518 (1928).
[18] K. Fajans: Science, 72, 99-107 (1930).
[19] R. Ganssen (Gans): Centr. Mineral. Geol., 1913, 699-712, 728-741.
[20] K. K. Gedroiz: Kolloidchem. Beihefte, 29, 149-260 (1929).
[21] V. M. Goldschmidt: Trans. Faraday Soc., 25, 320-345 (1929).
[22] S. B. Hendricks and W. H. Fry: Soil Sci., 29, 457-479 (1930).
[23] F. M. Jaeger: Trans. Faraday Soc., 25, 320-345 (1929).
[24] H. Jenny: Kolloidchem. Beihefte, 23, 428-472 (1927).
[25] H. Jenny: Missouri Agri. Exp. Sta. Research Bull., 162 (1931).
[26] H. Kappen: "Bodenazidität" (1929).
[27] W. P. Kelley: J. Am. Soc. Agr., 22, 977-985 (1930).
[28] W. P. Kelley, W. H. Dore, and S. M. Brown: Soil Sci., 31, 25-45 (1931).
[29] H. W. Kerr: J. Am. Soc. Agr., 20, 309-355 (1928).
[30] F. Kohlrausch and W. Hallwachs: Z. physik. Chem., 12, 538-539 (1893).
[31] W. Kossel: Ann. Physik, 49, 229-362 (1916).
[32] I. Langmuir: J. Am. Chem. Soc., 38, 2221 (1916).
[33] J. E. Lennard-Jones and B. M. Dent: Trans. Faraday Soc., 24, 92-108 (1928).
[34] J. Liebig: Ann., 94, 373-384 (1855).
[35] A. R. Martin: Dept. Sc. Ind. Res. Tech. Paper, 1, London (1929).
[36] I. N. Mukherjee: Trans. Faraday Soc., 16, 103-115 (1921).
[37] St. Naray-Szabo: Z. physik. Chem., 1930, 356-377.
[38] H. Pallmann: Kolloidchem. Beihefte, 30, 334-405 (1930).
[39] F. W. Parker: Proc. Int. Congr. Soil Sc., 2, 164-173 (1928).
[40] W. Pauli u. E. Valko: "Elektrochemie der Kolloide" (1929).
[41] L. Pauling: J. Am. Chem. Soc., 51, 1010-1026 (1929).
[42] L. Pauling: Science, 71, 545 (1930).
[43] L. Pauling: J. Am. Chem. Soc., 53, 1367-1400 (1931).
[44] J. A. Prins: Naturwissenschaften, 19, 435-442 (1931).
[45] H. Remy: Z. physik. Chem., 89, 467-488, 529-569 (1915).
[46] F. Sestini: Landw. Versuchsst., 16, 409, 411 (1873).
[47] A. A. J. de Sigmond: Special publication, California Agr. Exp. Sta. (1927); Soil Sc., 21, 455-475 (1926).
[48] M. Trenel: Z. Pfl. Düng. Bodenk., 9A, 121-135 (1927).
[49] E. Truog: Ind. Eng. Chem., 8, 341-345 (1916).
[50] P. Vageler and J. Woltersdorf: Z. Pfl. Düng. Bodenk., A 15, 329-342 (1930); A 16, 184-204 (1930).
[51] E. W. Washburn: Jahrb. Radioakt. Elektronik, 5, 493-552 (1908); 6, 69-125 (1909).
[52] J. T. Way: J. Roy. Agr. Soc. England, 11, 313-379 (1850).
[53] T. J. Webb: J. Am. Chem. Soc., 48, 2589-2603 (1926).
[54] E. T. Wherry, C. S. Ross, P. F. Kerr: Colloid Symposium Annual, 1930, 191-193.
[55] G. Wiegner: J. Landw., 60, 111-150, 197-222 (1912).
[56] G. Wiegner: Kolloid-Z., 36 (Ergänzungsband), 341-369 (1925).
[57] G. Wiegner and H. Jenny: Kolloid-Z., 42, 268-272 (1927).
[58] G. Wiegner: Kolloid-Z., 51, 49-60 (1930).
[59] G. Wiegner: J. Soc. Chem. Ind., 50, 55-62, 65-71, 103-112 (1931).
[60] I. Zoch: Chem. Erde, 1, 219-269 (1915).

A STUDY OF THE STRUCTURE OF ELECTRODEPOSITED METALS.
PART II

BY L. B. HUNT

In an earlier paper[1] the writer has adumbrated a theory of the interference with crystal growth by ions, molecules or particles, other than those which constitute the metal being deposited, but no detailed suggestions were put forward of the precise mechanism by which this interference occurred. The present communication constitutes an attempt to elucidate this mechanism by means of a further and more detailed consideration of the processes occurring at the interface between cathode and electrolyte, in conjunction with the published data on the inclusion of foreign bodies within electrodeposits. In order to arrive at definite conclusions it has been necessary to start from the fundamental mechanisms of crystal growth and metallic cohesion, with particular reference to the concept of the two-dimensional lattice, and thence to develop a mechanical picture of the formation of this lattice from a more highly disperse phase during cathodic deposition. The ground having been cleared in this way, two further lines of thought have been developed. In the first place the problem has been treated as a case of surface chemistry. The interface cathode-electrolyte presents unusual and complicating features which render generalisation difficult. The constant renewal of surface which is occurring is particularly favourable to adsorption, but various bodies are present which may be adsorbed to a greater or less extent. Several workers have ascribed the influence of substances such as gelatin to adsorption, but have given no clear indication of the manner of this adsorption.

Secondly, the two-dimensional lattice idea has been further considered, and a new concept has been introduced of a two-dimensional lattice distortion, leading to changes of orientation and consequent refinement of grain. This concept has been applied to the data on the electro-deposition of alloys and of those metals with which hydrogen is co-deposited. Two distinct types of interference have thus been recognised, occurring respectively between, and during, the formation of the two dimensional lattices. It is fairly certain, however, that the transition from one to the other is not discontinuous in such cases as the discharge of complex cations and solvent sheaths, i.e., when the interfering particles are already attached to the metal ions. There is also the possibility, of course, of both types of interference occurring in any one case.

A number of investigators have referred to two other processes as influencing the structure of electrodeposited metals, viz. cataphoresis, and "mechanical inclusion" of the electrolyte or of colloidal particles. Now although cataphoresis may account for the arrival of particles at the cathode, some such process as adsorption must be brought into play to cause their ultimate cohesion to the cathode, whilst mechanical inclusion is of doubtful existence, and in any case has no fundamental bearing on the problem in hand. These two processes have therefore been omitted from consideration at the present time.

The Mechanism of Lattice Formation

Current ideas on the subject of crystal growth are definitely in favour of a discontinuous process occurring by layers. It is a simpler matter to visualise the formation of a two-dimensional lattice in the process of crystallisation from the molten state, in which case the distribution in the two phases is substantially the same. Any attempt to form a mechanical picture of this lattice formation during cathodic deposition, however, introduces several complications, chief among which is the very great difference in distribution of the metal ions in the two phases. Other factors tending to obscure the picture are the deposition of only one kind of ion, in contradistinction to the building up of crystals of inorganic salts, and the nature of the electrical forces involved which on a priori grounds makes any suggestion of a pause in the process of deposition difficult to uphold. More so than with any other process of crystal growth, it is obviously impossible for deposition to be a continuous process, or for a two-dimensional lattice to be laid down in its entirety. The only alternative is therefore a gradual laying down of the lattice in such a way as to satisfy the conditions of distribution and the supply of free electrons. Carrying the process of elimination a stage further, general considerations and experimental observations on crystal growth suggest the extreme unlikelihood of a random deposition of ions at more or less isolated points until a layer is complete. In those cases of deposition referred to in Part I as "cathodic reproduction" very extensive and uniform layers have clearly been formed in order to continue the orientation of the underlying crystals without imperfection.

Volmer[2] postulates an adsorption layer of ions in a state intermediate between that of the electrolyte and that which they will take up in the lattice, but bases his ideas of the subsequent lattice formation on the assumption of the surface mobility of the adsorbed ions. This concept is obtained by analogy with the growth of mercury crystals by deposition from the vapour phase. This process, however, involves uncharged atoms only, and it is quite likely that in this condition the mercury atoms arriving at the surface of the growing crystal may cohere primarily with van der Waals' forces and may possess lateral mobility. In the case of electrodeposition, on the other hand, positively charged ions are approaching a negatively charged surface, and the writer cannot agree that surface mobility in these conditions of powerful binding is possible. Volmer found by oscillographic measurements (during which the amount of current passing was so small that concentration polarisation was absent), that the polarisation accompanying the deposition of zinc on large well-formed zinc crystals was quite appreciable, whereas with zinc amalgam and finely crystalline zinc foil as cathodes, no perceptible polarisation was recorded. This result he ascribed to a retardation on the part of the metal ions entering the solid lattice, caused by fluctuations in thickness of the adsorbed layer, whilst in the case of the fluid electrodes, discharge and entry into the fluid phase constitute a single process. In the case of the finely crystalline electrodes the actual surface area may have been considerably greater than the apparent area.

The existence of an adsorption layer of metal ions on the surface of a cathode is a reasonably justifiable assumption in view of the work of Langmuir and others, coupled with the much older concept of a double layer due to Helmholtz and Lippmann. By making this assumption, however, the problem of the manner in which the layer is formed and maintained is still left unsolved. Presumably metal ions in the vicinity of the cathode will frequently be in collision with the cathode surface, and will tend to adhere thereto, prior to the passage of a current, although this will apply in greater or less degree to all ionic and molecular species present. On passing a current, however, the anions will be repelled violently, leaving an adsorbed layer of cations from which deposition can take place provided the potential requirements are satisfied. As deposition removes the metal ions the layer must be replenished by the process of diffusion. The process of deposition can therefore be roughly represented thus:

Diffusion ⟶ Adsorption ⟶ Lattice formation.

The final velocity will naturally be governed by the slowest stage in the process. The speed of diffusion will be determined by the concentration gradient across the diffusion layer, as also will the speed of adsorption. Increase of temperature, agitation of the solution and decrease of current density will thus promote diffusion, and adsorption from the diffusion layer. The concentration gradient, however, will depend upon the amount of deposition occurring, and thus on the current flowing. The delivery of electrons at the cathode surface is thus the determining factor, but certain complexities are introduced when the mechanism of this process is considered.

The Electron Theory of Metals and Metallic Cohesion

The majority of workers in this field have dealt mainly with the mathematical aspect of the problem, and it has become more and more apparent, as the wave nature of electrons has been established, that the formation of a mechanical picture should not be attempted. Certain general conclusions may, however, be drawn as to the inner structure of a metal as it affects the building up of a lattice at the cathode. This process consists fundamentally of the passage of the conduction electrons through the cathode until on reaching the surface they are captured by the metal ions, arriving from the opposite direction. There are therefore two points on which information is desired; firstly, as to the manner in which the electrons arrive at the cathode surface, and then as to the manner in which they cause the cohesion of the newly formed two-dimensional lattice to the bulk of the cathode.

In the first place, it is known that comparatively few of the electrons present in a metal are concerned in the conduction process, which comprises a relatively slow drift superimposed on the very rapid random movement of the electrons. The concepts of the manner in which the electrons exist in a metal vary from the interpenetrating lattice theory of Lindemann,[3] supplemented by Sir J. J. Thomson[4] to involve the movement of chains of electrons along the lattice, to the free electron-gas theory of Sommerfeld,[5] whilst Barlow[6] has suggested a resemblance to an incompressible fluid rather than to a gas. Bloch[7] has adopted the view that, whilst the conducting electrons are free, their motion is not completely haphazard, as postulated by Sommerfeld, but is a motion in a periodic field of force of which the period is the same as that of the atomic lattice. The electrons may then be regarded as both free and bound, i.e., as jumping from atom to atom and pausing for a time at each. Lennard-Jones and Wood[8] have further discussed the electronic distribution in metals and have obtained a partial solution which is particularly interesting from the present point of view. A complete solution for a three-dimensional metal was not attempted, but the problem was simplified to that of a hypothetical two-dimensional lattice. For further details and the resulting diagram the original paper must be consulted, but the authors concluded that regions of greater electron density exist between the nuclei, and that the electrons within these regions are to be regarded as shared between the four surrounding nuclei (still retaining the two-dimensional concept), since they cannot be definitely associated with any one nucleus. These shared electrons apparently constitute a lattice array interpenetrating that of the nuclei, similar to the suggestions of Lindemann and Sir J. J. Thomson, but differing in that the system is not static even at the absolute zero. Those electrons which have sufficient energy will cross the equipotentional lines and be able to travel from end to end of the metal, causing a continual interchange of electrons.

This, however, does not advance the solution of the problem of how the slow drift of the conduction electrons accounts for the cohesion of a metal ion *on every lattice point.* Barlow, however, observes that the pressure of the applied E.M.F. will be sufficient to cause only a limited number of gaps to be bridged by the conducting electrons, so that their flow will be restricted to paths that are continually changing. The electrons will always be attempting to move forward, but they must wait until an opportunity offers. It seems to the present writer that the most probable mechanism of the arrival of electrons at the surface, in the case of electrodeposition at all events, is in a succession of waves at right angles to the direction of flow, which will appear as somewhat analogous to a creeping barrage passing continually over the face of the cathode. It has already been said that the formation of a mental picture of this type is in many cases unjustifiable, but there are definite objections to being too easily dissuaded from the particle concept in the present case, such as the relations expressed in Faraday's laws, and the orderly arrangement of the lattices resulting from the interaction of metal ions and electrons, despite the indeterminate nature of the conduction process. If an imaginary plane is taken through the cathode, normal to the direction of flow of the current, and similar to Lennard-Jones' two-dimensional lattice, it is clear that all the conduction electrons cannot be moving simultaneously.

There must, therefore, be either a random here and there movement (an idea which is immediately discounted), or a wave-like oscillation, having an amplitude of the same order as the mean free path of the electrons themselves, and a frequency dependent upon the applied E.M.F. The passage of this wave train through the adsorption layer will naturally govern the formation of the next adsorption layer, and the whole process will thus be governed by these electron waves.

As regards the nature of metallic cohesion, Hume-Rothery[9] suggests that the reason underlying the formation of this particular type of bond is that there are insufficient valency electrons for each atom to complete its octet by sharing one electron with each of several neighboring atoms. An atom of Group N will normally tend to complete its octet by sharing one electron with each of $(8-N)$ other atoms. When, however, there are less than four available valency electrons, each atom can no longer share one electron with more than four other atoms. When this occurs a bond must be formed in which an electron can be associated with more than two atoms. This bond will thus resemble the normal covalent bond in which an electron is shared between two atoms, but differ in that a larger number of atoms will share a valency electron. The point then arises of the difference between the cohesive forces in adsorption and in lattice formation, i.e., the difference between an adsorbed ion and a "discharged atom." The obvious conclusion is that the difference is due to the presence of the excess valency electrons. If the supply of electrons were cut off, adsorption would also cease, since the adsorption layer would no longer be incorporated into the metal lattice, thus forming a new surface on which further adsorption can take place. It is probable, therefore, that the adsorption of metal ions comprises an electrostatic type of adhesion in which the adsorbed ions attach themselves by the mirror image forces to the surface, without interfering with the cohesion bonds in the lattice. The supply of electrons by conduction will then operate to incorporate the adsorbed layer by the covalent electron-sharing linkage. Reverting to the wave concept of electrons, the transition from ion to "atom" may then be considered not as a sharply defined process, but as a merging of one into the other.

Interfacial Phenomena

The existence of an adsorption layer at the interface cathode-electrolyte has been the basis of the foregoing discussion, and it now becomes necessary to examine in more detail the conditions in this layer with respect to the various ionic and molecular species present in the solution. The constant renewal of surface which occurs cannot but be favourable to pronounced adsorption effects, and in these circumstances the experimental fact that adsorption of species other than the metal ion takes place to a very limited extent requires a word of explanation. The point of immediate interest is to consider the forces operating on a metal ion approaching a cathode. Firstly, there is the force due to the electrical field, which is responsible for the migration of the ions, and extends throughout the electrolyte. Secondly, there is the short range electrostatic force between the cathode and the ion, and also the van der Waals' cohesive forces. In the opposite direction there are the retardations due to the anionic atmosphere and the solvent sheath respectively.

Now the ionic atmosphere, according to the Debye-Hückel theory, is continually building up in front, and dying away in rear, of a moving ion. When a cation reaches a point a few angstroms away from the cathode, therefore, the building up must cease and the dying away become more complete, owing to the repulsive forces on the anions prohibiting their close approach to the cathode surface. The resultant force on a metal ion passing through this part of its course will thus be first a slight retardation, followed by an increased attraction. The next event will be the repulsion of the solvent envelope, which will cause a further increase in potential energy of the ion, again followed by a sharp fall, to the point where the ion is held by the electrostatic forces, vibrating about the position of minimum potential energy, pending the arrival of one or more electrons to bring about ultimate cohesion. The potential energy of a metal ion as a function of its distance from the cathode surface is represented diagrammatically in Fig. 1 by curve A.

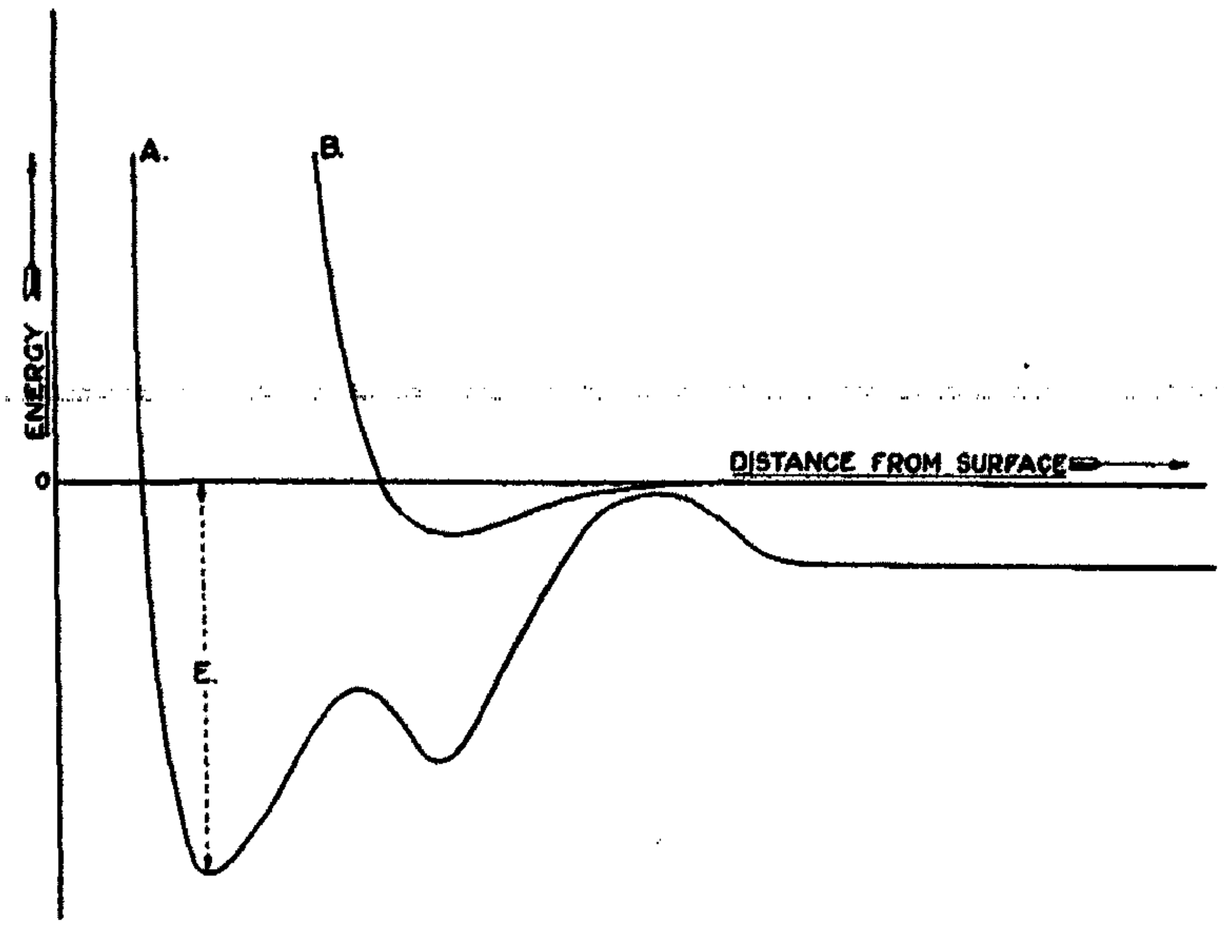


Fig. 1
Variation in potential energy with distance from cathode surface

This curve is at best a first approximation, largely owing to the complexities introduced by the superposition of an electrical field on the more or less normal adsorption phenomena, but it is now tentatively put forward as a basis for future discussion.

Discharge of the ion will occur only if the neutralisation potential E, of Gurney,[10] be greater than the work function of the metal ϕ, less the applied potential difference V. This neutralisation potential is defined by

$$E = I - W$$

where I is the ionisation potential of the ion, and W represents the energy of solvation, which must be replaced on discharge. The condition for discharge is then given by

$$E = I - W > \phi - V$$

Various other cations are usually present in the electrolytes employed for deposition, but except in cases of alloy formation, which will be dealt with later in the paper, they are never found in the deposit. The inference is that ions such as those of the alkali metals are not only incapable of being discharged, but on colliding with the cathode, have less tendency to be adsorbed, and are more likely to be reflected into the solution, in accordance with their relative ionisation potentials. This will result, however, in a building up of the concentration of alkali metal salts in the vicinity of the cathode, with a consequent decrease in the dissociation of the metal ions.

The adsorption of molecules will not be affected by the electrical field, but the ions of the metal lattice will cause the formation of induced dipoles in the molecules, which together with the long range van der Waals' forces will bring about adsorption. The potential energy of a molecule or solvent dipole is represented in Fig. 1 by curve B. There will be a small minimum at a greater distance from the surface than was the case with a metal ion, from which it is clear that molecules may be adsorbed in a layer above the ionic layer. They will, however, be comparatively loosely bound, and will thus possess an appreciable chance of escaping back into solution. They will also possess a certain amount of lateral mobility, according to Volmer's observations,[2] and it may be necessary for stable nuclei or groups to be formed in this way before adsorption becomes possible.

Solvent sheaths present a transitional case, in that the molecules are already bound to the metal ions, and that they arrive in more or less stable groups. However, the chance of their survival as far as the adsorption layer is considerably reduced by the increased concentration of metal ions in the two dimensional state. The possibility of their inclusion is nevertheless not to be ignored, as was indicated in Part I of this paper.[1] The above explanation merely accounts for the infrequency of the process. In this connection some results obtained by Aten, Hertog and Westenberg,[11] in the absence of solvation are instructive. Experiments were carried out with fused electrolytes and it was found that although the grain-size of electrodeposited silver, copper and nickel, was still dependent upon temperature and composition of bath, the wide differences which exist between the structures of these metals when deposited from solution disappeared. In general the grain-size was much larger than in deposits from solution. Van Liempt[12] has also obtained coarse-grained deposits of tungsten from fused electrolytes.

A similar transitional case is presented by the deposition of complex cations, such as Fuseya[13] and his co-workers have investigated in copper sulphate electrolytes. Here again the molecular species arrive at the cathode already bound to the metal ion, but their concentration will not be reduced to the same extent as will that of the solvent molecules. The probability of their becoming adsorbed and included is thus much greater. Fuseya ascribed his results to "discharge" of the complex ions, but his curves bear every resemblance to adsorption isothermals. Fuseya,[14] however, could not obtain the same results with lead and zinc electrolytes, although complex ion formation was found. This failure he ascribed to the decomposition of the complex ions in the film of more alkaline solution near the cathode.

The Inclusion of Basic Matter

A more interesting phenomenon which has recently received attention concerns colloidal hydroxides or basic salts precipitated in the cathode film owing to the decrease in hydrogen ion concentration caused by the discharge of hydrogen. This was first investigated by O'Sullivan,[15] who concluded that in the case of nickel sulphate electrolytes the hydroxide entered the deposit and influenced its structure. Macnaughtan and Hammond[16] have recently extended this line of work, using Brinell hardness as a criterion of grain size in the deposit. It was found that the acidity of the electrolyte exerted a marked influence upon the hardness and structure of the deposit. In general a low acidity favoured the formation of hard deposits having a finely crystalline structure, whilst greater acidity favoured the formation of softer deposits having a larger grain size. Further, it was found that the hardness did not increase uniformly with increasing pH, but rose suddenly after a certain critical pH value had been reached. The present writer,[17] however, has drawn attention to the somewhat illogical method used to represent the results of these workers, namely, the plotting of Brinell hardness against pH. By recalculating to hydroxyl ion concentration and plotting the results obtained

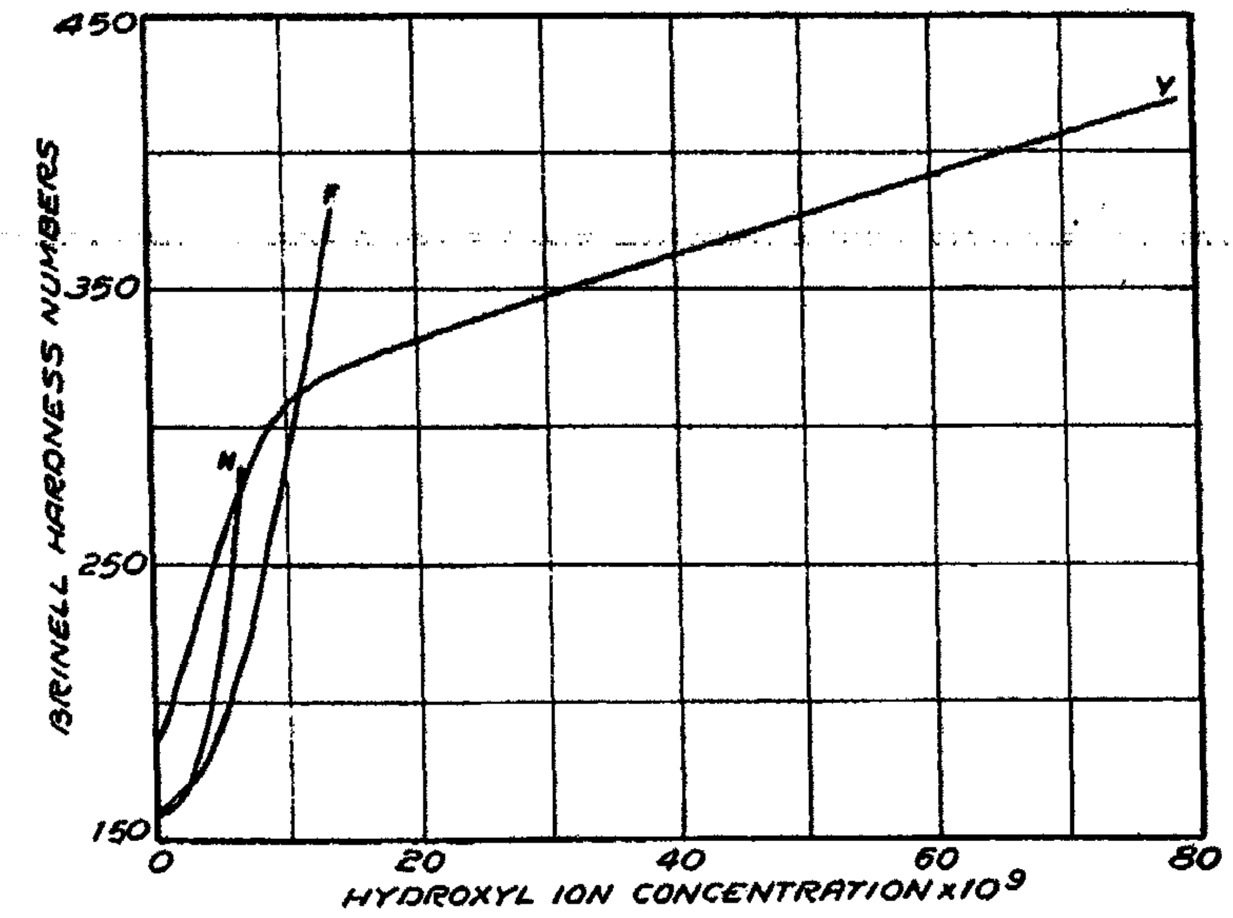


FIG. 2

against Brinell hardness the writer has obtained curves of a different type, shown in Fig. 2 which bring out more clearly the differences between the electrolytes containing ammonium ions and those free from ammonia, owing to the different types of buffer action exerted. It appeared that whereas with the electrolytes N and F containing boric acid and sodium fluoride the amount of inclusion increased rapidly with increasing hydroxyl ion concentration, in the solution γ, containing ammonium sulphate the rate of increase of hardness fell away as hydroxyl ion concentration increased. While the latter effect might well be due, as suggested by the authors, to the tendency of the precipitated matter to redissolve in the ammoniacal solution in the vicinity of the cathode, the mechanism of the inclusion remains unexplained.

Adsorption in the true sense of the term is clearly insufficient to account for the increase in the amount of inclusion with increasing hydroxyl ion concentration, which fact of itself suggests a more direct mechanism of inclusion. The writer would therefore suggest that this mechanism consists of the discharge *of a complex ion containing the metal hydroxide, or of an ion to which the colloidal basic matter is attached.* In this connection it is interesting to note that Brdicka[18] has recently investigated the hydrolysis of cobaltous chloride solutions at the dropping mercury cathode, and has concluded that deposition may occur from the ion $[Co(H_2O)_5\,OH]^{\cdot}$.

The deposition of basic matter is also a factor of importance in the electrodeposition of chromium.

Sargent[19] stated that the first stage in the process of electrolysis of chromic acid was the formation of a film of basic chromium chromate on the cathode. This was followed by a partial reduction of chromic ions to chromous ions, and deposition from both types with simultaneous evolution of hydrogen. Liebreich[20] suggested that metallic chromium was obtained by secondary reduction of the divalent hydroxide $Cr(OH)_2$, in the cathode film, basing his statement on the fact that the metal is found beneath a layer of hydroxide when deposited from almost neutral electrolytes. The smaller the OH' concentration the greater would be the tendency for chromium to be deposited free from hydroxide. Müller[21] agreed that the film at the cathode was composed of chromic oxide or chromic chromate, but maintained that deposition took place from the hexavalent ion. The sulphate radical was supposed to destroy the film and allow chromic acid to reach the cathode and be reduced, whilst in the absence of the sulphate or other radical the diaphragm (then invisible) was assumed to be "ideal." Small ions such as the hydrogen ion would be able to pass through the diaphragm, but large anions would be unable to follow. This concept has been criticised by Ollard,[22] who showed that electrophoresis, which was held by Müller to be responsible for pressing the diaphragm against the cathode, was unfavourable in the chromic acid solutions employed.

As regards the actual inclusion of basic matter in the deposit, Adcock[23] found that chromium contained considerable amounts of oxygen in a form from which insoluble Cr_2O_3 was produced by heating in vacuo. The original oxygenic matter dissolved in dilute acid without residue, suggesting that it was not Cr_2O_3, and no evidence of the presence of the electrolyte could be found on crushing the deposit. The inference is that basic matter was included in the deposit in a manner analogous to the inclusions found by O'Sullivan and by Macnaughtan and Hammond.

Britton and Westcott[24] have also recorded the deposition of basic matter from solutions of chromic sulphate and chromic chloride. Furthermore these workers[25] have recently found as much as 13% of hydroxide matter included in the apparently metallic portions of the deposit. The writer considers that the concept introduced above to explain the inclusion of basic matter in nickel deposits will also suffice to account for the presence of such inclusions in chromium deposits, and also for the observed diaphragm formation. The colloidal particles are considered to be attached to the metal ions in the adsorption layer, and whilst this layer is static it will naturally not be visible. When deposition occurs, however, with the accompanying evolution of hydrogen, large amounts of basic matter will be brought up to the cathode. Small amounts will certainly remain adsorbed, and so become included in the deposit, but the major portion will be separated from the metal ions. The adsorbed layer will then thicken and become detached from the surface, thus becoming visible as a diaphragm in contradistinction to the breakdown of a molecular film, which merely results in molecular dispersion or solution. This concept appears to agree well with the results of Förster and Deckert[26] who, working with stannous sulphate electrolytes to which m-cresolsulphonic acid had been added, found that whilst the effect of adsorbed molecules was prolonged, the colloidal matter was rapidly exhausted, the effect increasing with increasing current density. In the case of basic matter, of course, the supply of colloidal particles is continuous owing to the constant evolution of hydrogen causing a rise in pH of the cathode layer. The process will differ considerably from the normal phenomenon of adsorption in that the amount of inclusion will increase regularly with increasing concentration of basic matter in the cathode film. The number of metal ions having colloidal or basic matter attached will necessarily be only a small fraction of the total number of metal ions proceeding to the cathode, this fraction being dependent on the hydroxyl ion concentration.

The Deposition of Foreign Cations

In certain cases of electrodeposition there are two principal cations entering the deposit. One of these may be the hydrogen ion, as is the case with the metals of the transitional group, or both may be metal ions, leading to the formation of an alloy. Now deposits formed in this way from two ions are well known to possess finely crystalline structures. For instance, nickel, cobalt or iron, deposited from solutions of their simple salts, are invariably of much finer structure than metals such as copper and zinc deposited under similar conditions. Further, deposits of two metals which normally yield coarsely crystalline deposits alone, are found to give fine-grained alloys. In the foregoing discussion foreign bodies which presumably enter, or rather cause, the grain boundaries of the deposited metal, have been the chief concern, but it is clear that foreign ions which enter the lattice have also to be taken into consideration. In the case of alloy deposition the variable factors such as current density, temperature, agitation, etc., instead of influencing the structure of the deposit, merely serve to bring about alterations in its composition. No explanation of this finely crystalline structure has as yet been forthcoming.

The constitution of electrodeposited alloys has been investigated by a number of workers. Nakamura[27] found that the lattice constant of electrolytic brass containing 82% of copper showed no apparent difference from that of cast brass of the same composition. The deposit may therefore be presumed to consist of the normal α-solid solution of zinc in copper. Roux and Cournot[28] examined electrodeposits of copper-zinc, cadmium-silver, cadmium-zinc, and cadmium-nickel alloys, and found that the X-ray spectra could not be reproduced by superposition of those of the constituent metals, indicating that compounds or solid solutions, or both, were formed. Similarly Fuseya and Sasaki[29] examined their deposits of chromium-iron alloys and found them to consist of solid solutions. Stillwell[30] showed that in cadmium-silver alloys a number of phases consisting of both solid solutions and compounds were present.

Unfortunately the systems hydrogen-metal have received very little attention, and it is as yet quite impossible to state whether these systems represent solid solutions of the substitutional type, or solid solutions of the interstitial type (in which the solute ions are situated in the spaces between those of the solvent) or compounds. Yamada[31] and McKeehan[32] obtained the characteristic X-ray pattern for palladium, but found that the lattice was uniformly expanded by the presence of hydrogen. Linde and Borelius[33] concluded that both solid solution and compound formation occurred in the system palladium-hydrogen, whilst Hanawalt[34] considered that the compound Pd-H was formed. Evidence of the formation of a solid solution was obtained by Hüttig and Brodorb,[35] who found that the presence of hydrogen in electrolytic chromium caused a widening of the lattice without altering its form.

It is now established that the ions of a metal entering into solid solution replace those of the solvent metal in the lattice, so that the two kinds of ions are situated at random in a common lattice. If, however, the limit of solid solubility is exceeded a new phase must be formed in which the crystal structure differs from that of the pure metals, and which may consist partly of an intermetallic compound. The details of the concept of substitution in solid solutions have been worked out by Rosenhain[36] who in explaining the increased hardness of these phases suggested that solute atoms distort the lattice of the solvent metal, thus causing an increased resistance to slip. The writer proposes to adapt this hypothesis of lattice distortion to the case of a two dimensional lattice in course of formation. In the solid three-dimensional state it is comparatively easy to visualise distortion producing hardness, but with a two-dimensional lattice the hardness factor is absent, and rigidity is greatly reduced. The writer suggests, therefore, that the presence of stranger ions in the two-dimensional lattice will cause distortion and breaking up of this lattice with consequent changes in orientation and grain refinement. If the limit of solid solubility is exceeded a new phase must be formed, which will again be conductive to grain refinement. This type of interference with lattice formation clearly occurs in a plane parallel to the cathode, in contradistinction to the other types of interference which have been considered. The result of lattice distortion is therefore the production of a fibrous type of deposit, such as is invariably found with deposits of the transitional metals and of alloys.

Conclusion

The various types of interference with lattice formation which have been described are shown diagrammatically in Fig. 3, which represents the passage of the ionic and molecular species from the electrolyte to the cathode.

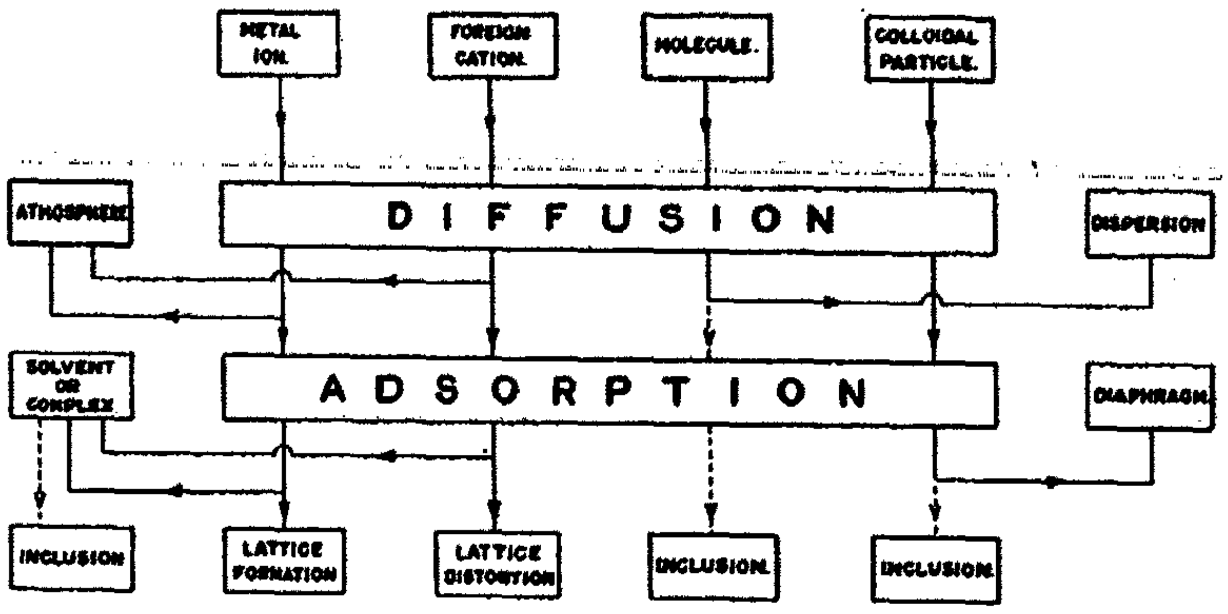


FIG. 3
The processes occurring at a cathode

Continuous lines indicate the major processes, and broken lines the processes of infrequent occurrence. The branching lines indicate the removal of certain types of ions and molecules from the cathode layer. Thus the first event on the approach of a cation to the cathode will be the loss of its anionic atmosphere, which will be followed by the loss of the solvent sheath or the complex portion of the ion. The latter may, as shown, remain adsorbed to a slight extent and thus be included in the deposit. The difference between the removal of molecules and colloidal particles is also indicated. Molecules adsorbed from the cathode will return into solution, whereas colloidal matter will not, and may accumulate temporarily as a diaphragm a short distance from the cathode, prior to its redistribution by diffusion or electrophoresis. Further, certain colloidal particles, more particularly those consisting of basic matter, will be adsorbed more firmly and in greater amount owing to their attachment to the metal ion, and will behave in a similar manner to complex ions.

The theory of interference with crystal growth proposed by the writer[1] receives considerable support from the lines of thought which have been developed in this paper. It is clear that no simple hypothesis, such as that based on changes in polarisation, can be expected to account for the variations in structure of electrodeposited metals. Each species present in the electrolyte must be considered on its own merits with respect to the forces acting upon it, and its behaviour under these forces. It is considered that the adoption of this method has resulted in a more detailed insight into the mechanism of interference with crystal growth, and although the writer hopes to be able to present experimental data and more exact information bearing on the relative potency of the interfering bodies, it is his opinion that the first essential is an attempt to present a clear and logical account of the subject. By applying existing knowledge in the co-ordination of the available data and the further development of the hypothesis it is hoped that this object has been achieved.

References

[1] Hunt: J. Phys. Chem., **36**, 1006 (1932).
[2] Volmer: Z. physik. Chem., **139**, 597 (1928).
[3] Lindemann: Phil. Mag., **29**, 127 (1915).
[4] Thomson: Phil. Mag., **44**, 657 (1922).
[5] Sommerfeld: Z. Physik, **47**, 1 (1928).
[6] Barlow: Phil. Mag., **8**, 289 (1929).
[7] Bloch: Z. Physik, **52**, 555 (1928).
[8] Lennard-Jones and Wood: Proc. Roy. Soc., **120A**, 734 (1928).
[9] Hume-Rothery: Phil. Mag., **9**, 65 (1930).
[10] Gurney: Proc. Roy. Soc., **134A**, 137 (1931).
[11] Aten, Hertog and Westenberg: Trans. Am. Electrochem. Soc., **47**, 265 (1925).
[12] Van Liempt: Z. Elektrochemie, **31**, 249 (1925).
[13] Fuseya and Nagano: Trans. Am. Electrochem. Soc., **52**, 249 (1927).
[14] Fuseya and Yumoto: J. Soc. Chem. Ind. Japan, **31**, 80B (1928).
[15] O'Sullivan: Trans. Faraday Soc., **26**, 89 (1930).
[16] Macnaughtan & Hammond: Trans. Faraday Soc., **27**, 633 (1931).
[17] Hunt: Discussion on above.
[18] Brdicka: Coll. Czech. Chem. Comm., **3**, 396 (1931).
[19] Sargent: Trans. Am. Electrochem Soc., **37**, 479 (1920).
[20] Liebreich: Z. Elektrochemie, **29**, 208 (1923).
[21] Müller: Z. Elektrochemie, **32**, 299 (1926).
[22] Ollard: *Metal Ind. (London)*, **31**, 437 (*1927*).
[23] Adcock: J. Iron Steel Inst., **115**, 369 (1927).
[24] Britton and Westcott: Trans. Faraday Soc., **27**, 809 (1931).
[25] Britton and Westcott: Private Communication.
[26] Förster and Deckert: Z. Elektrochemie, **36**, 901 (1930).
[27] Nakamura: Sci. Papers Inst. Phys. Chem. Research, Tokyo, **25**, 287 (1925).
[28] Roux and Cournot: Industrie electrique, **37**, 455 (1928).
[29] Fuseya and Sasaki: Trans. Am. Electrochem. Soc., **59**, 209 (1931).
[30] Stillwell: J. Am. Chem. Soc., **53**, 2416 (1931).
[31] Yamada: Phil. Mag., **45**, 241 (1923).
[32] McKeehan: Phys. Rev., **20**, 82 (1922).
[33] Linde and Borelius: Ann. Physik, **84**, 747 (1927).
[34] Hanawalt: Phys. Rev., **33**, 444 (1929).
[35] Hüttig and Brodkorb: Z. anorg. Chem., **144**, 341 (1925).
[36] Rosenhain: Proc. Roy. Soc., **99A**, 192 (1921).

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STATIC SORPTION ISOTHERMALS. ADSORPTION OF CARBON DIOXIDE BY CHARCOAL

BY L. J. BURRAGE

1. Introduction

As the result of previous work on the discontinuous nature of sorption isothermals,[1] in themselves largely the outcome of a new method for the determination of sorption isothermals,[2] it was decided to carry out a further series of experiments using the static technique. This has the obvious advantage that the discontinuity cannot in any measure be due to the method employed.

The criticism which has been levelled at all previous work is that in no cases have points been taken closely enough together, in many instances a dozen points or so being deemed sufficient to cover the complete range of the isothermal. In the present work it was decided to start from a pressure of about 80 mm. and obtain points as close together as was possible, the main object in view being to determine, if possible, the exact number and position of the breaks.

2. Experimental

The technique employed was similar to that described in a previous paper.[3] This was adopted after careful consideration of the only other method which was suitable for this type of work—the McBain Sorption Balance. It is not considered that the latter has any advantages over the method employed in the present work. In the sorption balance the quartz spring has first to be calibrated. This is achieved by noting the elongation of the spring on the addition of known weights to the cup, which is attached to the spring. When set up for use, charcoal is placed in the cup and the apparatus evacuated. A certain charge of vapour is admitted to the system, which is then allowed to come to equilibrium. One notes the position of the spring with a cathetometer to give the weight of substance adsorbed and reads off the vapour pressure on some type of manometer. This latter involves two readings on the cathetometer, if some type of U-tube manometer is employed.

In the method employed in the present work, it was necessary to know the volume of the apparatus accurately and then for each point on the isothermal four cathetometer readings were necessary, two for the initial pressure and two for the final pressure. It would appear that the accuracy of the latter method was not in any way inferior to that of the sorption balance, judging by the degree of reversibility which has been obtained.

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[1] Allmand and Burrage: Proc. Roy. Soc., **130A** (1931); J. Phys. Chem., **35**, 1692 (1931).

[2] Burrage: J. Phys. Chem., **34**, 2202 (1930).

[3] Proc. Roy. Soc., loc. cit.

Several refinements have been instituted in the method described in a previous paper, and it would be of advantage to describe the method in detail. The complete train (Fig. 1) consists of a Leybold mercury condensation pump backed by a Hyvac Oil Pump, a McLeod Gauge, a small section of narrow tubing about 2½ inches long with taps at either end (A and B, the volume between these points being approximately 1.5 ccs.), and a freezer C, followed by a mercury manometer E. This is fitted with a tap in the 'closed' limb which is connected to the vacuum line, so that, if necesssary, the manometer may be pumped out on the closed side. This is useful in freeing the mercury from the last traces of air, when the apparatus is first set up.

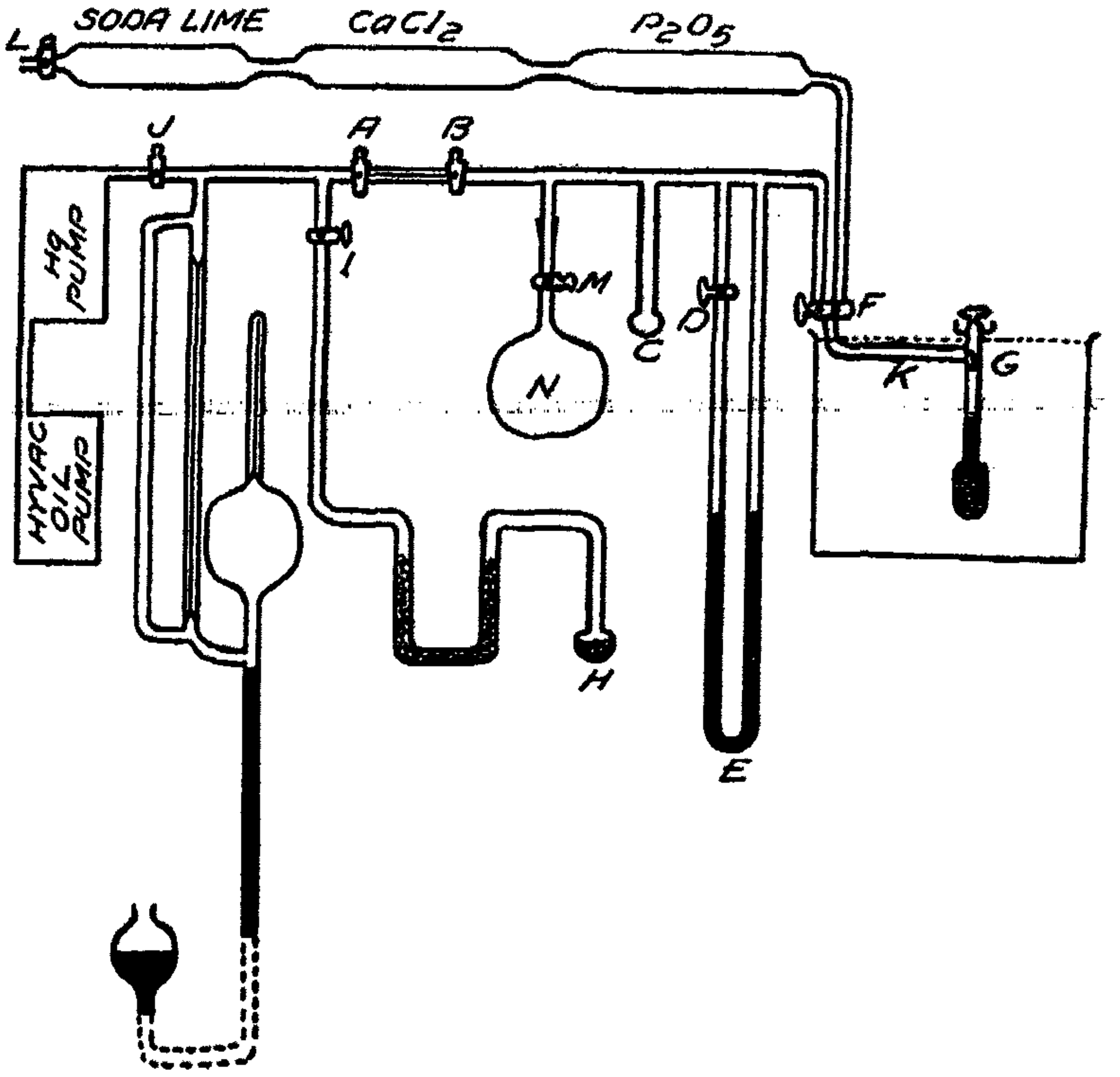

Fig. 1

F is a two-way tap, one limb being connected to the vacuum line and one to the air. Attached to this latter limb are a phosphorus pentoxide tube, calcium chloride tube, and a soda lime tube. The container for the charcoal was attached to the common limb of this tap. This container G, made in silica, was exactly similar to that described by Chaplin.[1] Between the mercury pump and the tap A, a T-piece was inserted leading to a bulb which was shut off from the apparatus by a tap. This constituted the supply bulb.

It has been suggested that interference with the position of the breaks might be caused by the CO_2 on the surface which is constantly being driven

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[1] Proc. Roy. Soc., 121A, 344 (1928).

off during the course of the experiment to a greater or lesser degree. Since the chief object in view in this investigation was the establishment of the exact pressures at which breaks occur, and also the quantity increment per break, when these are unaffected by disturbing conditions, it appeared that carbon dioxide might be a suitable substance to employ.

Since the carbon complex, C_XO_Y, which covers the surface of the charcoal, exerts a pressure of carbon dioxide at ordinary temperatures, it seemed as though there was a probability that an isothermal with carbon dioxide might be somewhat less disturbed by those complications which have been present heretofore.

It was decided to work with a charcoal which was known to have a large capacity for carbon dioxide[1] and, D 1, a steam-activated coconut charcoal, (packing density = 0.575) was selected. About 2 gms. of this was sieved (10-12 mesh) and heated in an air oven at 150° to remove most of the adsorbed water to facilitate the evacuation. This is an important point in the evacuation of charcoals, which has been previously overlooked, as it lowers the time necessary for evacuation down to 10^{-4} mm. by at least 75%. This half-dried charcoal was packed into the silica container and attached to the evacuation apparatus, and pumped down to 10^{-4} mm. at room temperature. The temperature was then raised to 110°C. and the charcoal evacuated to the same pressure as before. The container was detached, cleaned with alcohol and ether, and weighed, and finally attached to the apparatus proper, the joint being made vacuum-tight with Everett's Wax.

The supply bulb on the apparatus was filled with sodium bicarbonate and the whole apparatus evacuated to a pressure of 10^{-4} mm., the tap on the container being kept shut during this operation. Between the supply bulb and the main apparatus a small U-tube, filled with phosphorus pentoxide, was inserted to free the carbon dioxide from water as it passed into the apparatus.

The taps J, leading to the pumping system, D, forming the closed limb of the manometer, and A, leading to the main apparatus were closed. Tap I was opened and the supply bulb H warmed until gas was evolved. A Dewar flask containing melting methylcyclohexane was put on the freezer C and the taps A and B opened to admit a charge into the apparatus, the two-way tap F being open, connecting with G. The freezing bath removes any traces of water which may have passed the phosphorus pentoxide. Tap B was now shut and the pressure read off on the manometer E. Then tap G was opened and when the pressure was constant the manometer was read again. Knowing the initial pressure, the final pressure after sorption, and the volume of the apparatus, the weight of carbon dioxide sorbed was found. This was repeated several times until sufficient carbon dioxide had been adsorbed to give a pressure of about 100 mm.

Tap G was then shut, and liquid air placed around the freezer C, the carbon dioxide between B and G being frozen out. The two-way tap F was then turned to admit air and the container removed for weighing. The air that is

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[1] Allmand and Burrage: Proc. Roy. Soc., **130A**, 610 (1931).

let into this portion of the apparatus is freed from water and carbon dioxide by passing over soda lime, calcium chloride and phosphorus pentoxide. Immediately the container has been removed, the open end of the tube K, where the container had been attached, was closed by a waxed glass stopper.

In this way the container can be removed at any time during the experiment without interfering with the pressure of carbon dioxide in the apparatus. The container was next reattached, the air being removed from the side arm system by means of a hand pump attached at L, the liquid air removed and the whole apparatus evacuated down to 10^{-4} mm. Taps A and B were closed and the container tap opened. When equilibrium had been obtained (which was almost instantaneous) the pressure was read off. Knowing the volume of the apparatus and the pressure, the weight of carbon dioxide lost by the charcoal can be calculated and hence the quantity corresponding to the new pressure.

The container tap was now shut and tap B opened and shut immediately, the time interval being approximately $\frac{1}{5}$th second. By this means the pressure in the main apparatus was lowered to a very slight degree. The pressure was read off and the container tap opened, causing the pressure to rise slightly. The carbon dioxide lost by the charcoal was again calculated. Tap A was opened to the pumps and the carbon dioxide between A and B removed. Tap B was then shut and the apparatus was now ready for the next point. In this manner points may be obtained as closely as one may desire. When the pressure was low it was necessary to remove gas several times before a sufficient drop in pressure was obtained in the main apparatus.

If it was desired to remove the container during the course of the run to check the weight, the carbon dioxide in the apparatus between B and G was first frozen out in the manner which has been previously described.

The volume between B and G was determined by a sharing method and checked by a second process. A bulb N, provided with a tap, was joined to the apparatus by means of a ground glass joint M, sealed with Everett's wax. The volume of the bulb below the tap was accurately determined both by evacuation and filling with water—96 ccs. The bulb was filled with nitrogen at atmospheric pressure and attached to the main apparatus which was then evacuated. On opening M, a pressure developed in the apparatus. Knowing the initial and final pressures and the volume of the bulb, the volume of the main apparatus was calculated. The calibration was carried out with the container G in position. This determination was repeated several times, close agreement being obtained.

The volume was checked by filling G with charcoal and charging with vapour. In this way the loss in weight of the container gave rise to a certain pressure in a similar fashion to the first calibration. Good agreement was again obtained, the average value being 359 ccs. A correction was applied for the change in volume with change of level in the manometer tube but this was almost negligible, except at the higher pressures. The change in volume does not affect the pressure, since the latter is in equilibrium with the adsorbed carbon dioxide. It affects, however, the calculated quantity of carbon dioxide adsorbed, which is in equilibrium with that pressure, but it was found that the error introduced in the calculated weight was exceedingly small.

The container was surrounded by a thermostat and the rest of the apparatus enclosed in a constant temperature box by which means an accurate temperature control was exercised. The dead-space volume of the container was very small and could be neglected since the variation in the weight of carbon dioxide occupying this area was negligible in comparison with the weight adsorbed. In weighing the container a counterpoise of the same material and of approximately the same displacement and surface was used.

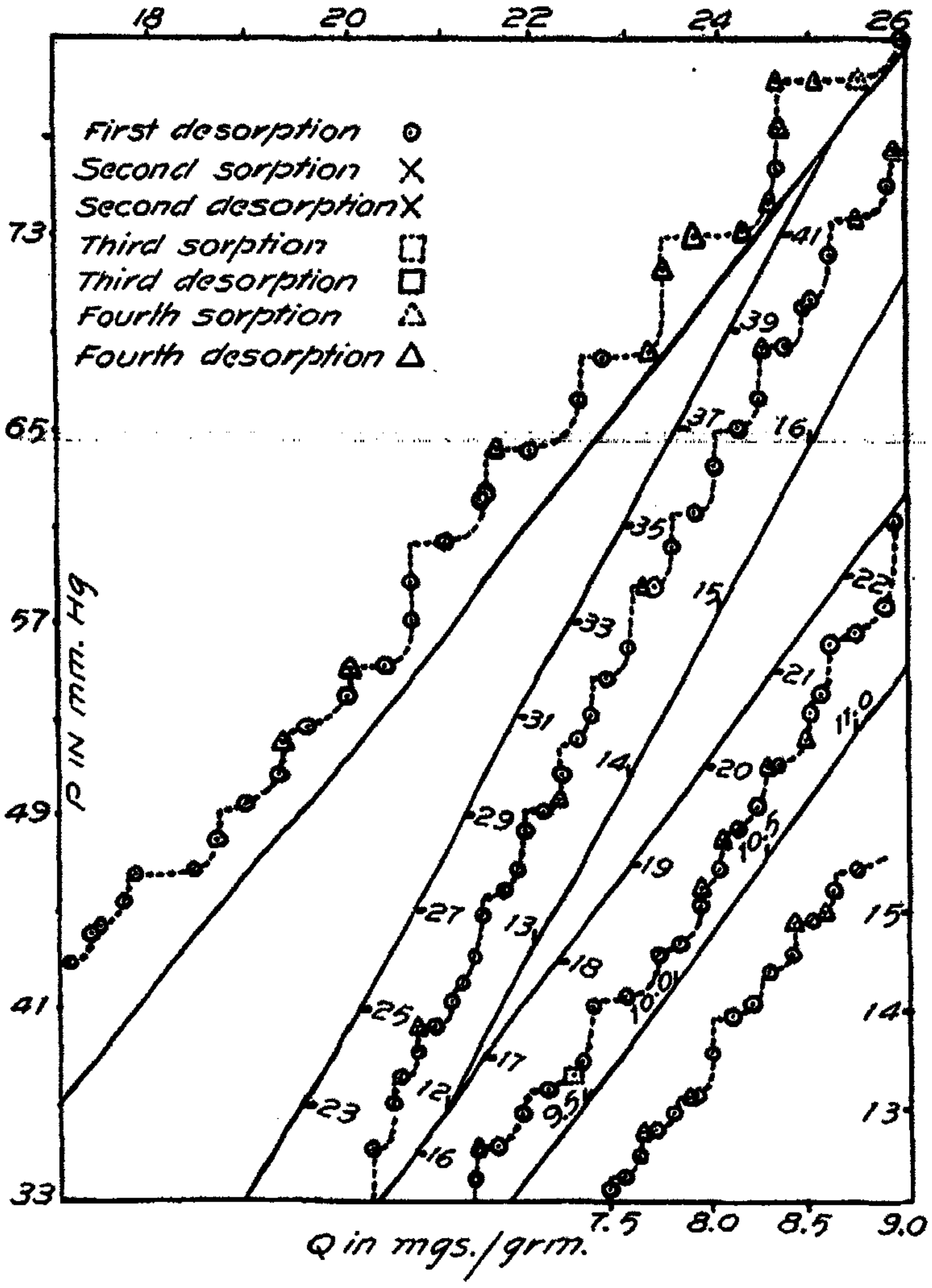

Fig. 2

It should be mentioned that the frozen carbon dioxide, after its liberation from the bicarbonate was exhausted before measuring its pressure at 25°C. in the apparatus, to remove any traces of permanent gas, this process being repeated several times. Tests for permanent gas were also made at intervals during the experiment but the results were always negative.

3. Results

Approximately 350 points have been obtained on the isothermal within the pressure range 81 mm. — 10^{-2} mm. at 25°. This comprises a desorption curve, a resorption, then a redesorption, followed by a second resorption and a further redesorption.

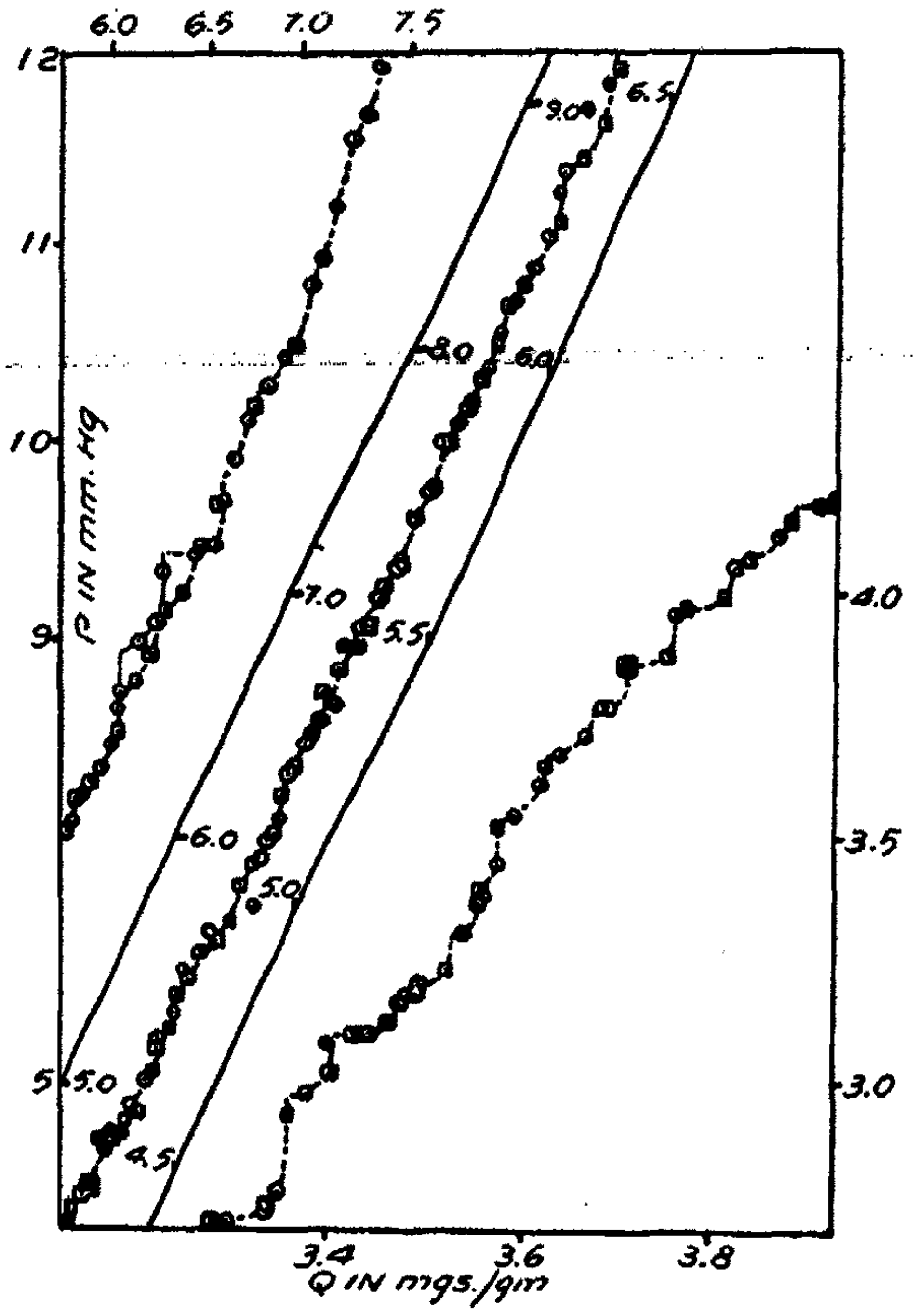

FIG. 3

Finally sorption was carried out to the initial pressure and then desorption to a considerable distance along the isothermal.

The pressure measurements were obtained with a cathetometer reading to 0.01 mm. and the pressure readings could always be reproduced to this figure. This was demonstrated by freezing out the carbon dioxide and then allowing it to vaporise and also by a redetermination of the meniscus after resetting the cathetometer.

For the sake of brevity all tables of figures have been omitted and the complete results are expressed graphically in Figs. 2-4.

One is justified in drawing the curves through each point and not taking a mean, since the experimental error of each point is very low, as is instanced by the reproducibility. If there were any serious error this reproducibility could not be obtained in an experiment employing this technique.

It should be noted, in passing, that the breaks are in no way due to drift as there was no change in the pressure 0.66—(Point 217) after the charcoal had been allowed to stand in contact with the vapour for 76 hours; similarly there was no change in the pressure 0.20 mm (Point 223) after 168 hours, while at 2.48 mm. (Point 304) on the next desorption series there was no change on standing for 5 months.

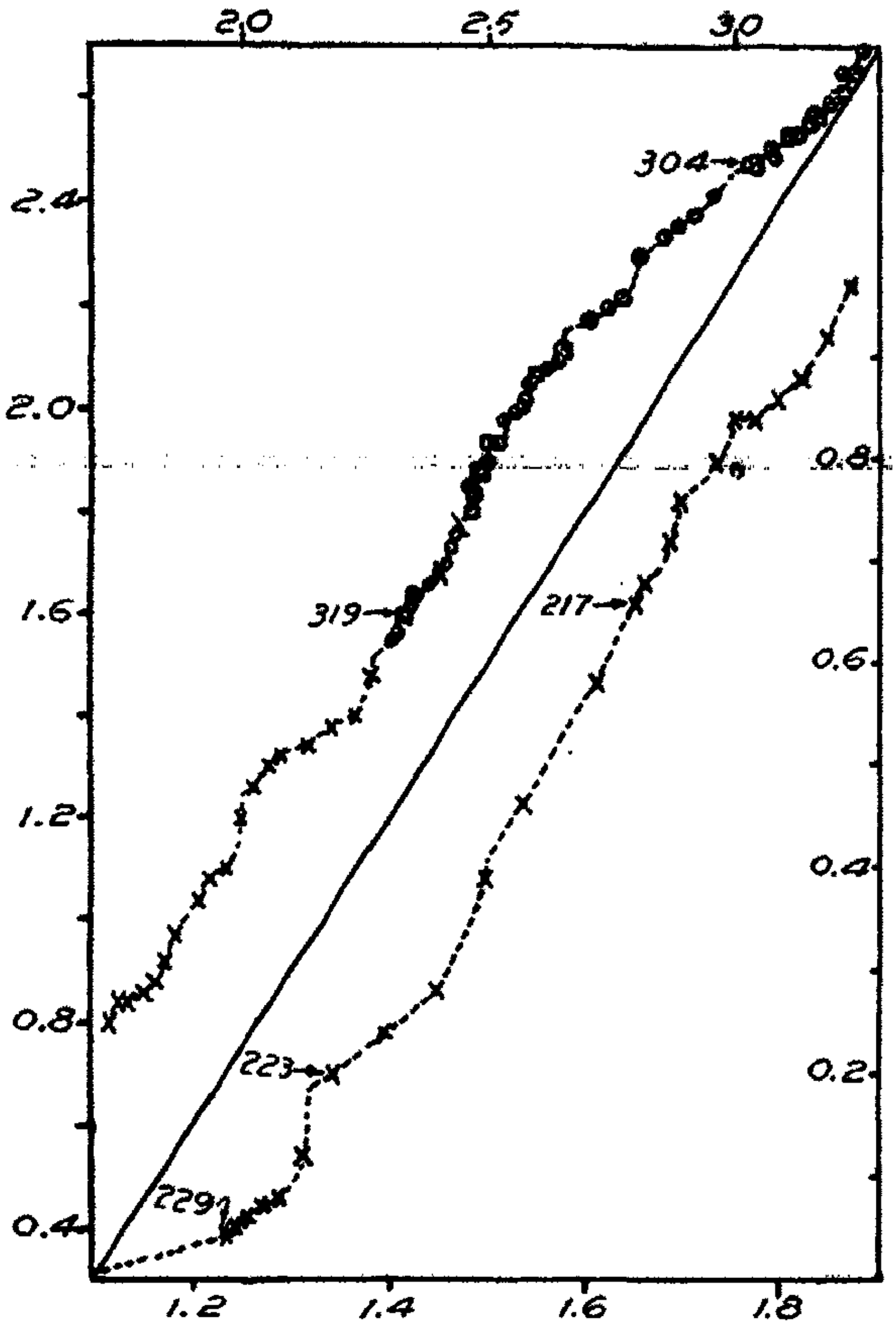

Fig. 4

Once or twice during the course of the experiment the container was detached and weighed and the quantity so obtained compared against that obtained by the 'pressure change' method employed in this work.

At 0.04 mm. Quantity = 1.23 mgs/gm (Pressure Change)
(Point 229) = 1.5 mgs/gm (Weight)

At 1.6 mm. Quantity = 2.33 mgs/gm (Pressure Change)
(Point 319) = 2.6 mgs/gm (Weight)

It was not possible to compare the weights at the end of the experiment as, owing to an accident, air was allowed to enter the container.

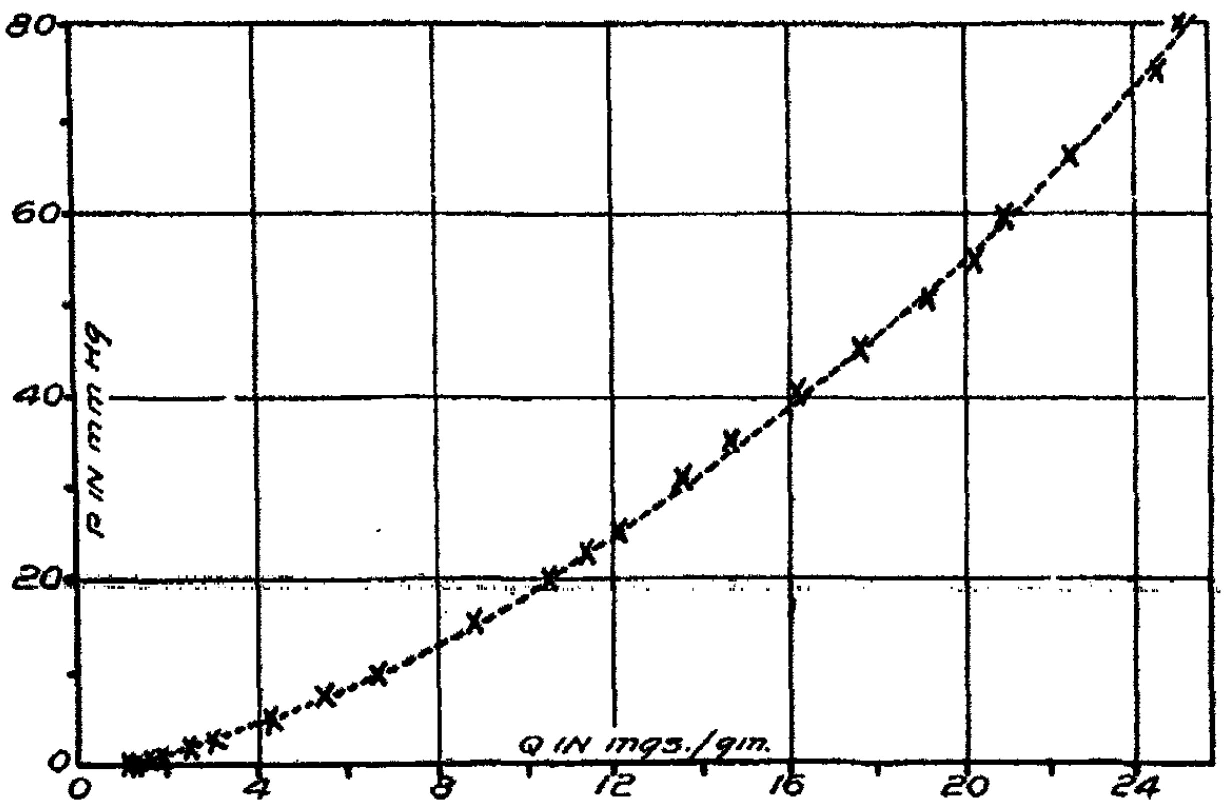

FIG. 5

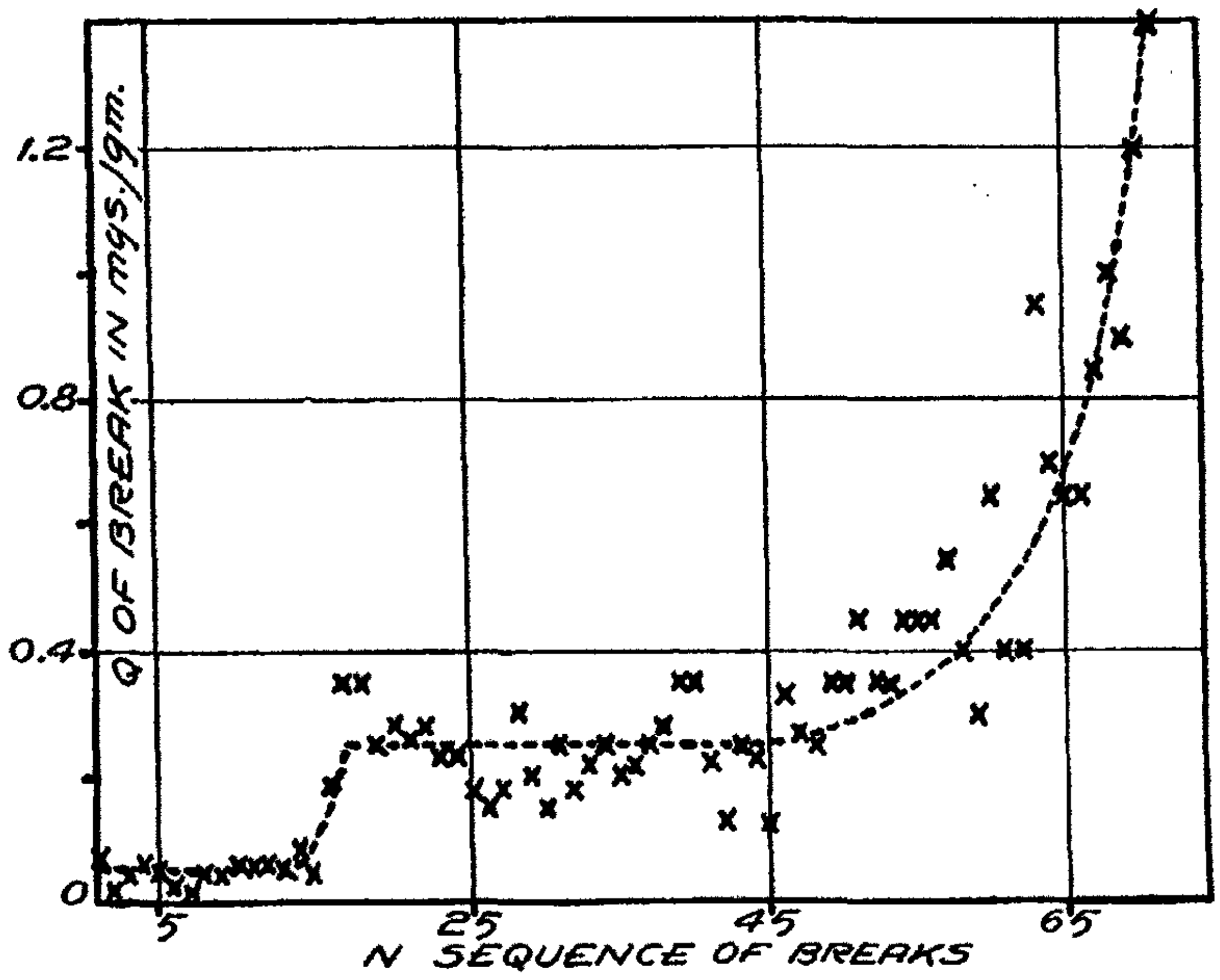

FIG. 6

The cause of the discrepancy between the weighed and calculated figures is not known and in any case is very small since a weight error of 0.5 mgm would account for the difference.

In Fig. 5 a selection of points from Figs. 2-4 have been plotted giving the course of the isothermal throughout the entire range investigated. As will be seen from the diagram a smooth curve has been drawn through the points, giving a normal type of isothermal. If this isothermal were plotted on the same scale, which is normally employed for vapours on charcoal (1 cm. = 1 mm. pressure or 10 mgs/gm quantity), a straight line could be drawn through practically all the points; this is in agreement with other results obtained in this laboratory.[1]

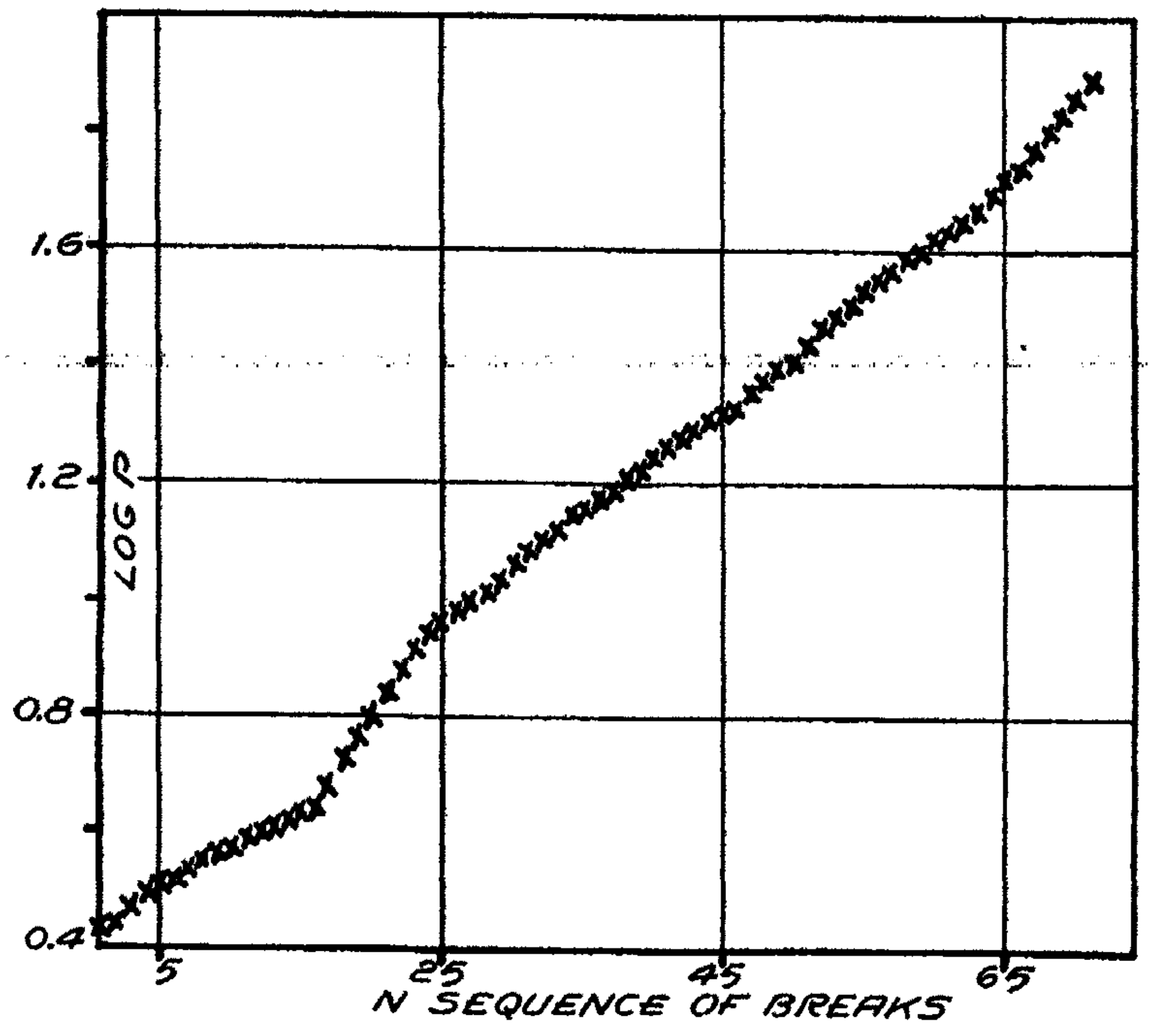

Fig. 7

Discussion

From Figs. 2-4, it will be seen that excellent reversibility has been obtained. The structure of the isothermal was found to be very complicated and a verification has been obtained of the discontinuities which have been found in other cases using different methods. The discontinuities previously noted, have only been observed up to a pressure of approximately 30 mm. In the present work this range has been practically trebled and still the breaks persist up to this pressure.

From this it would appear reasonable to predict that they would be found at whatsoever pressure the experiment was carried out, provided that the pressure exceeded 0.1 mm. and that the surface of the charcoal was not com-

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[1] Allmand and Chaplin: Proc. Roy. Soc., 132A, 460 (1931).

pletely covered by the adsorbed molecules. In this connection it should be noted that in some high pressure adsorption measurements carried out by McBain and Britton[1] marked breaks were obtained. The authors, however, do not comment on this.

At higher pressures the breaks are almost rectangular, but this form tends to disappear somewhat at lower pressures when the pressure and quantity increments per break become very small.

In Figs. 6 and 7, respectively, the pressures at which the breaks occur, and the pressure increments for each break, have been plotted against the sequence of the breaks, commencing at a pressure of 2.72 mm., as the pressures and more especially the quantity values of the breaks are too small to allow of accurate definition below that point.

One interesting detail, which must be noted in passing, is that there is a very definite break at 0.06 mm., whereas in other cases there are no breaks below 0.1 mm. In a previous paper[2] mention is made of a break at 0.6 mm. in a water isothermal and this was considered to be due to carbon dioxide on the surface which had not been cleaned-up by the water vapour. Since carbon dioxide itself has a break in this region and vapours like carbon tetrachloride, which remove carbon dioxide with comparative ease, have not, providing that the surface has been sufficiently cleaned, this would appear to be a correct assumption.

Allmand and Puttick[3] found a break in this region using carbon tetrachloride, but a desorption isothermal carried out after further resorption to a much higher pressure gave a break at approximately 0.1 mm., showing that the surface could not have been completely cleaned-up in the first case.

In Fig. 6, the log of the pressure of the break has been plotted against the sequence of the breaks, calling the first break plotted No. 1, etc. and in Fig. 7 the quantity increment per break has been plotted against the sequence of the breaks. Both of these plots show a marked tendency to regularity, especially that representing log P/n. This was only to be expected since the pressure is probably less affected by foreign influences than is the quantity.

Assuming that each break marks the completion of a ring of molecules round all the activated points, then if foreign molecules are already present in the space where a given ring will form, the number of adsorbed molecules necessary to complete that ring will be fewer than would be expected and hence the quantity value for a given break is too small. There must, of necessity, be some effect on the pressure, but this will not be very marked unless a very large number of foreign molecules are present. Under these conditions, when the pressure reaches a value at which the ring should form, it is insufficient to anchor the molecules concerned and a greater force is needed, so as to expel the foreign molecules and thus allow the ring to be formed. Hence the pressure for a given break would be too high.

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[1] J. Am. Chem. Soc., 52, 2198 (1930).

[2] Allmand and Burrage: J. Phys. Chem., 35, 1692 (1931).

[3] Proc. Roy. Soc., 130A, 197 (1930).

Although the diagram representing the curve in which q is plotted against N may not appear to be very regular, yet when it is noted that 1 cm. on the vertical scale = 0.1 mgs/gm, it will be seen that experimental errors will be greatly magnified.

In Fig. 3 the curve in the region of 9 mm. pressure is seen to be non-reversible over a range of approximately 0.7 mm. The second desorption cycle is to the right of the first pointing to a definite cleaning of the surface between the carrying out of these two cycles. Since the points coincide below this portion of the isothermal, it would appear to be due to a purely local disturbance. It cannot be ordinary experimental error as the figures would not have overlapped below this point.

It is not proposed to go into any theoretical discussion in detail as that will be reserved until further work, which is now in progress, has been completed. One thing, however, would appear to arise from this investigation, namely, that instead of carbon dioxide on charcoal giving rise to the simplest conditions, in point of fact it gives rise to the most complicated. It would appear that the carbon dioxide, which is adsorbed, changes over continuously into the complex C_XO_Y, (a kind of surface compound) dependent on the pressure. As the pressure of carbon dioxide is increased more C_XO_Y will form and *vice-versa*. This means that with increase of pressure the complex builds itself up outwards from the surface of the charcoal, forming a spongy mass, of which the molecules nearest the charcoal actually form the complex, with a continuous gradation to ordinary carbon dioxide molecules on the surface.

This hypothesis tends to shed light on the anomalous results previously obtained with carbon dioxide on charcoal[1] D_1. It follows from the hypothesis that the amount of carbon dioxide adsorbed depends very largely on the degree of evacuation and this, in turn, depends on the ease with which carbon dioxide can diffuse away from the charcoal surface.

Again, from the hypothesis, it follows that the higher the initial charging pressure the more carbon dioxide may be more or less permanently transformed into the carbon complex. Since, in the previous work, the initial charging pressure at 25° was 4.58 mm. and at 40°, 8.04 mm., the statement that it would appear that less carbon dioxide was taken up at 25° than at 40°, could be easily explained.

The portion of the isothermal which will be principally affected by these conditions is the section which runs along the quantity axis, in other words, that quantity adsorbed, which is so firmly held, that it gives rise to practically zero pressure.

If this assumption be correct, it is obvious why such a complex curve should be obtained since one is dealing with two simultaneous effects. (1) The sorption of carbon dioxide and (2) the conversion of some of the previously adsorbed carbon dioxide to the complex C_XO_Y. It is these two processes occurring together which probably prevents the rectangular steps being observed.

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[1] Allmand and Burrage: Proc. Roy. Soc., loc. cit.

Summary

1. A careful study has been made of the carbon dioxide isothermal at 25° over a pressure range 81 mm. – 0.04 mm., some 350 points being determined.

2. The pressure and quantity increments of the breaks have been observed.

3. A hypothesis has been suggested for the complex nature of the isothermal.

The author wishes to express his thanks to Professor A. J. Allmand for the interest he has taken in this work.

King's College,
London.
February 29, 1932.

A MODIFICATION OF THE FREUNDLICH ADSORPTION ISOTHERM

BY WILLIAM ROGERS, JR. AND MARTIN SCLAR

Of the numerous theoretical and empirical adsorption equations which have been proposed,[1] that of Freundlich has been found to describe best the experimental facts, and hence has been used almost exclusively. The Freundlich isotherm may be used to calculate: (a) the mass of adsorbent necessary to cause a desired change in concentration or pressure, except where the equilibrium concentration or pressure is zero, and (b) the equilibrium concentration or pressure, when the initial concentration or pressure, the volume of solution or dead space, and the mass of adsorbent are known. But the latter calculation is very laborious even when carried out in the simplest manner.[2] The purpose of this paper is to modify Freundlich's equation so that it may be used for all the above purposes with the same efficiency, but with much greater ease. The modified equation also has the advantage that it may be used to calculate the mass of adsorbent just necessary for total adsorption.

Freundlich's isotherm for adsorption from solution is

$$x/m = k\,C^n_2$$

where x is the amount adsorbed, m is the mass of adsorbent, C_2 is the equilibrium concentration of the solute, and k and n are empirical constants.

For an infinitesimal adsorption the isotherm becomes

$$dx/dm = k\,C^n$$

But dx = V dC, where V is the volume of the solution, so that

$$VdC/dm = k\,C^n \quad \text{and} \quad VdC/C^n = k\,dm.$$

This equation may be integrated as follows:

$$V\int_{C_1}^{C_2} C^{-n}\,dC = k\int_{m}^{0} dm$$

where C_1 is the initial concentration of the solution.

$$V/m\,(C^r_1 - C^r_2) = k\,r$$

where $r = (1-n)$. Let $k\,r = K$ since both k and r are constants.
Then

$$V/m\,(C^r_1 - C^r_2) = K \quad \text{......................} (1).$$

Solving equation (1) for C_2:

$$(C^r_1 - K\,m/V)^{1/r} = C_2 \quad \text{.....................} (2).$$

When C_2 is taken as zero:

$$C^r_1\,V/m_o = K \quad \text{and} \quad C^r_1\,V/K = m_o \quad \text{...............} (3).$$

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[1] Swan and Urquhart: J. Phys. Chem., 31, 251 (1927).

[2] Rogers and Sclar: J. Phys. Chem., 35, 2758 (1931).

Equation (1) is to be used to calculate the values of r and K if the method of trial and error is to be used. Equation (2) is used for a calculation of the equilibrium concentration when C_1, m, and V are known. Equation (3) is used for a calculation of the mass of adsorbent, m_o, just required for total adsorption of the solute.

It is interesting to note that equation (3) is similar to one previously derived[3] in a different manner. The latter equation, however, is restricted to constant volume.

The method used to derive equations (1), (2), and (3) may be used to derive a similar set of equations for the adsorption of gases.

The Freundlich isotherm for the adsorption of gases is

$$x/m = k\,P^n{}_2$$

where P_2 is the equilibrium pressure, and the other terms retain their previous meanings. If x is expressed in mols, then $x = n_1 - n_2$, where n_1 is the number of mols admitted to the adsorption chamber, and n_2 is the number of mols not adsorbed. Corresponding to n_1 and n_2 there would be an initial pressure P_1 and an equilibrium pressure P_2 respectively. The volume of the adsorption chamber less the volume of the adsorbent is V. Then assuming a perfect gas,

$$P_1V = n_1\,RT \qquad P_2V = n_2\,RT$$

$$n_1 = P_1V/RT \qquad n_2 = P_2V/RT$$

$$x = V/RT\,(P_1 - P_2) \qquad dx = V/RT\,dP$$

For an infinitesimal adsorption the Freundlich adsorption isotherm would become,

$$dx/dm = k\,P^n.$$

Substituting in this equation the value of dx from above,

$$V/RT\,.\,dP/dm = k\,P^n \quad \text{and}$$

$$\int_{P_1}^{P_2} dP/P^n = kRT/V \int_m^0 dm$$

Proceeding exactly as in the derivation of the equation for adsorption from solution, the results are:

$$\frac{V}{m\,RT}\,(P^r{}_1 - P^r{}_2) = K \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4).$$

$$P_2 = (P^r{}_1 - \frac{K\,RT}{V}\,m)^{1/r} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5).$$

$$m_o = P^r{}_1\,\frac{V}{K\,RT} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6).$$

Equations (4), (5), and (6) are to be used similarly to equations (1), (2), and (3) respectively.

Since $P_1V = n_1RT$

$$P_1/n_1 = RT/V$$

and these may be used interchangeably in any equation if to do so is more convenient.

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[3] Freundlich, translated by Hatfield: "Colloid and Capillary Chemistry," 3rd Ed., 178.

The validity of equations (2), (3), and (5) will be seen in the following data. There are no data presented (because they are not available) in support of equation (6). But its validity may be assumed without much apprehension because of its similarity to equation (3), and its following directly from equation (5), both of which equations are supported by the data presented.

In the data listed, experimental and calculated values of equilibrium concentrations and pressures are compared. A brief examination of the data, especially that for adsorption of gases, will show that were the experimental and calculated values of x/m compared, as is the custom in demonstrating the validity of adsorption isotherms, the agreement would be better.

TABLE I[4]

Adsorption of Benzene in Ethyl Alcohol on Pure Carbon

C_1 mol frac.	H/m millimols/g.	C_2 obs. mol frac.	C_2 calc. mol frac.
0.00653	372.2	0.00513	0.00504
.01286	333.6	.01050	.01057
.02604	356.5	.02289	.02298
.05273	366.8	.04854	.04861
.1090	354.7	.1033	.1031

$r = 0.54$ $1/r = 1.852$ $K = 3.20$

TABLE II[4]

Adsorption of Ethyl Carbonate in Ethyl Alcohol on Pure Carbon

C_1 mol frac.	H/m millimols/g.	C_2 obs. mol frac.	C_2 calc. mol frac.
0.00339	525.0	0.00323	0.00324
.00696	455.2	.00667	.00667
.0142	399.9	.0136	.00137
.0293	514.2	.0286	.0286
.0610	404.3	.0596	.0594

$r = 0.28$ $1/r = 3.57$ $K = 1.37$

H in Tables I and II is the total number of millimols of both solute and solvent in the solution.

TABLE III[5]

Adsorption of Calcium Hydroxide on Basic Calcium Phosphate

m = 0.8614 g. in each bottle

C_1 g./l.	V cc.	C_2 obs. g./l.	C_2 calc. g./l.
1.176	224.69	1.099	1.089
0.6706	224.69	0.5910	0.599
.3335	224.69	.2805	.278
.1514	224.69	.1130	.110
.0907	224.69	.0579	.0572
.0470	224.69	.0207	.0216
.0205	221.69	.0029	.0034

$r = 0.65$ $1/r = 1.54$ $K = 14.1$

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[4] F. E. Bartell and C. K. Sloan: J. Am. Chem. Soc., 51, 1640-1641, Tables II and III (1929).

[5] Lorah, Tartar, and Wood: J. Am. Chem. Soc., 51, 1103, Table II (1929).

Table IV[5]

Adsorption of Calcium Hydroxide by Tricalcium Phosphate

m = 0.3838 g. in each bottle

C_1 g./l.	V cc.	C_2 obs. g./l.	C_2 calc. g./l.
0.4990	224.69	0.4525	0.4374
.2848	224.69	.2388	.233
.1390	212.69	.0989	.0961
.0699	224.69	.0348	.0379
.0278	224.69	.0043	.0059
.0188	224.69	.0011	.0010
.0110	224.69	.0002	.0000

r = 0.7 1/r = 1.43 K = 31.5

Table V[6]

Adsorption of Sodium Hydroxide on Silica Gel

V = 1000 cc. in each case

C_1 mol/l.	m g.	C_2 obs. mol/l.	C_2 calc. mol/l.
0.0127	43.8	0.0	0.0
.0264	42.8	.0016	.0015
.0371	43.5	.0036	.0036
.0667	43.6	.0118	.0130
.1325	43.5	.0447	.0427

r = 0.4 1/r = 2.5 K = 3.73

Table VI[7]

Adsorption of Sulphuric Acid on Wool

V = 250 cc. in each case
m = 1 g. in each case

C_1 millimols/250 cc.	C_2 obs. millimols/250 cc.	C_2 calc. millimols/250 cc.
0.08	0.04	0.032
.16	.09	.088
.23	.13	.14
.38	.24	.26
.61	.43	.46
1.15	.91	.94
1.91	1.64	1.64
3.06	2.71	2.71
4.60	4.18	4.17
6.14	5.70	5.63

r = 0.5 1/r = 2 K = 26

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[6] Patrick and Barclay: J. Phys. Chem., **29**, 1401, Table I (1925).

[7] Paddon: J. Phys. Chem., **33**, 1107, Table I (1929).

Table VII[8]

Total Adsorption of As by $Fe(OH)_3$ (with the addition of H_2SO_4)

V = 100 cc. in each case T = 0°C

C_1 mg./100 cc.	m_0 obs. mg.	m_0 calc. mg.	C_1 mg./100 cc.	m_0 obs. mg.	m_0 calc. mg.
0.1	1.6	1.97	200.	970.	1000.
5.0	56.	48.6	300.	1450.	1400.
30.	210.	211.	400.	1800.	1770.
60.	360.	373.	500.	2220.	2120.
100.	570.	567.	1.0	13.	13.

r = 0.82 K = 7.7

Table VIII[8]

Total Adsorption of As by $Fe(OH)_3$ (without the addition of salt or acid)

V = 100 cc. in each case T = 0°C

C_1 mg./100 cc.	m_0 obs. mg.	m_0 calc. mg.	C_1 mg./100 cc.	m_0 obs. mg.	m_0 calc. mg.
0.1	2.2	2.2	200.	1050.	971.
5.0	48.0	50.8	300.	1360.	1340.
30.	212.	213.	400.	1660.	1690.
60.	376.	370.	500.	1930.	2020.
100.	580.	558.	1.0	14.	14.

r = 0.8 K = 7.14

In the following tables, the "free space" is the volume, reduced to N.T.P., of helium or any other unadsorbable gas, required to fill the bulb containing the adsorbent at the equilibrium pressure.

V, the dead space of the adsorption bulb, is the total volume of the bulb minus the volume occupied by the adsorbent.

P_1 is the pressure which the gas admitted would exert if it occupied the dead space at the temperature of the experiment without being adsorbed.

Table IX[9]

Adsorption of Hydrogen on Platinum Black

m = 4.269 g. V = 10.8 cc. T = 25°C

Gas admitted cc. at N.T.P.	Free space cc. at N.T.P.	P_1 calc. mm. Hg.	P_2 obs. mm. Hg	P_2 calc. mm. Hg.
17.34	10.00	1332.	768.	739.
14.73	7.52	1131.	577.	551.
12.27	5.15	942.	393.	377.
9.10	2.13	699.	162.4	160.
7.71	0.88	592.	67.8	71.
6.94	.31	533.	23.5	25.
6.07	.01	466.	1.1	—

r = 0.9 1/r = 1.111 $K = 3.628 \times 10^{-6}$ R = 62350

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[8] Lockeman and Lucius: Z. physik. Chem., **83**, 743, Tables IV, VIII (1913).

[9] Benton: J. Am. Chem. Soc., **48**, 1859, Table II (1926).

Table X[10]

Adsorption Measurements on Platinized Gel

V = 29.3 cc. m = 1 g. T = 0°C

Gas admitted cc. at N.T.P.	Free space cc. at N.T.P.	P_1 calc. mm. Hg.	P_2 obs. mm. Hg	P_2 calc. mm. Hg
2.70	1.31	70.0	34.00	31.9
7.20	3.63	186.7	94.00	97.5
15.20	8.25	394.2	214.00	225.
24.80	14.35	643.3	372.00	386.
35.68	20.60	925.5	553.00	573.
46.17	28.40	1198.	735.70	759.
Ethylene	r = 0.185	1/r = 5.4	K = 5.1×10^{-7}	R = 62350
4.00	1.60	103.8	41.50	38.3
9.60	4.07	249.0	105.50	110.
16.50	7.63	428.0	197.50	208.
26.50	13.55	687.2	351.45	360.
42.75	23.35	1109.	604.50	618.
Carbon Dioxide	r = 0.21	1/r = 4.76	K = 8.6×10^{-7}	R = 62350
3.10	2.30	80.4	59.90	65.3
7.50	6.24	194.6	161.50	161.
14.75	13.15	382.5	340.50	321.
22.00	19.70	570.5	509.50	480.
31.90	28.70	827.4	743.00	702.
Carbon Monoxide	r = 0.1	1/r = 10.	K = 5.6×10^{-8}	R = 62350

The dead space in Tables IX and X was calculated by converting the free space to the corresponding equilibrium pressures and taking the average of the converted volumes.

Since x/m, in the reference from which the data in Table X was obtained, was seen to be the volume of gas admitted minus the free space value, m was assumed to be one gram.

In Tables IX and X, P_1 was calculated from "the gas admitted at N.T.P." by the perfect gas equation.

Table XI[11]

Adsorption of Carbon Dioxide on Charcoal

V = 5.94 cc. m = 4.5332 g. T = 0°C

P_1 calc. mm. Hg	x/m cc./g.	P_2 obs. mm. Hg	P_2 calc. mm. Hg
14360	24.6	90.4	—
32470	55.3	399.4	385.
38080	64.7	552.6	561.
43530	73.8	734.0	762.
48730	82.4	950.2	979.
54330	91.6	1207.1	1237.
58250	97.9	1478.2	1434.
71943	119.1	2864.8	—
r = 0.2	1/r = 5.	K = 3.616×10^{-7}	R = 62350

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[10] Ryerson and Swearingen: J. Phys. Chem., 31, 96, Table V (1927).

TABLE XII[11]

Adsorption of N_2O on Charcoal

$V = 5.94$ cc. $m = 4.5332$ g. $T = 0°C$

P_1 calc. mm. Hg	x/m cc./g.	P_2 obs. mm. Hg	P_2 calc. mm. Hg
15194	26.0	61.5	—
32220	55.1	262.6	255.
37720	64.4	369.2	383.
43130	73.5	504.3	533.
48640	82.7	674.4	708.
53370	90.5	881.4	877.
58730	99.3	1138.4	1087.
71623	118.6	2842.3	—

$r = 0.2$ $1/r = 5.$ $K = 3.804 \times 10^{-7}$ $R = 62350$

The initial pressures in Tables XI and XII were calculated in the following manner. The volume which 5.94 cc. of gas at one of the observed equilibrium pressures would occupy at 760 mm. was calculated by the perfect gas equation. The value of x/m for the observation was multiplied by m. To this last volume was added the volume previously calculated. The pressure this total volume, which is at 760 mm., would exert if it occupied 5.94 cc. was calculated by the perfect gas equation. This pressure was P_1.

The largest and smallest values of P_2 in the reference cited are given in Tables XI and XII. On examining the above data it is seen that the constants do not cover the entire range. But the constants do well to cover a range of 1000 mm. so efficiently when one makes allowance for the following facts: (a) the adsorption in Tables XI and XII is enormous, (b) equation (5) assumes a perfect gas, which is not the case for CO_2 and N_2O at the high pressures used at zero degrees, (c) P_1 is calculated from the available data on the assumption that CO_2 and N_2O are perfect gases.

Calculation of the Constants. From the method by which equations (1) and (4) were developed it would appear that $r = 1-n$ and $K = (1-n)k$, where n and k are the constants for the Freundlich adsorption isotherm. But this has been found not to be so. In order to find K and r one of the following procedures may be used. Equations for adsorption from liquids will be employed, but the procedures are similar for the adsorption of gases.

A. Equation (3) is $K = C^r_1 V/m_o$. If C_1 is one then $K = V/m_o$. Thus, by experimentally determining the mass of adsorbent required to remove all the solute from a volume, V, of solution, K may be experimentally found. Now, if a single measurement is available in which C_1 is not one and C_2 is zero, then from equation (3) $r = \dfrac{\log (Km_o/V)}{\log C_1}$. Or, if a measurement is available in which C_1 is one and C_2 is not zero, then, from equation (2)

$$r = \frac{\log (1-Km/V)}{\log C_2}.$$

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[11] Richardson and Woodhouse: J. Am. Chem. Soc., 45, 2644, Table I (1923).

But a value of r obtained by one of the above methods is not usually efficient for the calculation of equilibrium values or m_o. However, by retaining the value of $K = V/m_o$ and varying r in the region of the calculated value, an efficient value of r may be found. This procedure is permissible since r is an empirical constant.

B. If data of the kind required by the first method are not available, then the method of trial and error may be used with equation (1). Various values of r may be used with each set of measurements until the most constant value of K is obtained.

In Table VII, when C_1 equals one (1 mg./100 cc.), $K = V/m_o = 100/13 = 7.7$. In the same manner, in Table VIII, $K = 7.14$. Using these values of K, values of r have been found for these tables which give good results. The data in these two tables, together with that in Table XIII, which are the results of an experiment carried out by the contributors of this article, indicate indubitably that $K = V/m_o$ when C_1 equals one.

TABLE XIII

Adsorption of NaOH in Water on Silica Gel

$C_1 = 1.00$ centimols per liter in each case

$V = 100$ cc. in each case

m obs. grams	C_2 obs. cmols/l	C_2 calc. cmols./l.	$V(C_1 - C_2)/m$ obs cmols./g.	$V(C_1 - C_2)/m$ calc. cmols./g.
2.0247	0.15	0.18	0.042	0.040
3.0210	.07	.06	.031	.031
4.1309	.03	.01	.024	.024
5.9941	.01	.0	.017	.017
6.0993	.0			

$r = 0.24$ $1/r = 4.17$ $K = 16.4$

The silica gel was used as supplied by the Silica Gel Corporation with no further treatment; it was 40 to 200 mesh. The usual precautions were taken to keep out CO_2 in all steps of the experiment. In seeking m_o the masses of adsorbent were increased by approximately 0.1 gram because it was felt that the K so obtained would be sufficiently accurate. Because of the low concentrations, experimental and calculated values of $V(C_1 - C_2)/m$ as well as equilibrium concentrations are listed.

When C_1 is equal to one, $K = V/m_o$. K, therefore, is a measure of the adsorbability of the solute in that system to which the constant belongs.

From equation (3)

$$r = \frac{\log m_o - \log m_o^1}{\log C_1 - \log C_1^1}.$$

Therefore, r is the slope of the curve obtained by plotting $\log m_o$ against $\log C_1$.

Summary. An isotherm has been offered which describes adsorption from liquids and of gases. This isotherm contains a term for the initial concentration or pressure; it takes care of partial and total adsorption; it may be used to calculate equilibrium concentrations and pressures and the amount of adsorbent just required for total adsorption.

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March 26, 1932.

CHLORINE EQUILIBRIA AND THE ABSOLUTE ENTROPY OF CHLORINE

BY A. R. GORDON AND COLIN BARNES

The modern interpretation of the structure of band spectra provides a direct means of calculating the entropies, specific heats and heats of dissociation of many gases. The numbers so obtained have been used successfully in calculating various thermodynamic quantities which are not immediately obtainable from experiment. In particular, equilibria in homogeneous gas reactions can be predicted in many instances with an accuracy which leaves little to be desired from the point of view of the chemist. It is probably only a matter of time and of increased knowledge of molecular spectra before the method is recognised as the most natural and accurate way of obtaining the characteristics of gaseous mixtures. The absolute entropies of many gases have now been calculated for fairly wide ranges of temperature, and the numbers so obtained can be used with a confidence impossible in dealing with "third law" values.

An entropy value for a gas, derived from its molecular spectrum, contains certain contributions which, in the calculation of an entropy of reaction, cancel identically with similar contributions to the entropies of other constituents; thus the presence of nuclear spins and, as will be shown below, the existence of isotopes lead to contributions of this nature. If it were only desired to calculate equilibrium constants, such terms in the entropies could be omitted from the beginning, and calculation correspondingly simplified; but to obtain entropies which may be designated *absolute*, every contribution suggested by the theory must be included. In this connection the effect of isotopes on an entropy calculation can be illustrated in the case of chlorine; although the isotopes are chemically indistinguishable, it will be shown that they are without thermodynamic significance only because of a peculiar compensation. In the present paper we shall compute the absolute entropy of molecular chlorine, and use the values so obtained to predict the equilibrium constant for the Deacon reaction.

1. The Entropy of Chlorine

According to Aston, the atomic weights of the isotopes Cl_{35} and Cl_{37} are 34.98 and 36.98 so that in ordinary chlorine they are present in the proportions 0.761:0.239; if it be assumed that for the temperature range involved the formation of a chlorine molecule is statistically determined by the relative abundance of the isotopes, then in ordinary chlorine the proportions must be 35-35:35-37:37-37 = 0.579:0.364:0.057. The molar translational entropy S_T for a gas of molecular weight M at temperature T and pressure 1 atmosphere[1] is

$$S_T = -2.295 + 3R/2.\ln M + 5R/2.\ln T \tag{1}$$

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[1] $R = 1.9858$; $k = 1.372 \times 10^{-16}$, $h = 6.55 \times 10^{-27}$.

At 300°K, S_T is 38.675, 38.759 and 38.841 for the three molecular varieties, respectively. The rotational or vibrational entropy is found in the usual way by

$$S = R(\Sigma_2/\Sigma_1) + R.\ln\Sigma_1 \qquad (2)$$

where $\Sigma_1 = \sum_n p_n.e^{-\epsilon_n/kT}$, $\Sigma_2 = \sum_n p_n.(\epsilon_n/kT).e^{-\epsilon_n/kT}$

ϵ_n being the energy of the n'th rotational or vibrational state of weight p_n. For temperatures above 300°, the rotational entropy assumes its classical value when the sums are evaluated:

$$S_R' = R + R.\ln 8\pi^2 IkT/h^2 \qquad (3)$$

where I is the moment of inertia of the diatomic molecule. It is known that Cl_{35} has 5/2 units of spin; the spin of Cl_{37} has not been determined, but we shall assume that it is the same as for Cl_{35}.[1] If this be the case, the spins of each type of molecule Cl_2 contribute a term 2R.ln 6 to the molar entropy. Now the 35-35 and 37-37 varieties are homonuclear, which means that (if it were not for nuclear spin) alternate rotational levels would be missing, i.e. a term R ln 2 must be subtracted from S_R' in these two cases; no such correction is needed with the heteronuclear 35-37. Thus if S_R denote the contribution to the entropy from rotation and spins,

$$S_R(35\text{-}35, 37\text{-}37) = S_R'(35\text{-}35, 37\text{-}37) + 2R.\ln 6 - R.\ln 2$$
$$S_R(35\text{-}37) = S_R'(35\text{-}37) + 2R.\ln 6$$

The moments of inertia of 35-35 and 35-37 are 113.7×10^{-40} and 117.4×10^{-40} respectively,[2] and by simple proportion the moment of inertia for 37-37 is 121.1×10^{-40}. It is apparent from the work of Elliott,[2] however, that the moments of inertia increase by about 0.0070 of their values in the ground vibrational state per unit increase in the vibrational quantum number. In a molecule with as low a fundamental frequency as chlorine, this will introduce an appreciable error at high temperatures where the population of the higher vibrational states is large. A rough correction for this effect can be made by multiplying the numbers given above by $(1 + \Delta)$ where

$$\Delta = 0.0070(\Sigma n.e^{-\epsilon_n/kT})/(\Sigma e^{-\epsilon_n/kT})$$

in which ϵ_n is the energy of the n'th vibrational state. Since $\Sigma_2/\Sigma_1 = \partial\ln\Sigma_1/\partial\ln T$, this will introduce in the expression for the rotational entropy, a correcting term $s \approx 0.0070R(T.\partial\Delta/\partial T + \Delta)$. Including this correction,[3] S_R for 35-35, 35-37 and 37-37 at 300° is 22.151, 22.591 and 21.275, respectively.

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[1] If it should prove that Cl_{37} have a spin different from this, the change in the numbers obtained can be readily calculated; for example, if the spin should be 7/2 units instead of 5/2, the entropy of 37-37 will be increased by 2R ln 8/6 and that of 35-37 by R ln 8/6 so that the numbers for ordinary chlorine in Table I will be increased by 0.273. The molar entropies of hydrogen chloride in the same Table will be increased by exactly half this amount.

[2] Elliott: Proc. Roy. Soc., **123A**, 629 (1929); **127A**, 638 (1930).

[3] The numerical values of s are as follows:

T°K	300	400	500	600	700	800	900	1000
s	0.004	0.007	0.011	0.014	0.018	0.021	0.025	0.029

The vibrational energy levels are given by $\epsilon_n = (n + 1/2).\omega_0 - (n + 1/2)^2 \cdot b$ and the weights p_n are unity. Elliott[2] gives $\omega_0 = 564.9$ and $b = 4.0$ for 35-35; if it be assumed that ω_0 is inversely proportional to the square root of the reduced mass of the molecule, ω_0 for 35-37 and 37-37 will be 557.2 and 549.4, respectively. The vibrational entropy S_V for the three varieties is 0.545, 0.560 and 0.577 at 300°, so that the molar entropy at the same temperature is 60.37, 61.91 and 60.69. Therefore the entropy of one mole of chlorine at 300° is

$$0.579 \times 60.37 + 0.364 \times 61.91 + 0.057 \times 60.69 - 1.9858\ (0.579 \ln 0.579 + 0.364 \ln 0.364 + 0.057 \ln 0.057) = 62.63$$

The last item (= 1.683) is the entropy of mixing. The values of the entropy and heat capacity of ordinary chlorine for various temperatures are listed in Table I; the vibrational part of the heat capacity was computed from the vibrational energy levels in the usual way, and a term $R.\partial(T^2 \partial \Delta/\partial T)/\partial T$ was included to take into account the increase in the "average" moment of inertia through rise in temperature; the numerical value of this correction varies from 0.006 at 300° to 0.035 at 1000°.

2. The Entropies of Hydrogen Chloride and Oxygen up to 1000°

The translational entropy of HCl_{35} and HCl_{37} is given by Eq. 1 with $M = 35.99$ and 37.99, giving for 300° $S_T = 36.695$ and 36.857 respectively. The rotational entropy is given by Eq. 2 with $\epsilon_J = J(J + 1)h^2/8\pi^2 I$, $p_J = 12\ (2J + 1)$, and $I = 2.617 \times 10^{-40}$ for both varieties;[1] the factor 12 in the weight arises from the spins of the hydrogen and chlorine atoms. For 300° $S_R = 12.852$. The vibrational entropy[2] is given by Eq. 2 with $p_n = 1$ and $\epsilon_n = n\ (2990 - 53.4n)$, where $n = 1/2, 3/2, \ldots$ For 300° S_V is negligible and for 1000° is only 0.166, the isotope affect can be neglected in S_R and S_V. The entropy of ordinary hydrogen chloride as entered in Table I is given by

$$S = 0.761 S_{HCl_{35}} + 0.239 S_{HCl_{37}} - R(0.761 \ln 0.761 + 0.239 \ln 0.239)$$

the last term (= 1.093) being the entropy of mixing. If from the value for 300°, we subtract the spin entropy ($R \ln 12 = 4.935$) and the entropy of mixing, the result is 44.65, corresponding to 44.61 at 298°; Giauque and Wiebe[3] give 44.64 for this temperature; the difference is exactly accounted for by our use of $R = 1.9858$ instead of $R = 1.9869$.

In the case of oxygen, Giauque and Johnston[4] have computed the entropy for 298.1°; for higher temperatures, S_T is obtained from Eq. 1 with $M = 32.00$, S_R by setting[5] $I = 19.27 \times 10^{-40}$ in Eq. 3 and then adding $R \ln 3/2$ to the result, while S_V is computed from Eq. 2 with $p_n = 1$ and $\epsilon_n = 1565n - 11.4n^2$ where $n = 0, 1, 2, 3, \ldots$. Giauque and Johnston have shown that this method of

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[1] Czerny: Z. Physik, 45, 476 (1927).

[2] Kemble: J. Opt. Soc. America, 12, 1 (1926).

[3] Giauque and Wiebe: J. Am. Chem. Soc., 50, 101 (1928).

[4] Giauque and Johnston: J. Am. Chem. Soc., 51, 2300 (1929).

[5] Dieke and Babcock: Proc. Nat. Acad. Sci., 13, 670 (1927); Rasetti: Phys. Rev., (2) 34, 367 (1929); Birge: Int. Crit. Tables 5, 411.

approximation leads to the same numerical result at 298.1° as their more exact method based on the band spectrum formula for oxygen. The resulting values for the entropy and heat capacity are entered in Table I; for 298.1° the entropy is 49.00, which is 0.03 less than Giauque and Johnston's value; as in the case of hydrogen chloride, this discrepancy is exactly accounted for by our use of a smaller value of R.

TABLE I

Molar Entropies and Heat Capacities of Chlorine, Hydrogen Chloride and Oxygen

	Chlorine		Hydrogen Chloride		Oxygen	
T°K	S	C_p	S	C_p	S	C_p
300	62.63	8.12	50.68	6.95	49.04	7.02
400	65.02	8.43	52.68	6.96	51.08	7.19
500	66.92	8.62	54.23	6.99	52.71	7.42
600	68.50	8.73	55.51	7.05	54.09	7.65
700	69.85	8.81	56.61	7.14	55.28	7.86
800	71.03	8.87	57.57	7.26	56.34	8.03
900	72.08	8.91	58.43	7.39	57.30	8.17
1000	73.02	8.94	59.21	7.52	58.17	8.29

3. The Deacon Equilibrium $2Cl_2 + 2H_2O = 4HCl + O_2$

If Q be the heat of reaction at temperature T and if ΣS be defined by

$$\Sigma S = 2S_{Cl_2} + 2S_{H_2O} - 4S_{HCl} - S_{O_2}$$

the entropies being all for temperature T and pressure 1 atmosphere, then at equilibrium

$$R \ln K = R \ln (P_{Cl_2})^2(P_{H_2O})^2/(P_{HCl})^4(P_{O_2}) = -Q/T + \Sigma S$$

The heat of formation of hydrogen chloride[1] at 291° is 22030 cals; the heat of formation of water[2] at 298° is 68313 cals. and the heat of vaporization at the same temperature[3] is 10485 cals.; hence at 298°, Q = −27,500 cals. From this value, and the heat capacities of steam[4] and the other gases (Table I), the values of Q/T entered in Table II are found by tabular integration. ΣS, entered in the same table, is obtained from Table I above and from the known entropy of steam.[4] The resulting R ln K were used to construct the curve in Fig. 1; the experimental values of this quantity, as obtained from International Critical Tables,[5] together with some additional experimental results of von Falkenstein[6] and Neumann[7] are indicated on the figure. The following values are suggested for the reaction:

$$\Delta H^\circ_{298.1} = 27{,}500;\ \Delta S^\circ_{298.1} = 30.99;\ \Delta F^\circ_{298.1} = 18260.$$

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[1] Int. Crit. Tables, 5, 176.

[2] Rossini: Bur. Standards J. Research, (6) 1, 36 (1931).

[3] Int. Crit. Tables, 5, 138.

[4] Gordon and Barnes: J. Phys. Chem., 36, 1143 (1932).

[5] Int. Crit. Tables, 7, 233.

[6] von Falkenstein: Z. physik. Chem., 65, 371 (1909).

[7] Neumann: Z. angew. Chem., 28, 233 (1915).

TABLE II

The Equilibrium Constant for the Deacon Reaction

T°K	600	700	800	900	1000
−Q/T	46.70	40.17	35.27	31.46	28.42
− S	32.21	32.40	32.52	32.60	32.71
R ln K	+14.49	+7.77	+2.75	−1.14	−4.29

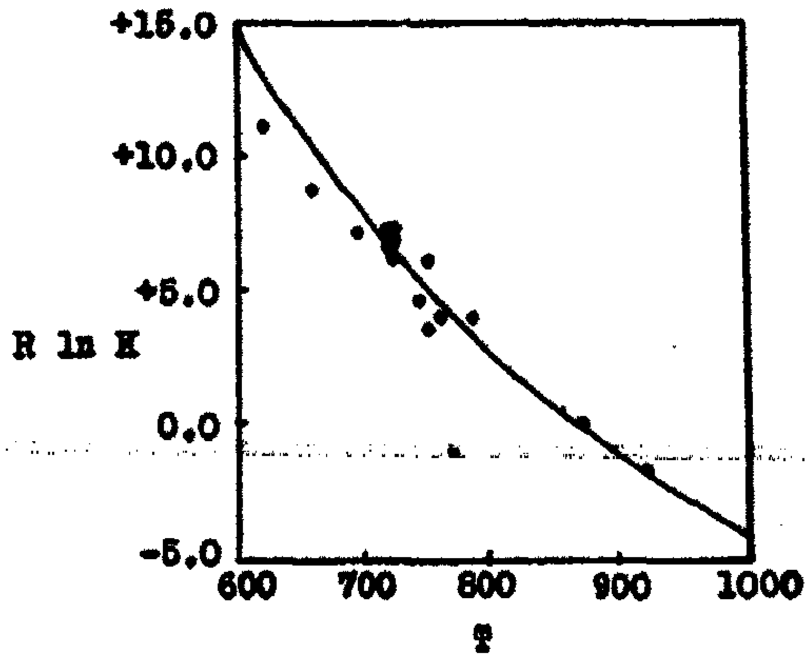

FIG. 1

4. Isotopes in Entropy Calculations

The entropy values of chlorine and hydrogen chloride as derived in Sec. 1 and 2 may be used to illustrate the general question of the effect of isotopes on an entropy calculation. Earlier calculations of the entropy of these two gases ignored the existence of isotopes in chlorine, and it is important to show the effect of this on the numbers obtained. To a first approximation, we may disregard the effect of isotopes on the values of S_R and S_V, and consider S_T as a linear function of the molecular mass M. With isotopes considered in chlorine, there occurs an entropy of mixing of 1.683, which is absent when these are disregarded. In addition, in a non-isotopic chlorine, all molecules would be homonuclear, and the extra entropy due to the heteronuclear nature of 35-37, viz. 0.364R ln 2, would not be present in the final entropy expression. Thus to ignore the existence of isotopes is to decrease the entropy of chlorine by $1.683 + 0.364R. \ln 2 = 2.18$. If for non-isotopic chlorine $M = 70.92$, $I = 116 \times 10^{-40}$, and $\omega_0 = 560$ cm^{-1}, the entropy can be readily evaluated and is found to be (at 300°) 60.46, which is just 2.17 less than the number in Table I. Now to disregard the chlorine isotopes in hydrogen chloride is practically equivalent to dropping the entropy of mixing, viz. 1.093, so that as far as the calculation of ΔS for the Deacon reaction is concerned, the effect of the isotopes cancels.

By writing down the general expression for the entropy of mixing for a diatomic gas X_2 having any number of isotopes in any relative proportions, and taking account of the $-R \ln 2$ which will occur in the molar entropy of any homonuclear combination, we can get the extra entropy due to isotopes. If we compare this with the entropy of mixing for molecules of the type AX, then in any reaction of the type

$$\ldots + 2A + X_2 = 2AX + \ldots$$

ΔS for the reaction is the same (to a first approximation) whether we consider the presence of isotopes or disregard them. Of course the temperature must always be so high that the rotational energy is classical (Eq. 3).

The indifference of ΔS to isotopes appears to be general, as would be expected for chemical reasons. The above type of cancellation can be shown to take place, for example, in the reaction

$$\ldots A + 2X_2 = AX_4 + \ldots$$

For simplicity, suppose that X has two isotopes X' and X'' in the relative proportions $\alpha, \beta = 1 - \alpha$. Then the entropy due to isotopes on the left hand side of the reaction is

$$\begin{aligned} &- 2R[\alpha^2.\ln\ \alpha^2 + \beta^2.\ln\ \beta^2 + 2\alpha\beta.\ln\ 2\alpha\beta] + 4R\alpha\beta.\ln\ 2 \\ &= - 4R(\alpha.\ln \alpha + \beta.\ln \beta). \end{aligned}$$

Now if AX_4 has the symmetry properties of methane, as may be assumed for the illustration, there is the following distribution of molecular types

Type	Proportion	Symmetry Number
AX_4'	α^4	12
$AX_3'X''$	$4\alpha^3\beta$	3
$AX_2'X_2''$	$6\alpha^2\beta_2$	2
$AX'X_3''$	$4\alpha\beta^3$	3
AX_4''	β^4	12

The column headed "Symmetry Number" determines the correcting term to be taken from the classical entropy expression to allow for the absence of a certain fraction of the energy states. Thus the symmetry number for the homonuclear varieties of chlorine is 2, and R ln 2 is to be subtracted from S_R' in Eq. 3; similarly the entropy of a mole of $AX_2'X_2''$ will be R ln 12/2 greater than that of a mole of AX_4' or AX_4'', and so on. Therefore, the isotope entropy on the right hand side of the reaction in question is

$$\begin{aligned} &- R[\alpha^4.\ln \alpha^4 + 4\alpha^3\beta.\ln\ 4\alpha^3\beta + 6\alpha^2\beta^2.\ln\ 6\alpha^2\beta^2 + 4\beta\alpha^3.\ln\ 4\alpha\beta^3 + \beta^4.\ln\beta^4] \\ &\quad + R[4\alpha^3\beta.\ln\ 4 + 6\alpha^2\beta^2.\ln\ 6 + 4\alpha\beta^3.\ln\ 4] \\ &\qquad = - 4R(\alpha.\ln \alpha + \beta.\ln \beta). \end{aligned}$$

This latter quantity is identical with that obtained for the left-hand side of the reaction.

Of course, one cannot assert that this type of cancellation will necessarily take place in every reaction, since the "symmetry number" is known for only the simplest types of molecules; in all the simple cases that can be treated by the method sketched above, however, it is found that the part due to mixing together with the part due to "symmetry" gives, on either side of the reaction, the same numerical result. To this extent, then, the effect of isotopes may be disregarded in questions of chemical equilibrium. The compensation is not exact, of course, for the mass effect of the isotopes has been disregarded, and this in general will not cancel, e.g. in the terms S_V of the entropies; this is a "second order" effect, however, amounting to (at most) a few hundredths of an entropy unit in the entropy of reaction.

Summary

The entropy of chlorine from 300° to 1000° is computed from the spectroscopic constants of Elliott; in conjunction with the known entropies of hydrogen chloride, oxygen and steam, the equilibrium constant of the Deacon reaction is calculated for the range 600°-1000°. The agreement between the calculated and observed values of the equilibrium constant is satisfactory. It is shown that to the first order, the entropy of reaction is not affected by disregarding the existence of isotopes in the calculation; the rule appears to be general.

Added in proof, June 28, 1932: Since this paper was sent to the Journal, Giauque and Overstreet (J. Am. Chem. Soc., 54, 1731 (1932)) have computed the entropy of chlorine by a method which takes exact account of the change in the spectroscopic constants in the higher rotational-vibrational states; they find 53.310 as the entropy of chlorine at 298.1°. If from our value at 300°, the spin entropy (7.116) and the isotope entropy (2.186) be subtracted, the result is 53.33, corresponding to 53.28 at 298.1°; with R = 1.9869, this last value becomes 53.31. A calculation by their method for 1000° shows that the entry in Table I is less than 0.02 in error.

The University of Toronto,
Toronto, Canada.
April, 1932.

PHASE RULE STUDIES ON THE PROTEINS. VII*

Non-aqueous Solutions

BY WILDER D. BANCROFT AND S. LOUISA RIDGWAY

Introduction

In a recent paper[1] the authors came to these conclusions: "Casein, gelatine and edestin showed compound formation with HCl in ethyl alcohol. Zein and gliadin showed only adsorption with HCl. Casein, gelatine, zein, gliadin and edestin showed compound formation with NaOH in ethyl alcohol plus marked adsorption, or adsorption alone with the adsorption practically complete at the lower concentrations." The method used in obtaining these results was briefly this. The protein was put in a given volume of the solvent, which was assumed to be inert to the system, containing the requisite amount of acid or base; after equilibrium had been attained, the excess acid or base was titrated using such indicators that any peptized protein or protein product would have no effect on the end-point. The practical difficulties involved in interpreting the curves obtained were pointed out. These were: (1) such complete adsorption that a flat appeared to be obtained; (2) lack of equilibrium in compound formation simulating an adsorption curve; and (3) change in the shape of the curve due to hydrolysis of the protein during the time required to reach equilibrium.

The object of the paper quoted was to determine whether proteins form adsorption complexes or true compounds with acids and bases. This has also been the object of the present research. A modification of the method previously used seemed to obviate some of the difficulties just mentioned. If the protein could be dissolved without chemical change in a small amount of some solvent and then poured into a large amount of a second solvent, in which the protein is insoluble, containing the acid or base, the protein would be precipitated in very small particles and equilibrium ought to be reached rapidly. The excess acid or base could be titrated very soon and there would be less chance for hydrolysis of the protein. Aside from the theoretical importance of this modification, the saving of time in experimental work would be enormous. The simplest example (and the only one actually used so far) is that of gelatine dissolved in water and poured into alcohol. The method is limited to proteins soluble in some medium which does not change them chemically—for instance gelatine and albumin in water, and the prolines in alcohol-water mixtures.

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[1] J. Phys. Chem., 36, 1285 (1932).

*This work has been done under the programme now being carried out by Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

Experimental

The experimental method was extremely simple. A gram of gelatine was dissolved in 10 cc. of warm water in a test tube, and the resulting solution was poured into a flask containing the desired amount of acid or base dissolved in 90 cc. of absolute alcohol. The test tube had been passed through a rubber stopper fitting the flask, so that the liquid could easily be shaken from one to the other. The gelatine precipitated as soon as it was poured into the alcohol, and in a short time agglomerated into one mass. In spite of this it seemed that equilibrium was reached very rapidly. After an hour or more an aliquot portion of the supernatant liquid was pipetted off and titrated for excess acid or base using standard base or acid in 95% alcohol. The red to yellow change of thymol blue was used to titrate excess acid, and thymolphthalein was used for excess base. Only strong acid or base was titrated by this method. The results of the titrations were corrected for the volume change incident to the mixing of water and alcohol. Some titrations were

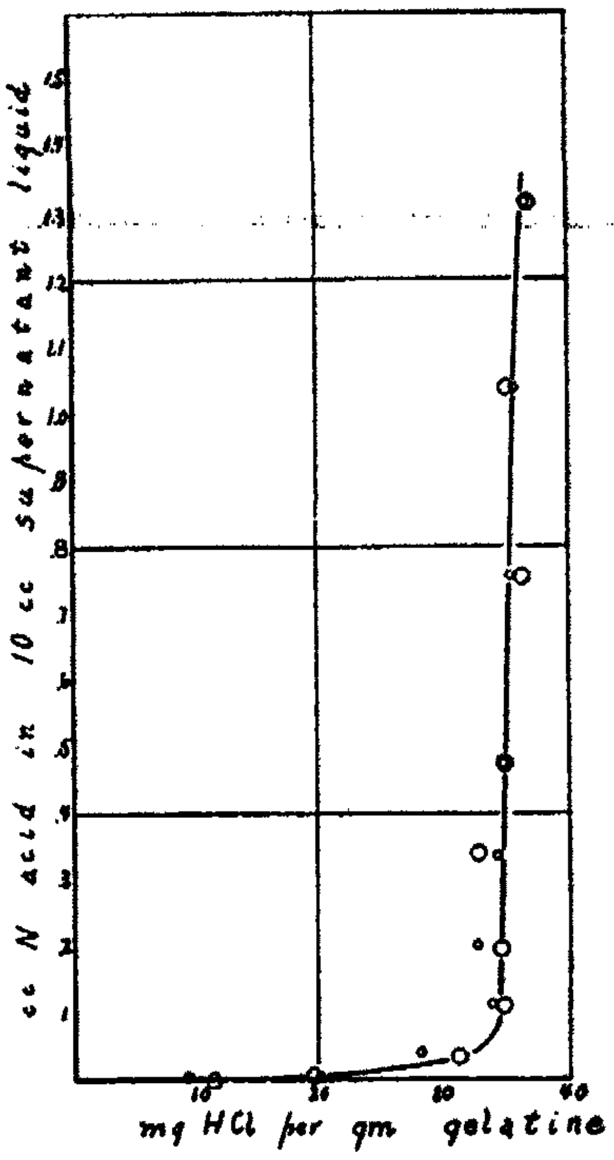

FIG. 1

Gelatine and HCl in 90% Ethyl alcohol
o = 0°C. O = Room Temperature

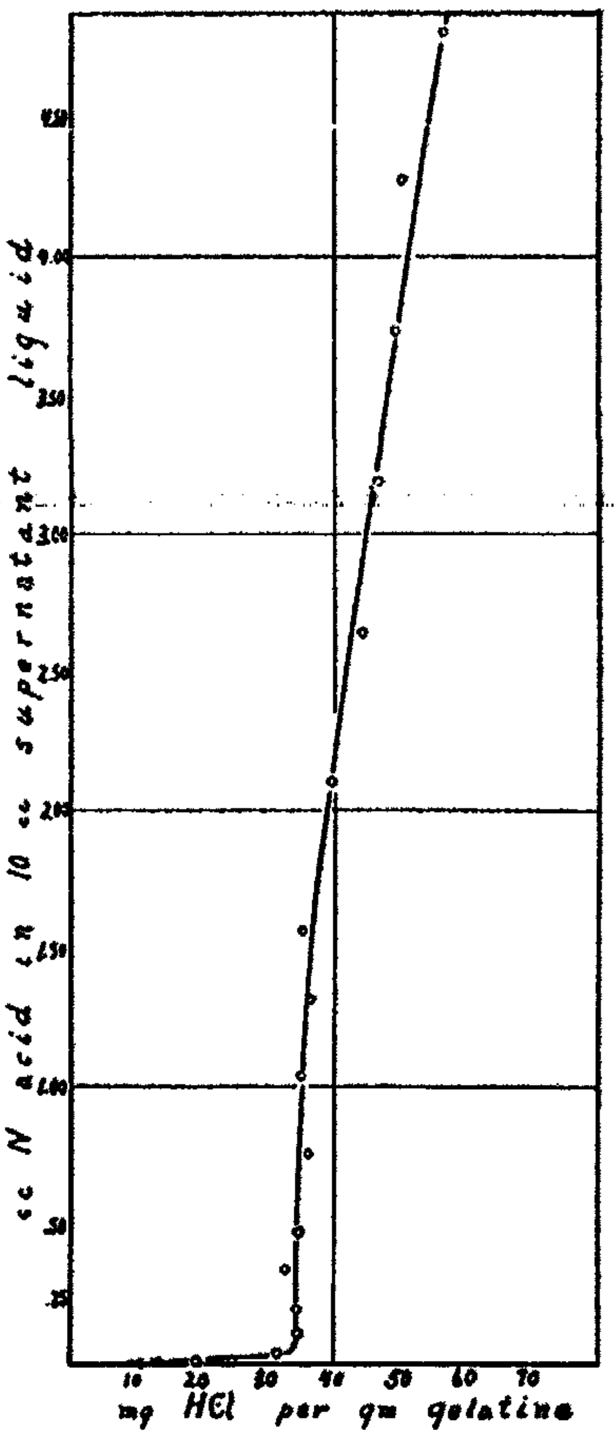

FIG. 2

Gelatine and HCl in 90% Ethyl Alcohol
High Acid Concentrations

made at 0°C. and the results of these were also corrected for the volume change due to temperature.

The amount of acid or base left in a definite volume of supernatant liquid was plotted against the amount used by a gram of dry protein. In the interpretation of the curves, the same principles used in the previous method were applied. A constant concentration of the supernatant liquid with varying values of the amount taken up indicated compound formation, while continuously varying values of both indicated adsorption.

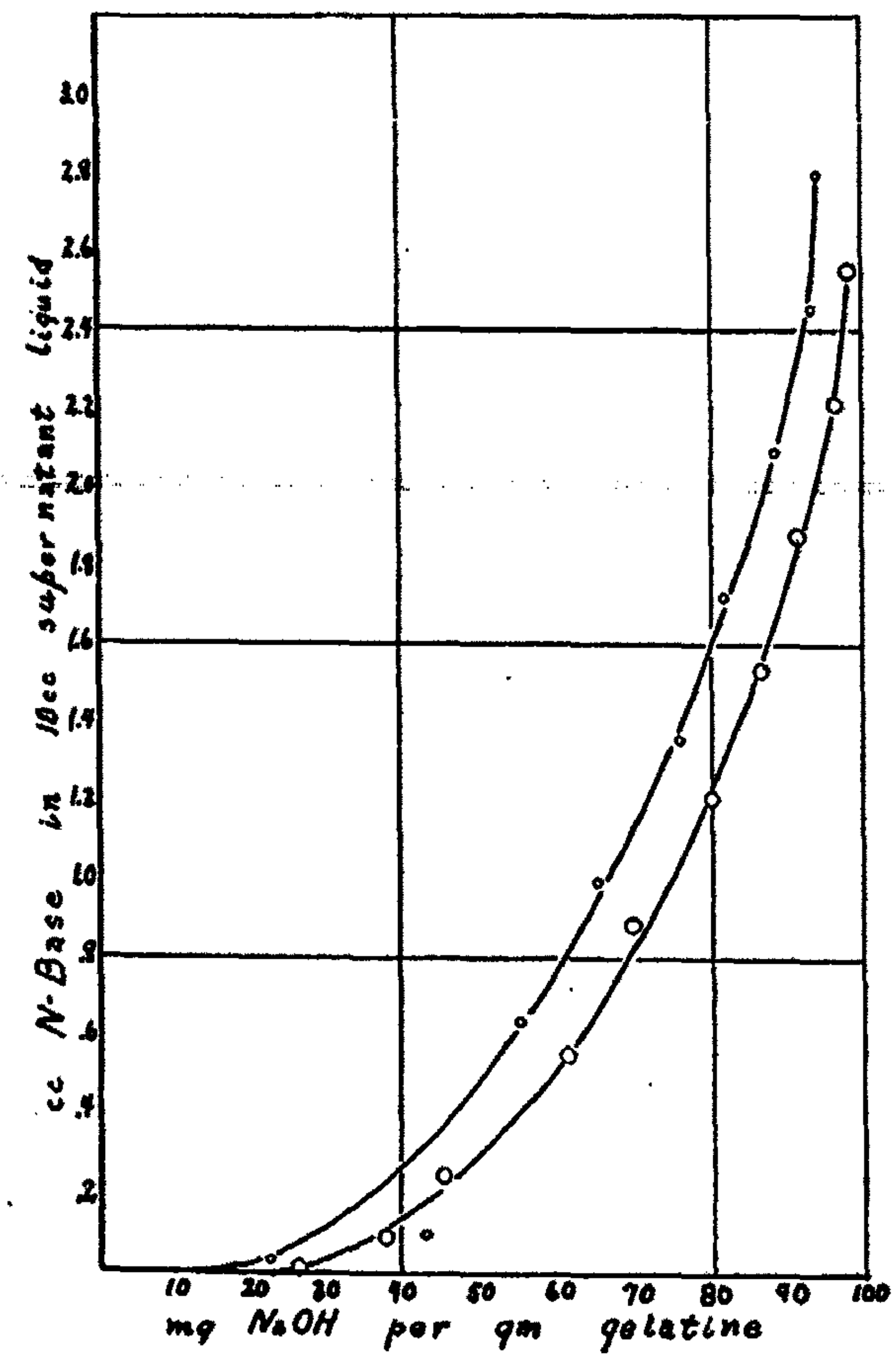

FIG. 3

Gelatine and NaOH in 90% Ethyl Alcohol
o = 0°C. O = Room Temperature

The first runs were made with HCl on the gelatine used in the earlier work. That particular lot of gelatine was exhausted before the new method was quite perfected and therefore no data are given. The results are important only because they are substantially the same as those obtained by the old method, and show the equivalence of the two.

The rest of the work was done on a sample of ash-free gelatine obtained from the Eastman Company. Runs were made with HCl at room temperature and at 0°C. A set of typical data for each are given in Tables I and II and plotted in Fig. 1. The data for a run made at higher acid concentrations is given in Table III and plotted, together with the data from Table I, in Fig. 2.

Single runs were made with NaOH at room temperature and at 0°C. The results are given in Tables IV and V, and plotted in Fig. 3.

TABLE I

Gelatine and HCl in 90% Ethyl Alcohol

1 g gelatine, equivalent to 0.891 g dry gelatine, used in each run. Volume of each run = 98.7 cc. Length of run = 2 hours.

Room temperature or approximately 25°C.

a = cc N HCl added; b = cc N base for 50 cc supernatant liquid; c = cc N acid in supernant liquid = b × 1.974; d = cc N acid in 10 cc supernatant liquid = b/5; e = cc N acid used per g gelatine equivalent × 10^{-3} (a − c)/0.891; f = mg HCl per g gelatine = e × 36.468.

a	b	c	d	e	f
0.28	0.00	0.00	0.00	0.31	11.4
0.56	0.04	0.07	0.01	0.54	19.7
1.11	0.17	0.34	0.04	0.86	31.4
1.94	0.55	1.09	0.11	0.95	34.8
2.78	0.98	1.93	0.20	0.95	34.5
4.17	1.70	3.36	0.34	0.90	32.8
5.55	2.38	4.70	0.48	0.96	34.0
8.33	3.77	7.44	0.75	1.00	36.4
11.11	5.19	10.25	1.04	0.96	35.0
13.89	6.58	12.99	1.32	1.01	36.8

TABLE II

Gelatine and HCl in 90% Ethyl Alcohol

1 g gelatine, equivalent to 0.891 g dry gelatine, used in each run. Volume of runs 1-3 = 100 cc.; volumes of numbers 4-10 = 98.7 cc. Temperature = 0°C. Length of run = 1½ hours.

a = cc N HCl added; b = cc N base for 50 cc supernatant liquid (cold); C = cc N acid in supernatant liquid = (b × vol)/51; d = cc N acid in 10 cc supernatant liquid = b/5.1; e = cc N acid used per g gelatine equivalent × 10^{-3} = (a − c)/0.891; f = mg HCl per g gelatine = e × 36.468.

a	b	c	d	e	f
0.28	0.02	0.04	0.004	0.26	9.3
0.56	0.03	0.06	0.006	0.56	20.3
1.11	0.21	0.42	0.04	0.78	28.3
1.95	0.58	1.12	0.11	0.93	33.8
2.78	1.02	1.98	0.20	0.90	32.6
4.17	1.72	3.33	0.34	0.94	34.3
5.56	2.43	4.71	0.48	0.96	34.8
8.33	3.86	7.47	0.76	0.97	35.4
11.11	5.29	10.24	1.04	0.98	35.7
13.89	6.72	12.99	1.32	1.01	36.7

TABLE III

Gelatine and HCl in 90% Ethyl Alcohol

1 g gelatine, equivalent to 0.891 g dry gelatine, used in each run. Volume of each number = 100 cc. Length of run = 2 hours.
Room temperature = about 25°C.
a = cc N HCl added; b = cc N base for 50 cc supernatant liquid; c = cc N acid in supernatant liquid = b × 2; d = cc N acid in 10 cc supernatant liquid = b/5; e = cc N acid used per g gelatine equivalent × 10^{-3} = (a − c)/0.891; f = mg HCl per g gelatine = e × 36.468.

a	b	c	d	e	f
16.49	7.81	15.63	1.56	0.97	35.4
21.99	10.51	21.02	2.10	1.09	39.8
27.49	13.21	26.41	2.64	1.21	44.3
32.98	15.92	31.84	3.18	1.28	46.7
38.48	18.64	37.28	3.73	1.35	49.4
43.98	21.38	42.75	4.28	1.38	50.2
49.48	24.04	48.09	4.81	1.46	56.9

TABLE IV

Gelatine and NaOH in 90% Ethyl Alcohol

1 g gelatine, equivalent to 0.891 g dry gelatine, used in each run. Volume of each number = 100 cc. Length of run = 2½ hours.
Room temperature = about 25°C.
a = cc N NaOH added; b = cc N acid for 50 cc in supernatant liquid; c = cc N base in supernatant liquid = b × 2; d = cc N base in 10 cc supernatant liquid = b/5; e = cc N base used per g gelatine equivalent × 10^{-3} = (a − c)/0.891; f = mg NaOH per g gelatine = e × 40.008.

a	b	c	d	e	f
0.69	0.05	0.10	0.01	0.66	26.6
1.73	0.44	0.88	0.09	0.95	38.0
3.46	1.22	2.45	0.25	1.14	45.4
6.92	2.78	5.55	0.56	1.54	61.2
10.37	4.41	8.82	0.88	1.74	69.7
13.83	6.03	12.05	1.21	2.00	80.0
17.29	7.68	15.36	1.54	2.17	86.8
20.75	9.36	18.73	1.87	2.27	90.7
24.21	11.03	22.06	2.21	2.41	96.6
27.66	12.74	25.48	2.55	2.46	98.2

TABLE V

Gelatine and NaOH in 90% Ethyl Alcohol

1 g gelatine, equivalent to 0.891 g dry gelatine, used in each run. Volume of each number = 100 cc. Length of run = 3½ hours.
Temperature = 0°C.

a = cc N NaOH added; b = cc N acid for 50 cc supernatant liquid (cold); c = cc N base in supernatant liquid = (b × 100)/51; d = cc N base in 10 cc supernatant liquid = b/5.1; e = cc N base used per g gelatine equivalent × 10^{-3} = (a − c)/0.891; f = mg NaOH per g gelatine = e × 40.008.

a	b	c	d	e	f
0.76	0.13	0.26	0.03	0.57	22.7
1.90	0.48	0.94	0.09	1.08	43.1
3.81	1.59	3.13	0.31	0.76	30.5
7.61	3.25	6.37	0.64	1.39	55.7
11.42	5.08	9.96	0.99	1.63	65.1
15.22	6.90	13.53	1.35	1.90	75.8
19.03	8.77	17.20	1.72	2.05	81.9
22.83	10.64	20.85	2.09	2.22	88.6
26.64	12.52	24.55	2.46	2.34	93.6
30.06	14.40	27.95	2.80	2.36	94.4

Discussion

The form of the curve obtained with HCl strongly suggests that a compound is formed, for it has two distinct portions with a fairly sharp break between them. It would be more conclusive if the "flat" really were flat instead of showing a very gradually increasing concentration of acid in the supernatant liquid. This may be due to a correspondingly small amount of hydrolysis of the assumed compound. If it is an adsorption phenomenon which is taking place, there should be more acid taken up by the protein at 0°C. than at room temperature for adsorption has a negative temperature coefficient. The curves are identical within experimental error, so that this is negative evidence for compound formation. Considering the whole evidence, we must return to our original conclusion that gelatine forms a compound with HCl in ethyl alcohol. At higher concentrations of acid, there is some adsorption on the compound formed. We predict that there would be increased adsorption at 0°C.

This sample of gelatine combined with somewhat more acid than the preceding one. The compound contained 92 × 10^{-5} equivalents or 33.5 mg. of HCl per gm. of dry gelatine, thus giving the gelatine a combining weight of 1090. This agrees well with much other work done on gelatine and HCl in water solution.[1] The other sample bound 86 × 10^{-5} equivalents.

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[1] Bancroft and Ridgway: J. Phys. Chem., **36**, 1311 (1932).

The curves with NaOH are typical adsorption curves. Theoretically the run at 0°C. should show more adsorption of NaOH, while the opposite is true. At present we have no explanation for this.

Conclusions

1. A new method for studying the acid and base binding power of certain proteins in non-aqueous solvents has been given.

2. Gelatine forms a compound with HCl in ethyl alcohol.

3. Gelatine probably adsorbs NaOH from ethyl alcohol without any compound formation.

Cornell University.

THE SORPTION OF ALCOHOL VAPORS BY CELLULOSE AND CELLULOSE ACETATES*†

BY S. E. SHEPPARD AND P. T. NEWSOME

The present paper deals with (a) the sorption equilibria of various alcohols with cellulose and cellulose acetates, (b) the rates of adsorption and desorption of alcohols by cellulose and cellulose acetates under definite conditions and (c) deductions regarding the sorption process and the fine and coarse structure of cellulose materials.

All measurements were made with an enclosed silica spring balance at 30°C. The cellulose materials used consisted of a series of primary and secondary acetates—primary acetates, extending from pure cotton linters (0% acetyl) to cellulose triacetate (44.8% acetyl), and secondary (hydrolyzed) acetates decreasing from 44.8% acetyl to 35.5% acetyl. As will be shown later, it is necessary to distinguish between adsorption by the "native" and by the "hydrate" crystalline forms of the various cellulose materials.

The secondary acetates all possess the "hydrate" form and the primary acetates are more or less converted from the "native" form of the original cotton linters to the "hydrate" form depending on the degree of dispersion in the acetylating mixture (the permanent conversion to hydrate form is probably complete above 40% acetyl).

Conversion to the hydrate form, expanded crystal lattice, results in an increased adsorbing capacity of pure cellulose and cellulose derivatives, as indicated by moisture adsorption experiments (see "The Sorption of Water Vapor by Cellulose and its Derivatives," Part I.[1]). The same result is also shown by the following alcohol adsorption data.

The relative rates of adsorption of methyl and ethyl alcohol vapors at the saturation pressure at 30°C. are independent of the acetyl content, although the maximum adsorption varies greatly with the acetyl content (see Figs. 1 and 2). However, the relative rates of adsorption of n-propyl and n-butyl alcohol vapors are definitely lower for the higher acetates (see Figs. 3 and 4). This indicates the existence of a difference in structure between the different acetates which was not apparent in the methyl and ethyl alcohol adsorption curves. A further discussion of this point will be given later in this paper.

In general, the rate of adsorption of alcohol vapor by any primary, or secondary acetate decreases as we go up the alcohol series (see Figs. 1, 2, 3 and 4). The difference in the rate of adsorption of water and various alcohols up to n-octyl alcohol by a secondary acetate (38% acetyl) is shown in Fig. 5. Higher alcohols are adsorbed more slowly than the lower alcohols because of lower vapor pressure and greater molecular size.

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* Presented at American Chemical Society Meeting, Buffalo, August, 1931.

† Communication No. 494 from the Kodak Research Laboratories.

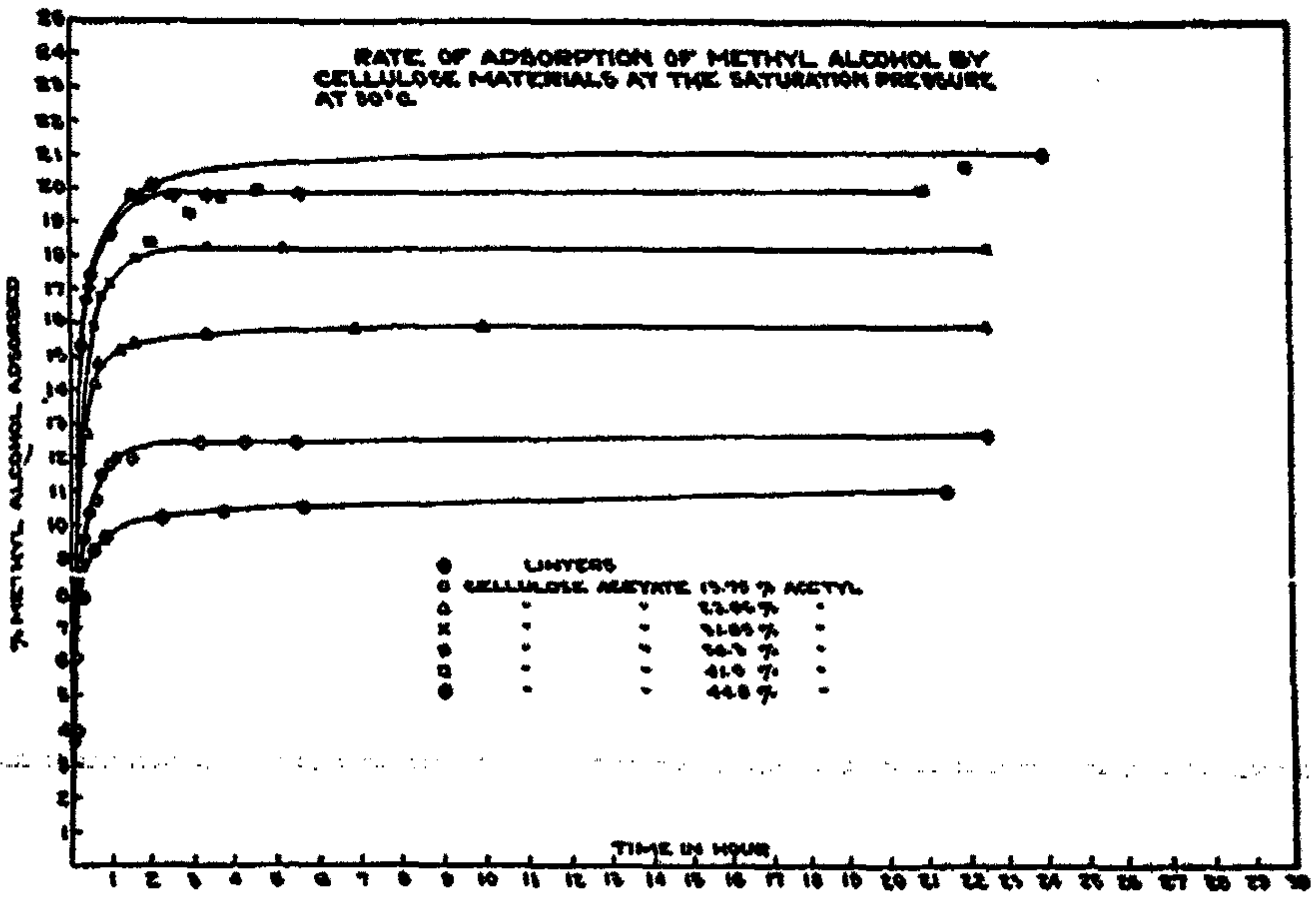
RATE OF ADSORPTION OF METHYL ALCOHOL BY CELLULOSE MATERIALS AT THE SATURATION PRESSURE AT 30°C.
● LINTERS
○ CELLULOSE ACETATE 13.75 % ACETYL
△ " " 23.64 % "
x " " 31.85 % "
⊕ " " 36.3 % "
□ " " 41.9 % "
● " " 44.8 % "
% METHYL ALCOHOL ADSORBED
TIME IN HOUR
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

Fig. 1

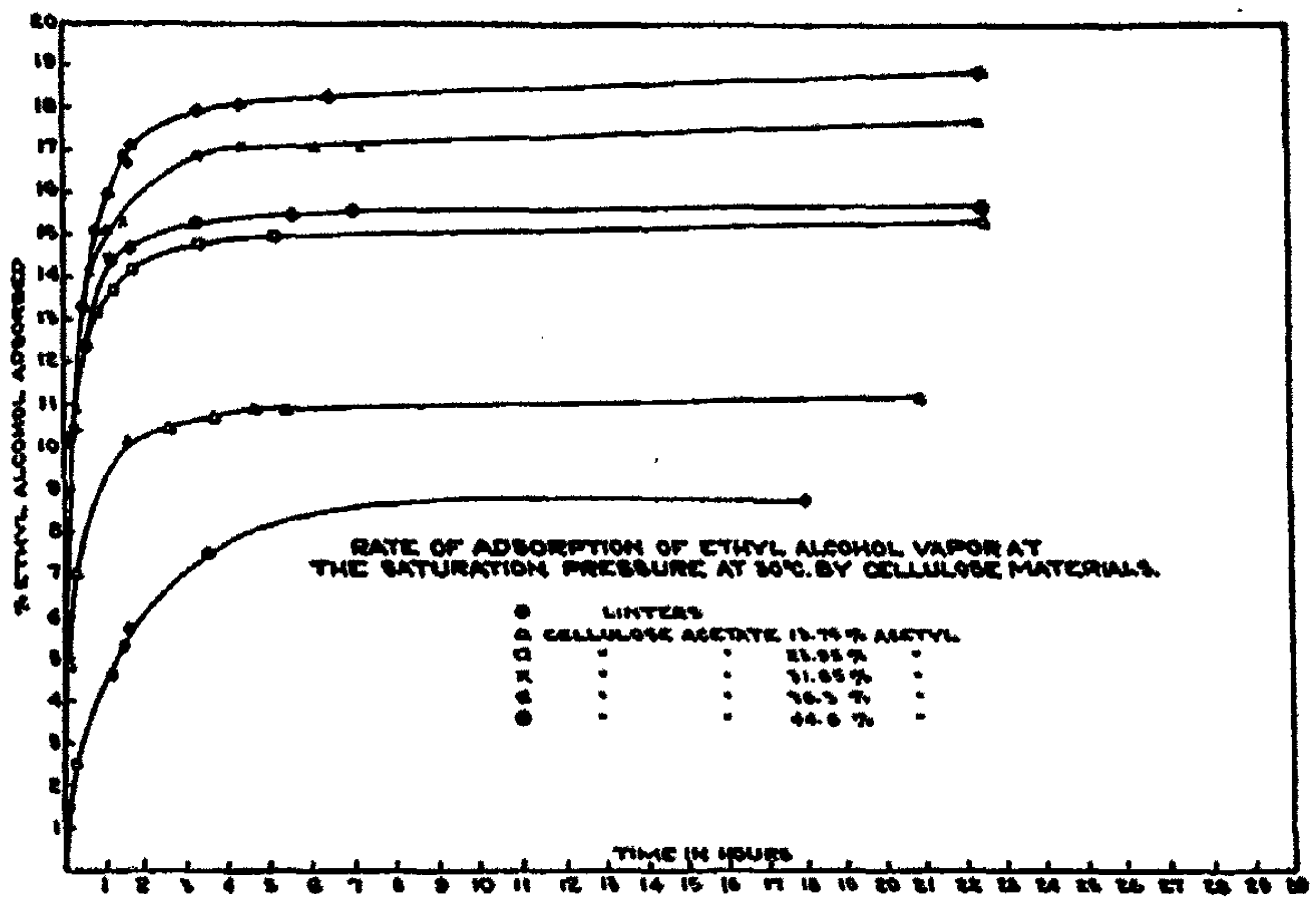
RATE OF ADSORPTION OF ETHYL ALCOHOL VAPOR AT THE SATURATION PRESSURE AT 30°C. BY CELLULOSE MATERIALS.
● LINTERS
△ CELLULOSE ACETATE 13.75 % ACETYL
□ " " 23.95 % "
x " " 31.85 % "
⊕ " " 36.3 % "
● " " 44.8 % "
% ETHYL ALCOHOL ADSORBED
TIME IN HOURS
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

Fig. 2

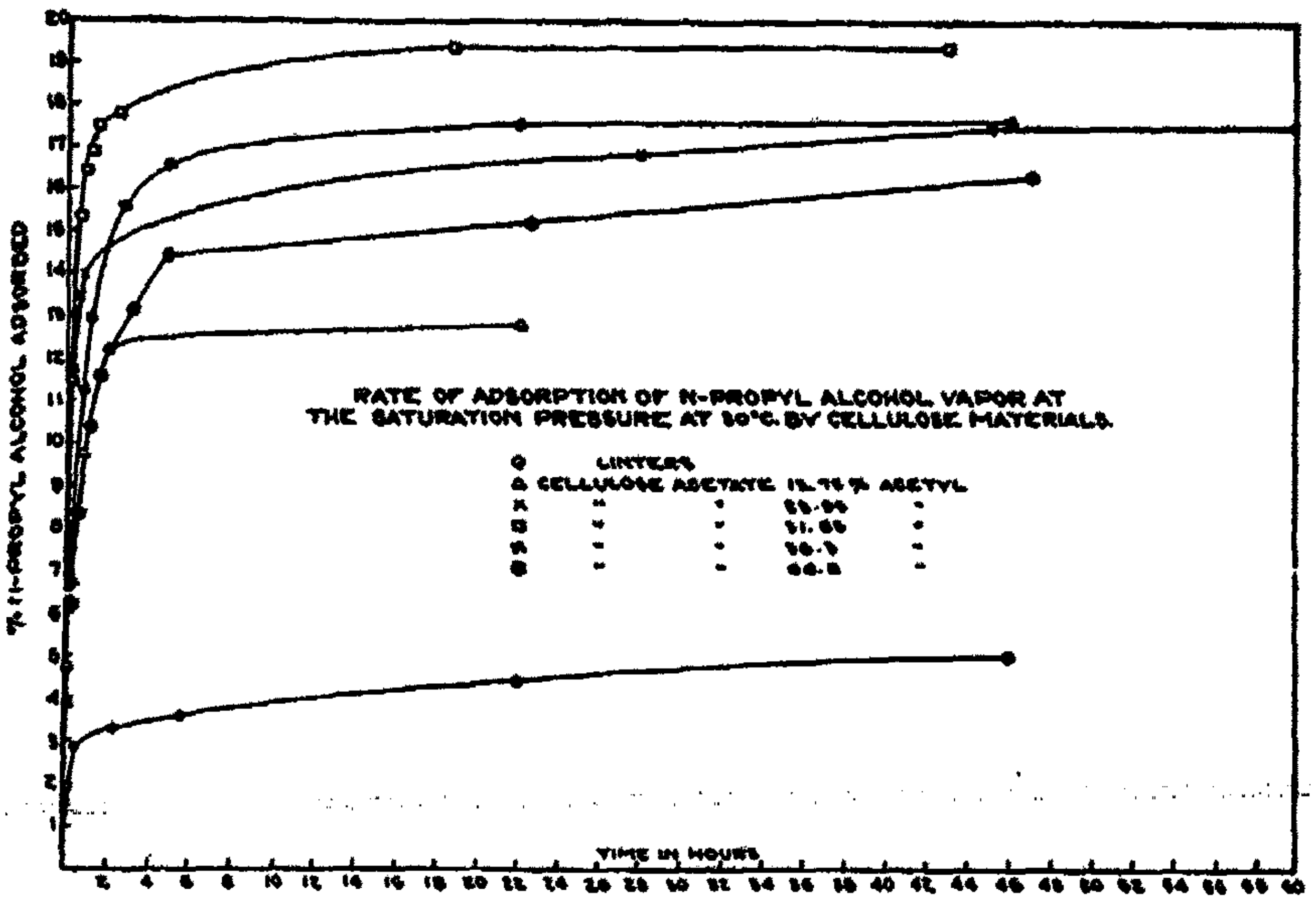
RATE OF ADSORPTION OF N-PROPYL ALCOHOL VAPOR AT THE SATURATION PRESSURE AT 30°C. BY CELLULOSE MATERIALS.
○ LINTERS
△ CELLULOSE ACETATE 13.75 % ACETYL
× " " 33.99 "
□ " " 31.85 "
" " 36.5 "
● " " 44.8 "
% N-PROPYL ALCOHOL ADSORBED
TIME IN HOURS
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Fig. 3

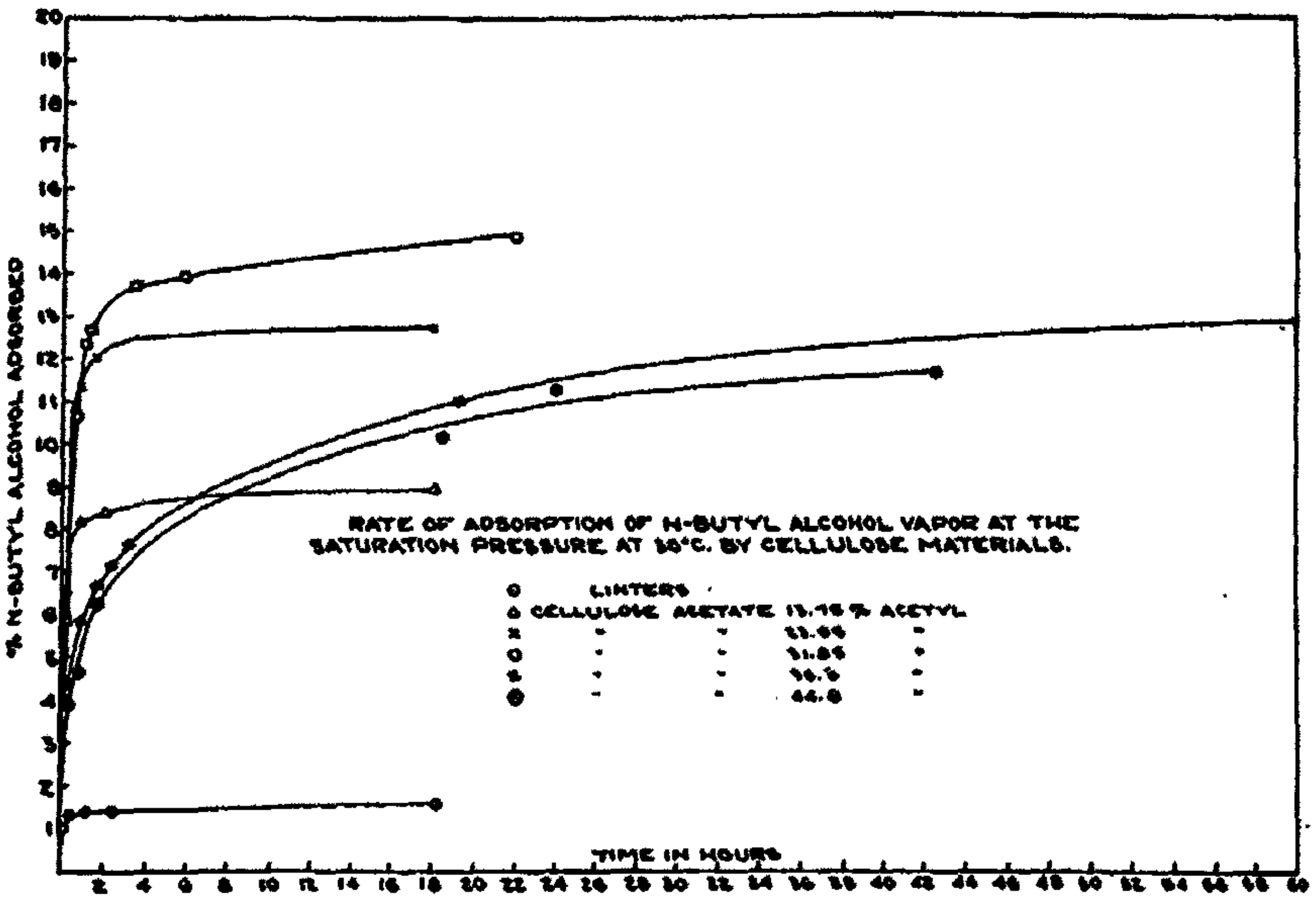
RATE OF ADSORPTION OF N-BUTYL ALCOHOL VAPOR AT THE SATURATION PRESSURE AT 30°C. BY CELLULOSE MATERIALS.
○ LINTERS
△ CELLULOSE ACETATE 13.75 % ACETYL
× " " 33.99 "
○ " " 31.85 "
" " 36.5 "
● " " 44.8 "
% N-BUTYL ALCOHOL ADSORBED
TIME IN HOURS
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Fig. 4

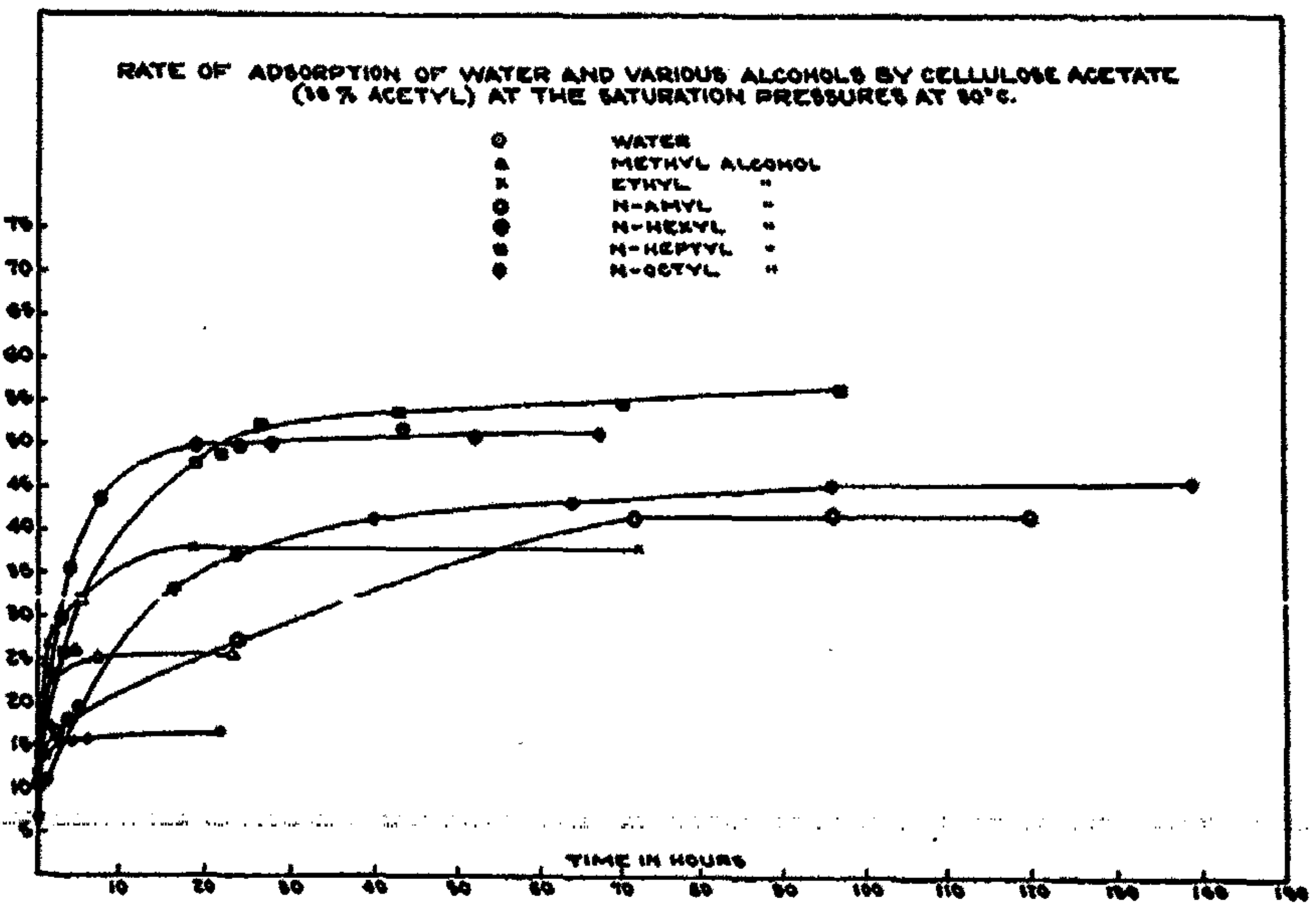

FIG. 5

The difficulty of maintaining a saturated atmosphere about the adsorbent increases with increasing molecular weight and lower vapor pressure of the alcohol. This is very important in a comparative study of adsorption rates at the saturation pressures. The rate of adsorption of the higher alcohols varies greatly depending on the shape of the apparatus even in the absence of air. Molecules of the higher alcohols diffuse slowly through long lengths of connection tubing. In all of the measurements recorded here the adsorbent was suspended from a silica spring balance in an air-free system not over 3 cm. above an area of 7 sq. cm. of liquid and the saturation pressure if known, was maintained as observed with a manometer.

Figs. 6 and 7 show the maximum adsorptions at the saturation pressures at 30°C. of water and alcohol vapors in per cent of the original dry weight and also in moles of the initially dry materials. The arrows in the figures indicate the direction of changing acetyl content (up to the triacetate and down again by hydrolysis).

The variation of maximum adsorption with acetyl content shown in Fig. 1 can logically be carried only as far as 41.5% acetyl, since the triacetate and three secondary acetates do not belong to the same series—the latter data are included in order to show the variation in adsorption of the different vapors by the same acetate. Nevertheless, it is clear that secondary acetates have a much greater adsorbing capacity for water and alcohol vapors than primary acetates of the same acetyl content.

The data of Fig. 7 show the variation in adsorbing capacity of a series of acetates all from the same batch. The water adsorption falls continuously

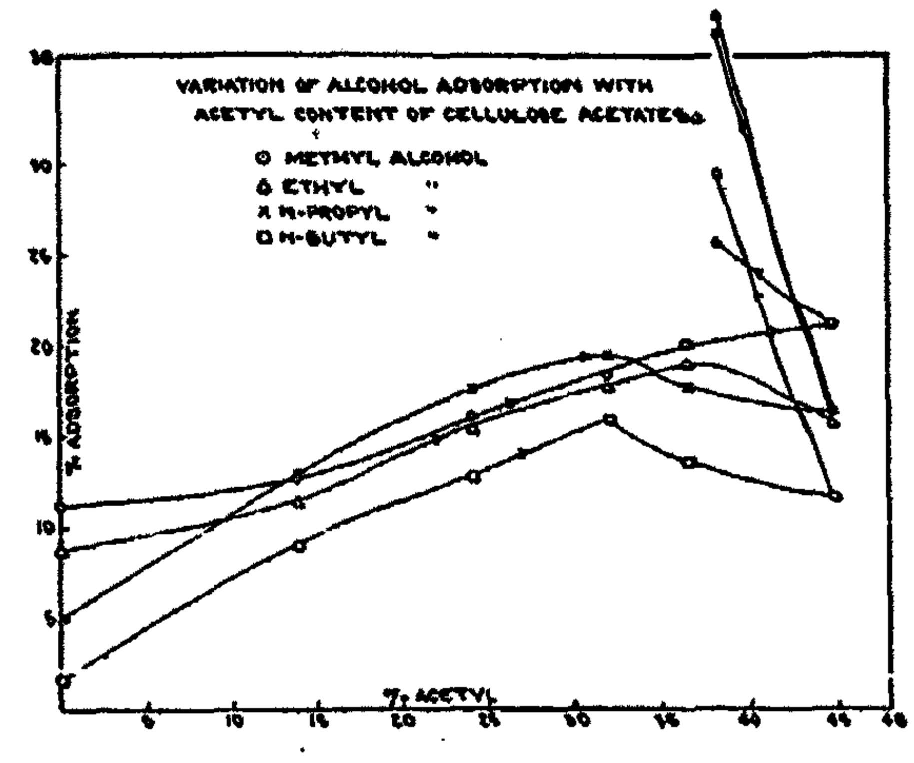

Fig. 6

with increasing acetyl content. The methyl and ethyl alcohol adsorptions rise continuously with increasing acetyl content while n-propyl and n-butyl alcohol adsorptions show maxima at 31.8% acetyl.

Werner and Engelmann[2] measured the adsorption of ethyl alcohol by sheets of cellulose (cellophane) and cellulose acetates when immersed in a solution of alcohol with 10% ether. A maximum adsorption was found at 37.7% acetyl. They also observed that the amount of water retained by the various sheets when immersed in liquid water and blotted dry decreased directly as the acetyl content increased from 0 to 44.8% acetyl. This is in fair agreement with our results on the sorption of water vapor by different cellulose acetates.[3] They point out relations between the variation of adsorption and solubility with acetyl content.

The amount of alcohol adsorbed by primary acetates, when expressed as moles per gram of dry material, decreases continuously in going up the alcohol series from methyl to n-butyl. But when the same adsorption is

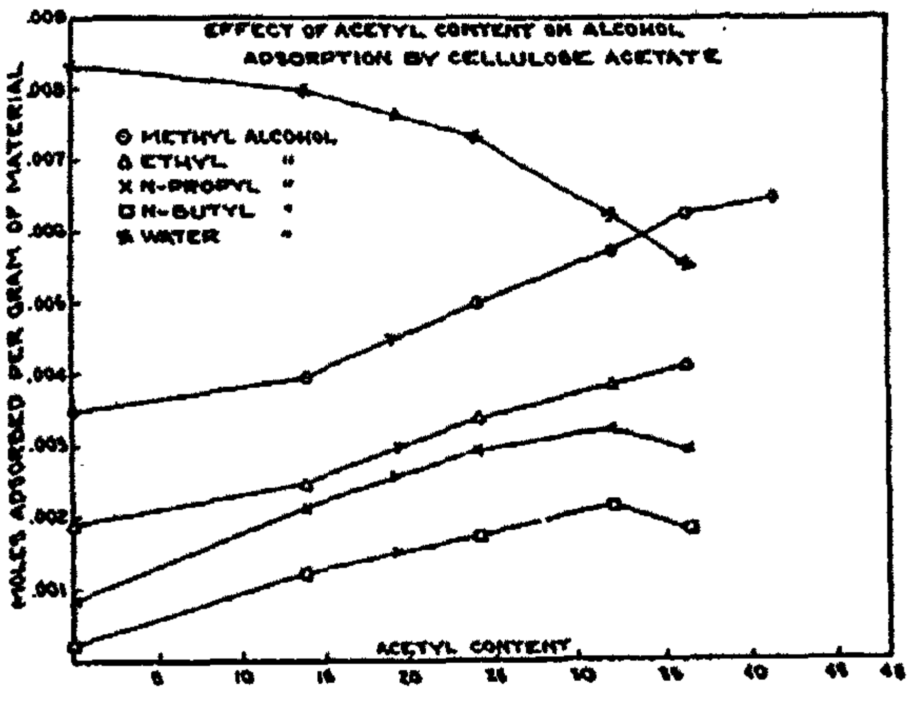

Fig. 7

expressed as per cent of the dry weight, this is not true because certain acetates adsorb more n-propyl alcohol than either methyl or ethyl alcohols (compare Figs. 6 and 7). Approximately 50% of adsorbed water appears to be held by hydroxyl groups in pure cellulose and any decrease in hydroxyl content produced by acetylation results in a decreased moisture adsorption. But the alcohols, also possessing polar hydroxyls, behave quite differently. A decrease in hydroxyls occasioned by acetylation results in an increased adsorption of alcohols by primary acetates, except for n-propyl and n-butyl, by acetates containing more than 32% acetyl. This behavior of the alcohols cannot be attributed to any gradual change of fine structure from native to hydrate form since both native and hydrate forms give, in general, the same results. (Compare our results with the native form to those of Werner and Engelmann using the hydrate form.) Neither is it entirely true that alcohols are held more strongly by acetate groups than by hydroxyls, since n-propyl and n-butyl alcohols show the reverse above 32% acetyl. Our results[4] show that increased dispersion as indicated by different viscosities does not increase the adsorbing capacity, since regenerated celluloses of low viscosity absorb less water than mercerized cellulose of high viscosity. However, Pringsheim, Kusenack and Weinreb[5] have found that the acetylation of cellulose, employing zinc chloride as catalyst, is accompanied by a decrease in particle size and that the conversion of primary triacetate into acetone-soluble secondary acetate involves a further disaggregation and theoretically, increased solubility in a given solvent will always be accompanied by increased adsorbability of the vapor of that solvent. Our results agree with this in that secondary acetates adsorb alcohols as well as water more strongly than primary acetates.

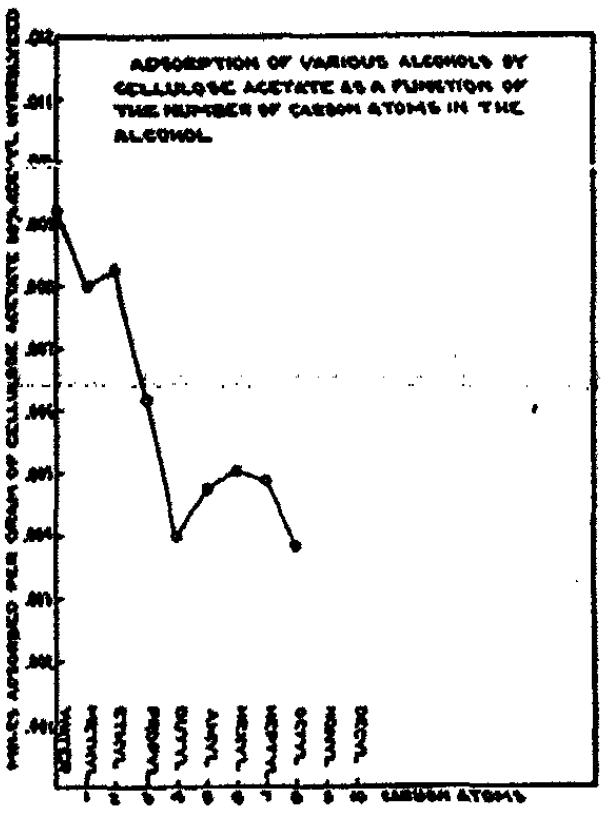

FIG. 8

Further measurements on the adsorption of different alcohols by cellulose materials of different crystalline structure, viscosity, chemical constitution, and external dispersity are necessary in order to clarify the problem. Such a study may also give an explanation of the wide divergence which has been found in the moisture regain of both dope and fibrous acetylated cellulose triacetates.

Fig. 8 and Table I show the adsorption of the saturated normal alcohols up to and including n-octyl by the same secondary acetate (38% acetyl). The molar adsorbing capacity of this acetate, contrary to the behavior of primary acetates, does not fall in a regular manner as we go to the higher alcohols. However, as an approximation, the molar adsorption falls rapidly from water with no carbon atoms to butyl alcohol with four carbon atoms and then remains constant at a value of 0.004 to 0.005 moles per gram of acetate. This behavior might be expected if we assumed that butyl alcohol just ceased to penetrate the cellulose units, and that from this alcohol onward, we have pure surface adsorption with the hydroxyls of the alcohols attached to the cellulose. Since the cross section of the alcohols remains the same with increasing number of carbon atoms, the molar adsorption would also remain constant, assuming uniformity of exposed surface and complete covering by the alcohols with the formation of a unimolecular layer.

A calculation of the total adsorbing surface of a gram of cellulose acetate may be made as follows:

According to N. K. Adam[6] the area occupied by the $-CH_2OH$ group when oriented on a surface is 21.7×10^{-16} sq. cm. Since we have 0.0045 moles of adsorbed alcohol, the total area occupied is $0.0045 \times 6.06 \times 10^{23} \times 21.7 \times 10^{-16} = 5{,}918{,}000$ sq. cm. per gram.

TABLE I

Adsorption of Various Vapors at Their Saturation Pressures at 30°C. by the same Cellulose Acetate (Hydrolyzed—38% acetyl)

Vapor	Boiling Point °C	V.P. mm. Hg. at 30°C	Mol. Wt.	% Adsorption	Moles Absorbed per gram	$\frac{\text{Moles per Gram}}{\text{V.P.}}$
Methyl alcohol	64.5	160.0	32.03	25.6	0.0080	0.00005
Ethyl alcohol	78.5	78.8	46.05	38.1	.00827	.000105
n-Propyl alcohol	97.8	27.6	60.06	37.2	.00618	.000224
n-Butyl alcohol	117.7	9.5	74.08	29.4	.00397	.000417
n-Amyl alcohol	137.9	5.5	88.10	41.9	.00476	.000858
n-Hexyl alcohol	155.8		102.11	51.5	.00504	
n-Heptyl alcohol	175.8		116.12	56.8	.00489	
n-Octyl alcohol	194		130.14	50.1	.00385	
Water	100	31.82	18.02	16.5	.00918	.000288
Acetic Acid	118.1	20.6	60.03	144.9	.02615	.00127

From a consideration of compression forces and thickness of adsorbed water layer Stamm[7] calculated the total adsorbing surface of wood material to be 310,000 sq. cm. per gram. The above value for cellulose acetate is probably high because of some formation of polymolecular layers of adsorbed alcohol.

The last column of Table I shows the adsorption in moles per gram of cellulose acetate divided by the vapor pressure of the adsorbate. The vapor pressures of n-hexyl, n-heptyl and n-octyl alcohols were not available. From methyl to amyl alcohols the above quantity doubles for each additional CH_2 group. The maximum adsorption at the saturation pressure at any temperature is independent of the absolute value of the vapor pressure of the liquid under consideration. The energy changes involved are dependent only on the relative vapor pressure. Thus, the work which a molecule does in evaporating from a liquid surface is $\phi = KT \ln P$, where ϕ is the work, K the Boltzmann constant, T the absolute temperature and P the relative vapor pressure. Also, the amount of work done in reversibly transferring one mole of vapor from the interior of the free liquid to a point on the adsorption surface is KT ln P, where again P is the relative vapor pressure. It seems that the difference in pressure influences only the rate of attainment of equilibrium at the saturation pressure.

Dewar[8] found that in general, the gas with the highest boiling point was most strongly adsorbed, while Schmidt and Hinteler[9] found apparently the reverse, that is, the adsorption on charcoal of a number of vapors at their saturation pressures was inversely proportional to the molecular volumes at the boiling point. However, the two general laws are applicable to entirely different portions of the adsorption isotherm and are not contradictory (see Pearce and Johnstone).[10]

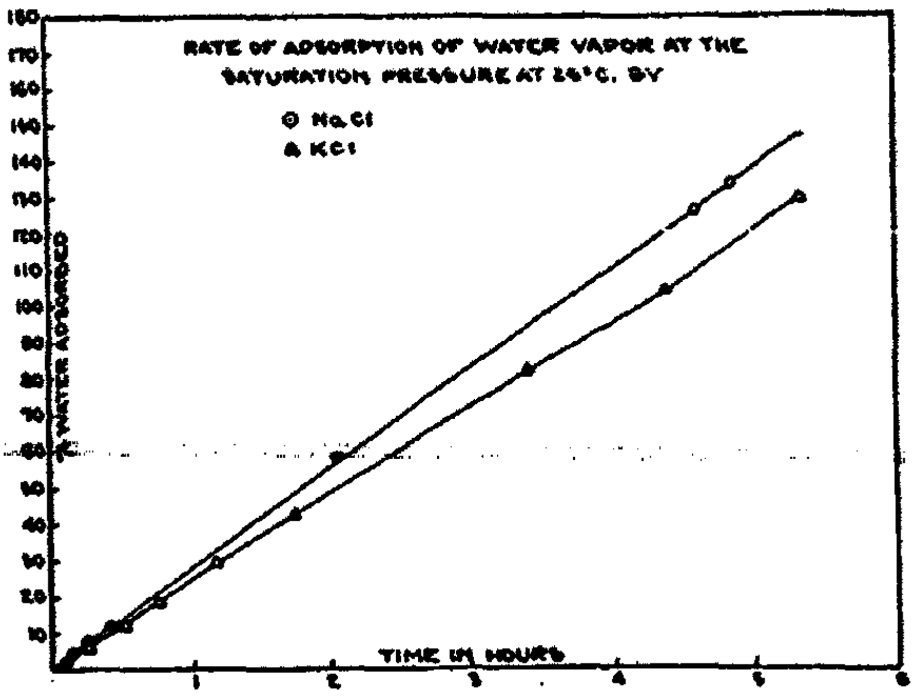

Fig. 9

Cellulose acetate (13.7% acetyl) adsorbed 12.3% benzyl alcohol at the saturation pressure.

Fig. 9 shows the rate of adsorption of water vapor by sodium chloride and by potassium chloride at the saturation pressure at 25° C. The rate curves are practically straight lines up to 130% adsorption. Before this point had been reached both salts had formed liquid solutions. These curves are introduced in order to show the type of rate curves to be expected in the adsorption of a solvent vapor by a solid. The adsorbed water is also rapidly removed from sodium chloride by evacuation at room temperature—only 0.7% remaining after 1 hour and none after 15 hours.

Fig. 10 shows the rate of adsorption of n-heptyl alcohol by a secondary cellulose acetate (37.25% acetyl) both in precipitated and in sheet form. The sheet adsorbs alcohol very slowly compared with the precipitated acetate. It is obvious that the exposed surface is an important factor. That the influence of molecular size of adsorbed vapor is also very great is seen when we consider that either precipitated or sheet cellulose acetate adsorbs water vapor at the same rate and to the same extent.

In general, we may conclude that the adsorption of non-solvent vapors is increasingly influenced by external surface, the greater the size of the vapor molecules.

It is practically certain that the rate of adsorption of all of the alcohols by precipitated acetates will vary depending on the state of aggregation.

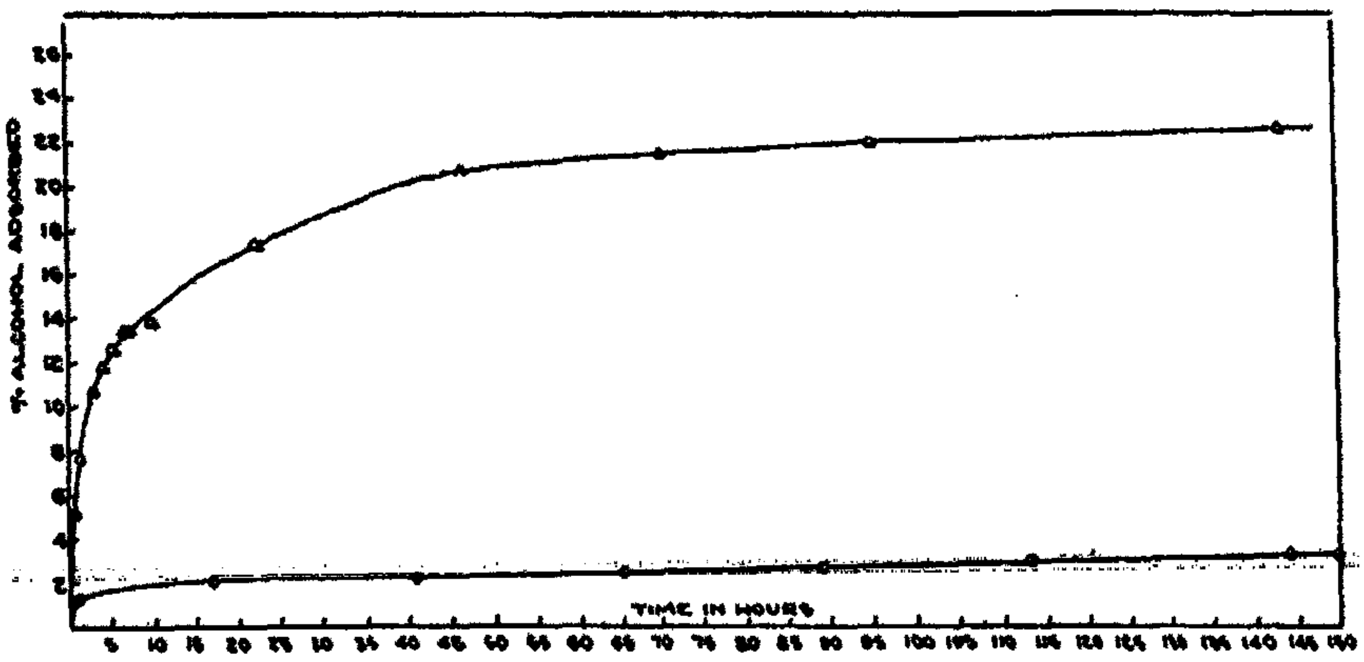

Fig. 10

Rate of adsorption of N-Heptyl Alcohol by Cellulose Acetate (37.25% Acetyl) in Precipitated and Sheet Form.

△ Precipitated ⊙ Sheet

Table II

Volume of Adsorption Space of Cellulose Acetate

Adsorbate	x/m	d	x/m/d
Water	0.165	0.998	0.165
Methyl alcohol	.256	.792	.323
Ethyl "	.381	.789	.483
n-Propyl "	.372	.804	.463
n-Butyl "	.294	.810	.363
n-Amyl "	.419	.817	.513
n-Hexyl "	.515	.820	.628
n-Heptyl "	.568	.817 (22°C.)	.696
n-Octyl "	.501	.827	.605

x/m = grams of vapor adsorbed per gram of acetate at the saturation pressure at 30°C.
d = density of liquid adsorbate at 20°C.
x/m/d = volume of adsorbed vapor.

Table II shows the volumes of the different alcohols adsorbed by a given secondary cellulose acetate (38% acetyl). The volume is not constant. Coolidge[11] found that the volume of a number of vapors adsorbed on charcoal at the saturation pressure at 0°C. varied only from 0.424 to 0.494 cc. per gram of charcoal, and he suggested that the adsorbent presents a fixed volume rather than a fixed surface. But cellulose materials being elastic gels, show neither a fixed volume nor a fixed surface.

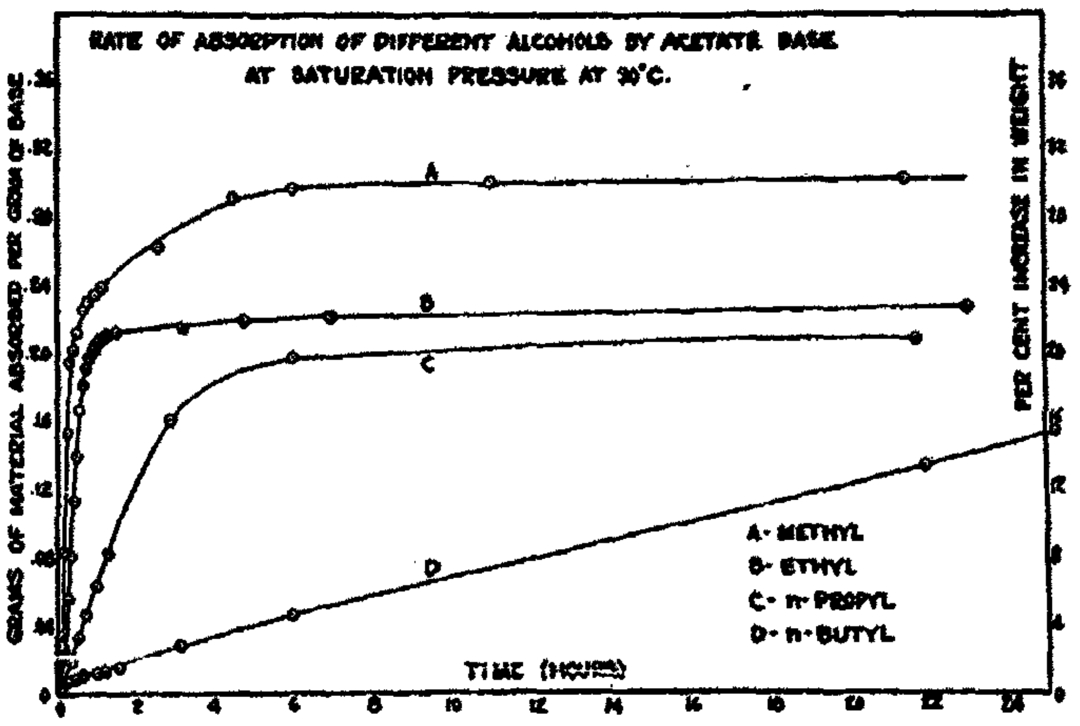

Fig. 11

Adsorption and Desorption of Alcohol Vapors by Cellulose Acetate Sheet

Whereas all of the data presented so far in this paper were obtained with samples of precipitated or fibrous material, the following measurements were made on a sample of cellulose acetate sheet, 0.003″ thick, prepared from a secondary cellulose acetate (38% acetyl) and acetone. The sheet was heated 24 hours at 105°C. to remove the acetone.

The difference in the rate of sorption of the different alcohols is much more pronounced in the sheet than in the precipitated form (see Fig. 11). The rate of adsorption as well as the maximum adsorption decreases regularly in going from methyl to n-butyl alcohol.

Fig. 12 shows the rate of desorption of the different alcohols by evacuation at 30°C. As the higher alcohols were more slowly adsorbed by the sheet, so

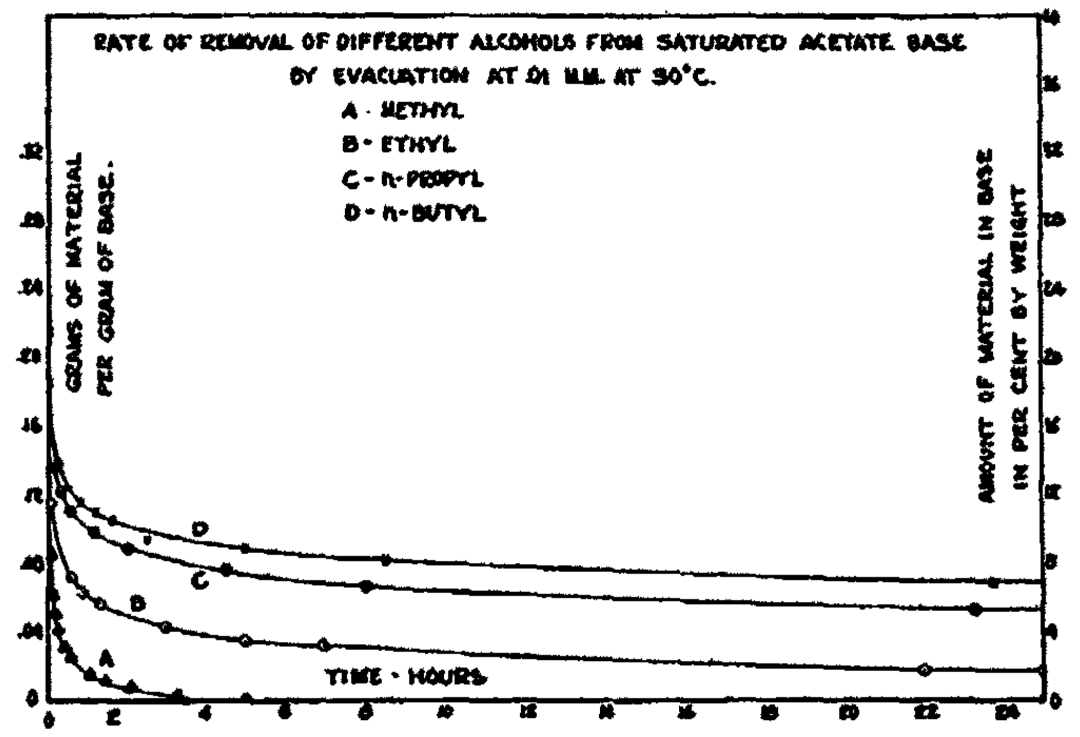

Fig. 12

they are more slowly removed from it independently of the total amount adsorbed at saturation. This behavior is to be expected because of the lower vapor pressure and greater molecular size of the higher alcohols with the consequent lowering of the diffusion rate. It should again be noted that all of the water adsorbed by a piece of sheet can be completely removed by the above evacuation procedure in about 30 minutes, whereas the lowest alcohol requires 5 hours.

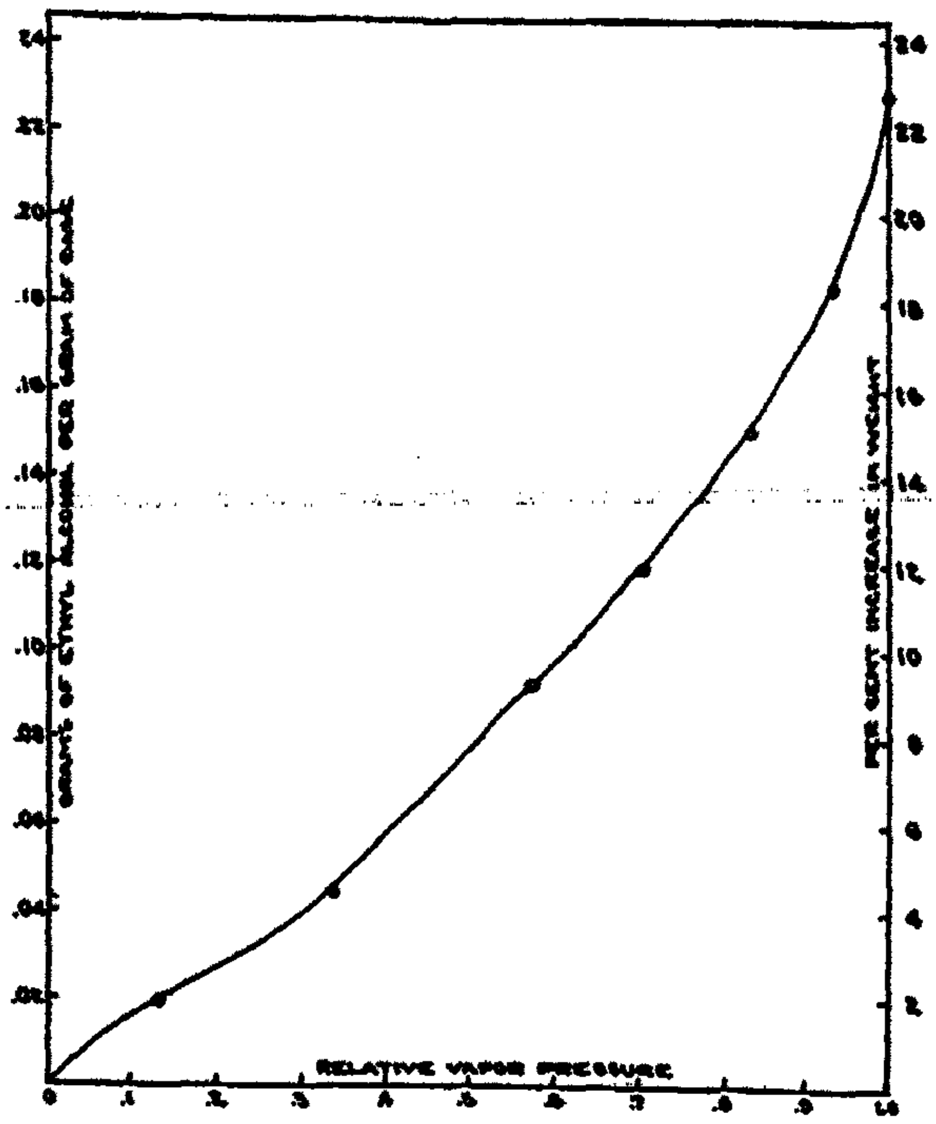

FIG. 13
Sorption of Ethyl Alcohol by Acetate Base at 30°C

Fig. 13 shows the maximum adsorption of ethyl alcohol vapor at different relative vapor pressures at 30°C. by a sample of the same sheet as used above. We have a typical S-shaped isotherm similar in all respects to the moisture adsorption isotherm. A calculation of the pore radius using the Kelvin equation gives the distribution curve shown in Fig. 14 with a most probable pore radius of 4.4 Å.U. in fair agreement with the value of 5.5 Å.U. obtained from the moisture adsorption isotherm.

Some information may be gained from a comparison of the alcohol and water adsorption data. Alcohol adsorption by cellulose and cellulose acetates is much more profoundly affected by chemical composition and mechanical structure than water adsorption and hence may yield more conclusive evidence regarding the mechanism of adsorption by such materials. The fact that water is adsorbed just as rapidly and to the same extent by a cellulose acetate in either sheet or precipitated form and that all of the water adsorbed at the saturation pressure may be removed by evacuation at room temperature within 10 minutes indicates that the mechanical structure offers no impediment to the diffusion of water molecules in such a material. Neither is there any indication here of pronounced chemical attraction between cellulose acetate and water although, since the moisture adsorption does vary with acetyl content, specific chemical forces must play a part. On the other hand, even the smallest alcohol molecule has difficulty diffusing in and out of the cellulose acetate material. Specific chemical or polar forces are insufficient to attract strongly any of the alcohols, yet a large molecule of a solvent vapor is strongly attracted and adsorbed. The attractive force overcomes the resistance to diffusion and the material swells and finally dissolves in the adsorbate. On desorption the last traces of this vapor are removed more slowly than adsorbed alcohols because of the stronger attraction between adsorbent and adsorbate and also increasing resistance to diffusion due to collapse of pore space.

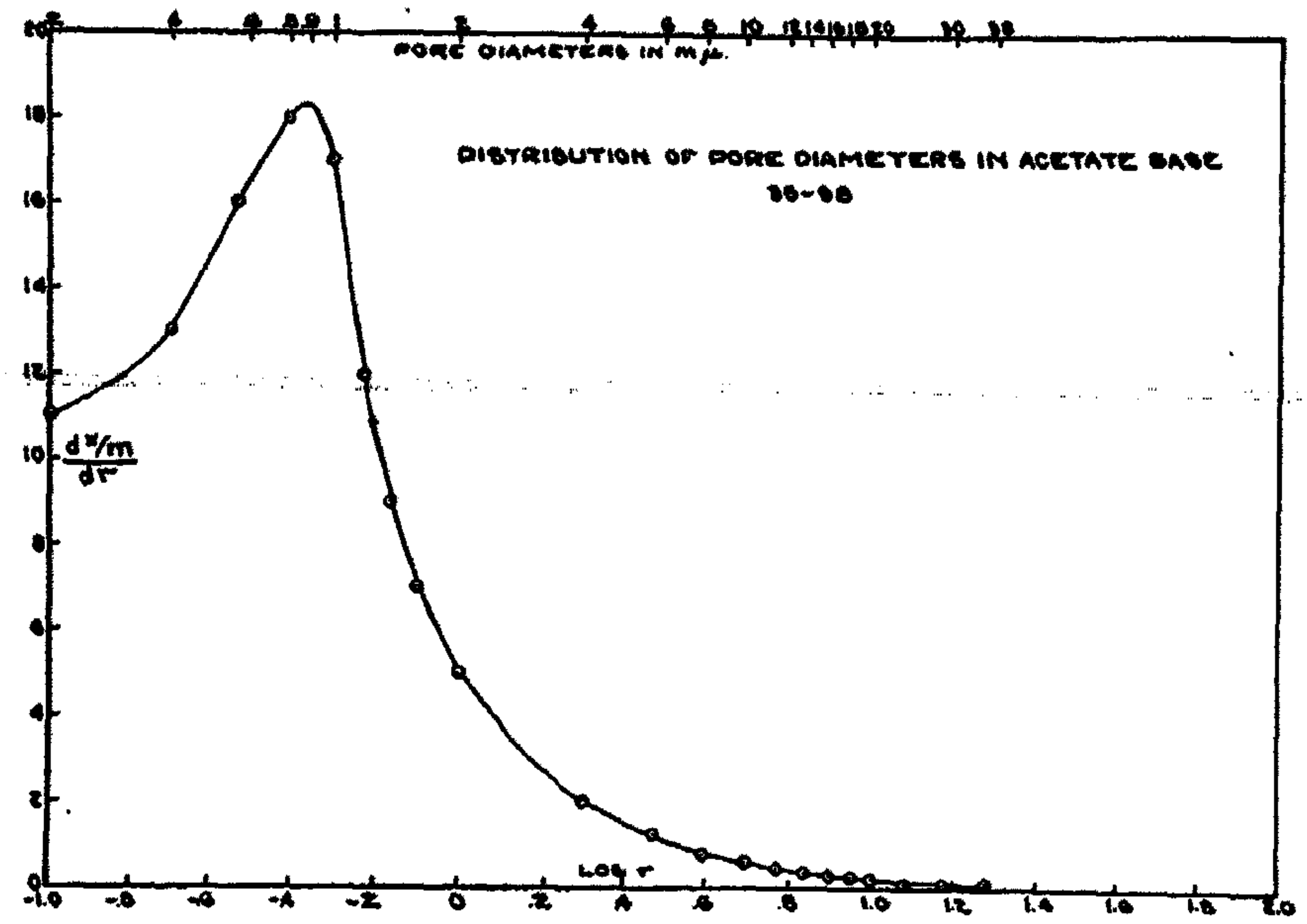

FIG. 14

Summary

The rates of adsorption of the normal saturated alcohols up to n-octyl by cellulose and a series of primary and secondary cellulose acetates were determined at the saturation pressures at 30°C. The rates of adsorption and desorption of methyl, ethyl, n-propyl and n-butyl alcohols by a certain cellulose acetate sheet were determined at 30°C. as well as a complete isotherm of the adsorption of ethyl alcohol by the same material at 30°C.

Alcohol adsorption by primary acetates increases with increasing acetyl content and n-propyl and n-butyl alcohols give maxima at 32% acetyl.

Secondary acetates show greater adsorbing power than primary acetates. In general, higher alcohols are found to be adsorbed and desorbed more slowly than the lower alcohols. Also, higher alcohols are adsorbed more slowly by cellulose acetate in sheet form than in precipitated form. It is found that the adsorption of different alcohols expressed in moles per gram of cellulose material decreases rapidly with increasing number of carbon atoms and becomes approximately constant at n-butyl.

References

[1] S. E. Sheppard and P. T. Newsome: J. Phys. Chem., **33**, 1817 (1929).
[2] K. Werner and H. Engelmann: Z. angew. Chem., **42**, 438 (1929).
[3] S. E. Sheppard and P. T. Newsome: loc. cit.
[4] S. E. Sheppard and P. T. Newsome: loc. cit.
[5] H. Pringsheim, W. Kusenack and K. Weinreb: Cellulosechemie, **9**, 48 (1928).
[6] N. K. Adam: Proc. Roy. Soc., **101A**, 452-72 (1922).
[7] A. J. Stamm: J. Phys. Chem., **33**, 398 (1929).
[8] J. Dewar: Chem. News, **94**, 173, 185 (1906); **97**, 4, 16 (1908).
[9] G. C. Schmidt and B. Hinteler: Z. physik. Chem., **91**, 103 (1916).
[10] J. N. Pearce and H. F. Johnstone: J. Phys. Chem., **34**, 1260 (1930).
[11] A. S. Coolidge: J. Am. Chem. Soc., **48**, 1795 (1926).

Rochester, N. Y.,
May 14, 1932.

THE STRUCTURE OF GELATIN SOLS AND GELS
Part IV. Fluidity and Hydrolysis*

BY S. E. SHEPPARD AND R. C. HOUCK

In a previous paper[1] there was presented an extended study of the effect of temperature change on the fluidity of gelatin sols. Using a de-ashed gelatin, fluidity-time curves at different pH values were obtained at 40°C., 50°C., 60°C., 70°C., and 85°C. Initially the curves sufficiently approached straight lines for their slopes to be taken as measures of the rate of change of fluidity. The slope, $\Delta\phi/\Delta t$, plotted as function of pH, gave at each temperature a curve showing a flat minimum. These curves sufficiently resembled the logarithmic form of the catalytic catenary[2] of Hudson to allow the conclusion that ϕ_k, the fluidity change constant, was proportional to log K, where K was the actual velocity constant of hydrolysis.[3] On the other hand, if ϕ_k is considered as proportional to the actual velocity constant of hydrolysis, then it is found that the comparison of the family of log $\phi_k \sim$ pH curves with Northrop's log K $\sim$ pH curves is somewhat closer. Fig. 1 shows the actual curves. Plotting the data in this manner indicates more clearly that the slopes of the straight line on the acid side and on the alkaline side of the flat portion of the log $\phi_k \sim$ pH curve are practically the same for all the temperatures employed. Further, it appears to be probably the better method of plotting since by considering ϕ_k the velocity constant, the usual methods employed in chemical kinetics for studying a reaction can be employed.

Further evidence, pointing to hydrolysis of gelatin molecules as the main cause of the decrease in viscosity with time, has been found by calculating the heat of hydrolysis from the ϕ_k values at constant pH and at different temperatures.

The heat of hydrolysis is calculated by application of the van't Hoff expression dealing with the relation of the velocity constant and temperature. This expression is as follows:

$$\frac{d \log k}{dT} = \frac{Q}{RT^2}$$

in which k = velocity constant
T = absolute temperature
Q = heat of reaction
R = gas constant expressed in calories

A study of this relation indicates that a linear relation should exist between the logarithm of the velocity constant and the reciprocal of the absolute temperature.

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*Communication No. 493 from the Kodak Research Laboratories.

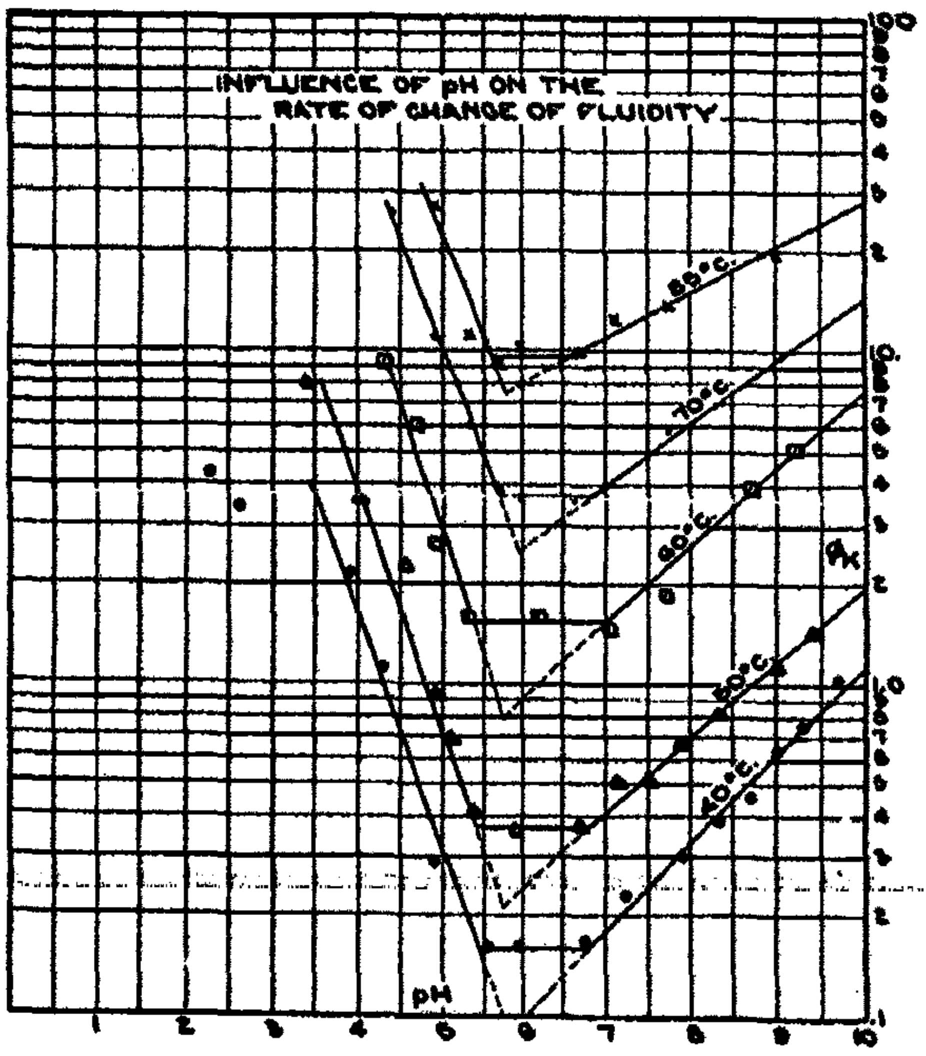

Fig. 1

Accordingly, log ϕ_k values at the same pH, but different temperatures, were plotted against the reciprocals of the absolute temperatures. The results obtained are shown by Figs. 2 to 3. With pH's up to 5.4, fairly good straight lines were obtained, provided the results at 85°C. were excluded. The ϕ_k values at this high temperature appear to be too low, possibly due to a change in the reaction products. A very satisfactory straight line was obtained over the pH range 5.6 – 6.8, in which the velocity constant is practically independent of pH at all temperatures studied. At pH 8.0 and above, straight lines were not obtained, indicating that probably there are other disturbing factors in this region as well as hydrolysis.

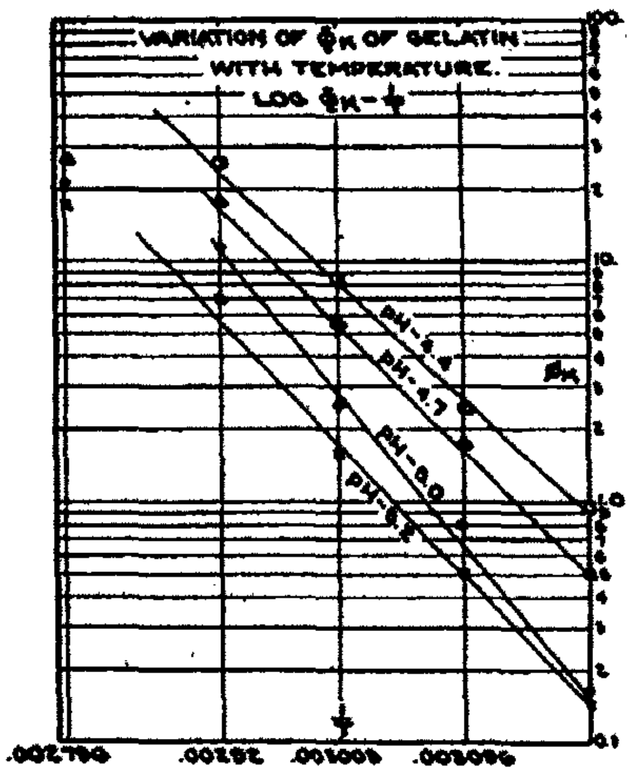

Fig. 2

Inspection of the van't Hoff equation, particularly in the integrated form:

$$\log_{10} \frac{K_2}{K_1} = \frac{Q}{2.303\ R} \cdot \frac{T_2 - T_1}{T_2T_1}$$

shows that the heat of the reaction is obtained by multiplying the slope of the log $\phi_k \sim 1/T$ curve by 2.303 R, where R is the gas constant expressed in calories and is equal to 1.98. This was done for those cases where the log $\phi \sim 1/T$ graph was a straight line. The results obtained are shown by Table I.

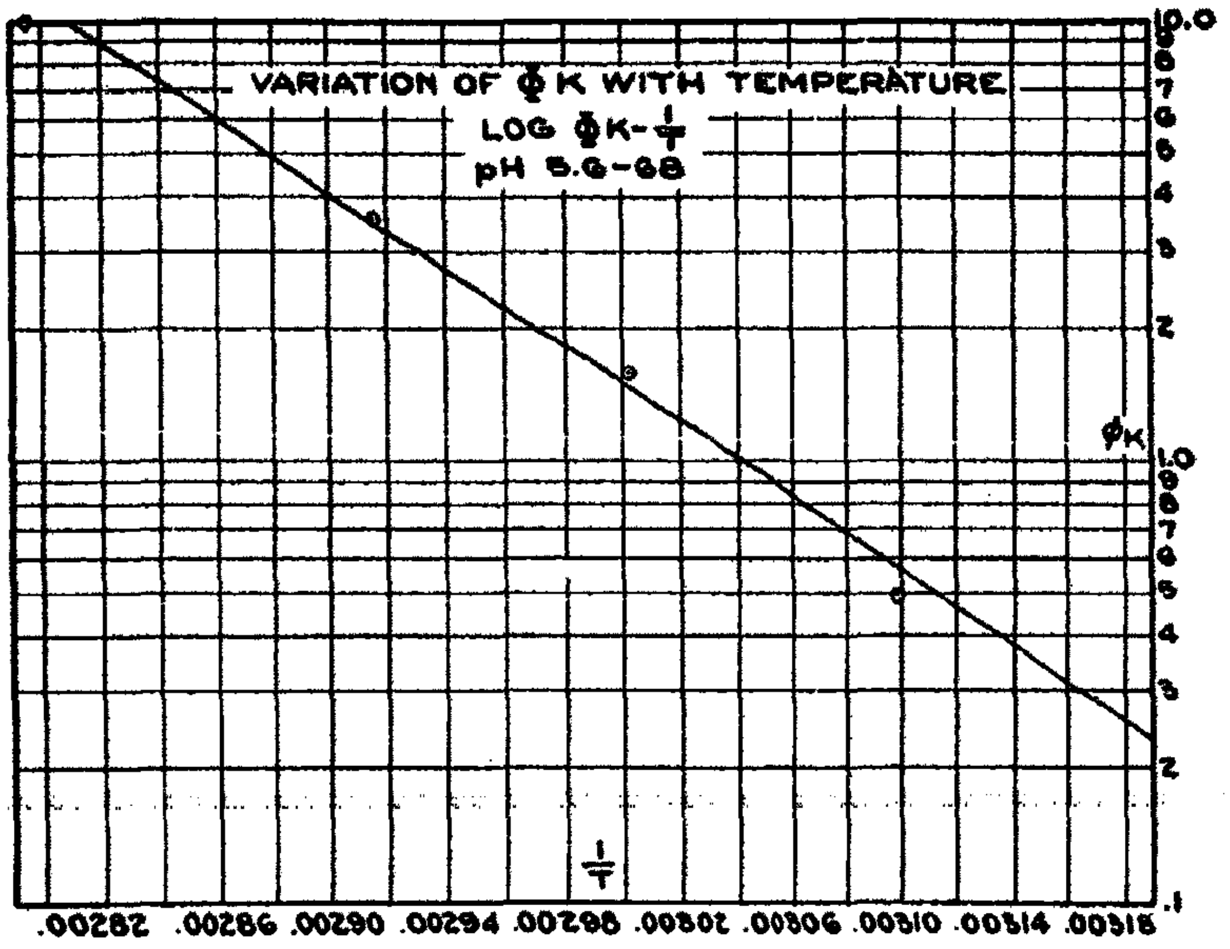
VARIATION OF ΦK WITH TEMPERATURE
LOG ΦK – 1/T
pH 5.6–6.8
ΦK
1/T
10.0
9
8
7
6
5
4
3
2
1.0
9
8
7
6
5
4
3
2
.1
.00282
.00286
.00290
.00294
.00298
.00302
.00306
.00310
.00314
.00318

Fig. 3

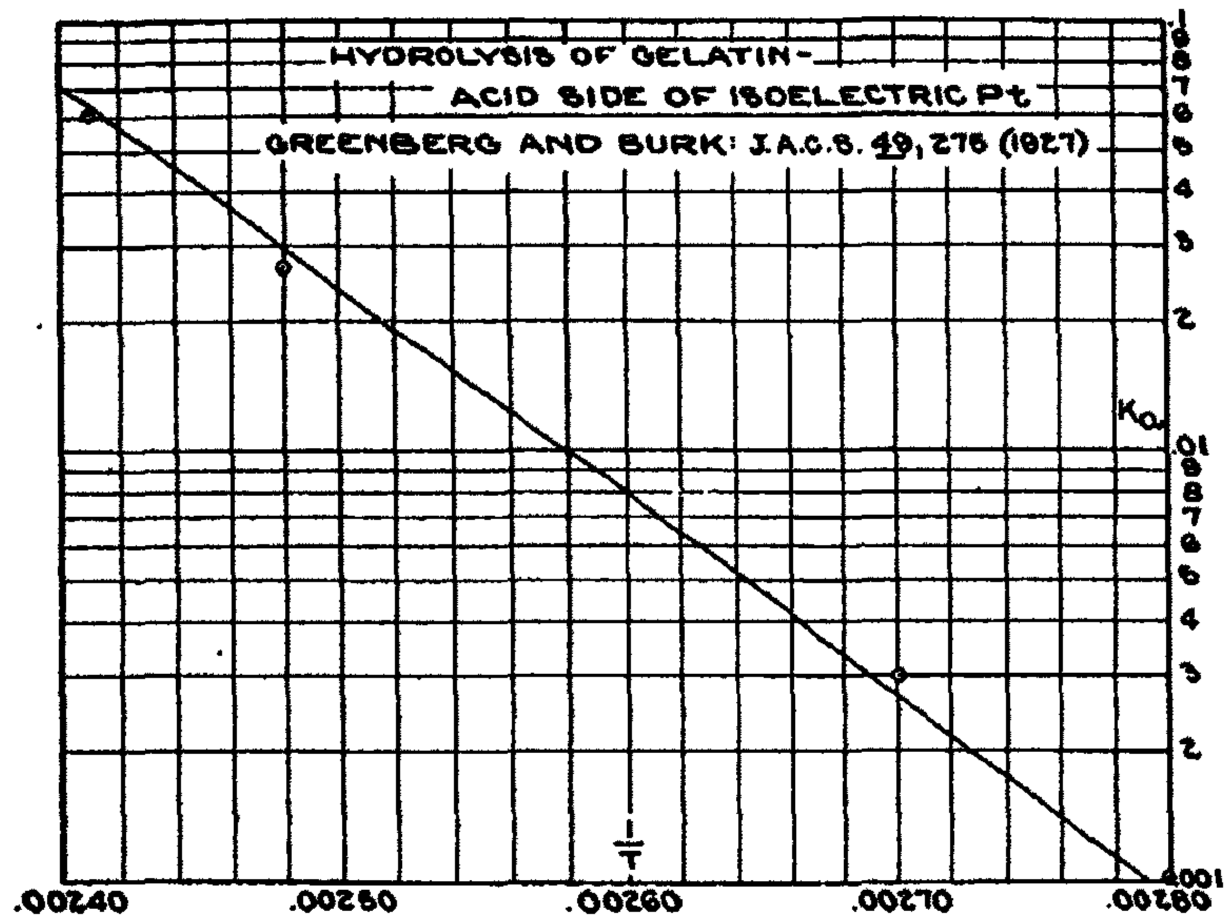
HYDROLYSIS OF GELATIN–
ACID SIDE OF ISOELECTRIC Pt.
GREENBERG AND BURK: J.A.C.S. 49, 276 (1927)
Ka
1/T
.1
9
8
7
6
5
4
3
2
.01
9
8
7
6
5
4
3
2
.001
.00240
.00250
.00260
.00270
.00280

Fig. 4

TABLE I

Heats of Hydrolysis of Gelatin No. 36

pH	Slope	Heat of Hydrolysis of Gelatin (calories)
4.4	5258	24,000
4.7	5522	25,200
5.2	5825	26,540
5.6 – 6.8	4735	19,920
		(Mean 23,915 cal.)

These values appear to be significant when comparison is made with the value for the heat of hydrolysis of gelatin calculated from velocity constants determined chemically. Greenberg and Burk[4] determined the velocity of hydrolysis of gelatin at high temperatures by autoclaving and measuring the amino-acid content by the Van Slyke method. They calculated a constant K_a, involving the activity coefficient. By plotting log K_a against $1/T$, a fair straight line is obtained, as shown by Fig. 4. The authors preferred to plot log K_a against T. Calculation of the heat of hydrolysis in the usual manner from the slope of the log $K_a \sim 1/T$ curve gives a value of 21,480 calories.

A comparison of this value of 21,480 calories with the values obtained from fluidity changes and shown in Table I indicate them to be of the same order of magnitude. It is believed that this agreement is further proof that the fluidity changes are mainly due to hydrolysis of molecules.

The hydrolysis in this case may be most simply represented as a splitting of peptide linkages.

$$-\mathrm{NH{\cdot}CO}- + \mathrm{H_2O} = \begin{matrix}-\mathrm{NH_2}\\ -\mathrm{COOH}\end{matrix}$$

It is known that this reaction does not proceed to complete hydrolysis (with formation of free amino-acids) save in very strongly acid solutions at temperatures of the order of 100°C. In strongly alkaline solution the hydrolysis is accompanied by racemization.[5] It may be considered probable, therefore, that above a certain temperature the end product of the reaction is different—and hence the final fluidity value. Since the initial slope $\Delta\phi/\Delta t$ depends both on the final state of the system, as well as on the reaction velocity, this may explain the discrepancy for the 85°C. value.

The high viscosity of gelatin sols—as of other solutions of "high molecular" bodies—has been frequently attributed to solvation, whereby it is assumed that the molecules or micelles are surrounded by a solvate sheath of solvent molecules of which the inner layers are held with stronger, the outer with weaker forces.[6] These solvate molecules would be under considerable compression, so that if the fluidity change on heating gelatin sols consisted in increase of free water molecules, or breakdown of solvate sheaths, one would expect a definite increase in specific volume. We have studied, therefore, the dilatometry of gelatin sols at the same time as the viscosimetry. The method employed was somewhat similar to that used by The Svedberg[7] and by Neville

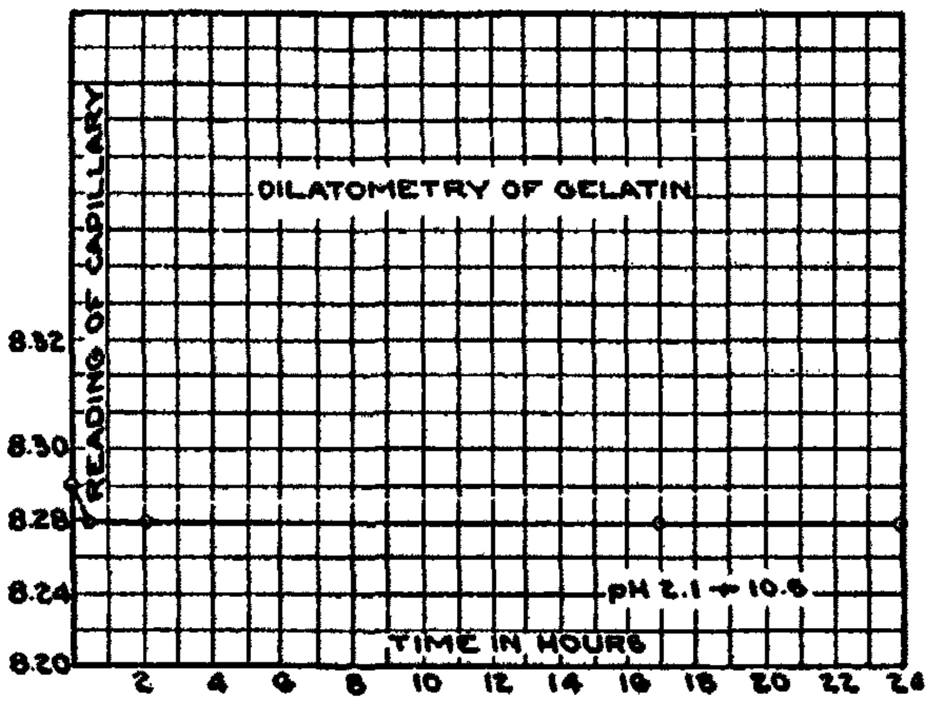

FIG. 5

and Jones.[8] A gelatin sol was prepared at the desired pH, and placed in the bulb of the dilatometer. The capillary was sealed on, and after evacuation the remainder of the bulb and capillary were filled. This method was adopted to avoid any uncertainty as to possible leaks around a ground-glass joint or stopcock. Volume changes were followed with a cathetometer.

The results at 50°C. for solutions between pH 2.1 and pH 10.5 are shown in Fig. 5. Over this range there is no change in volume during a period of 24 hours, while the fluidity has increased very considerably. After this time there usually followed a slight decrease (contraction). On the other hand, a sol of pH 12.0 showed a very noticeable increase in volume (Fig. 6). The fact that more far reaching changes occur in strongly alkaline solutions has already been noted. But the constancy of volume over the pH range 2 – 10, when the fluidity is steadily increasing, appears to exclude the explanation of the viscosity of protein sols in terms of solvate sheaths. Together with the shape of the pH ~ velocity curves, the temperature coefficient, and the calculated heat

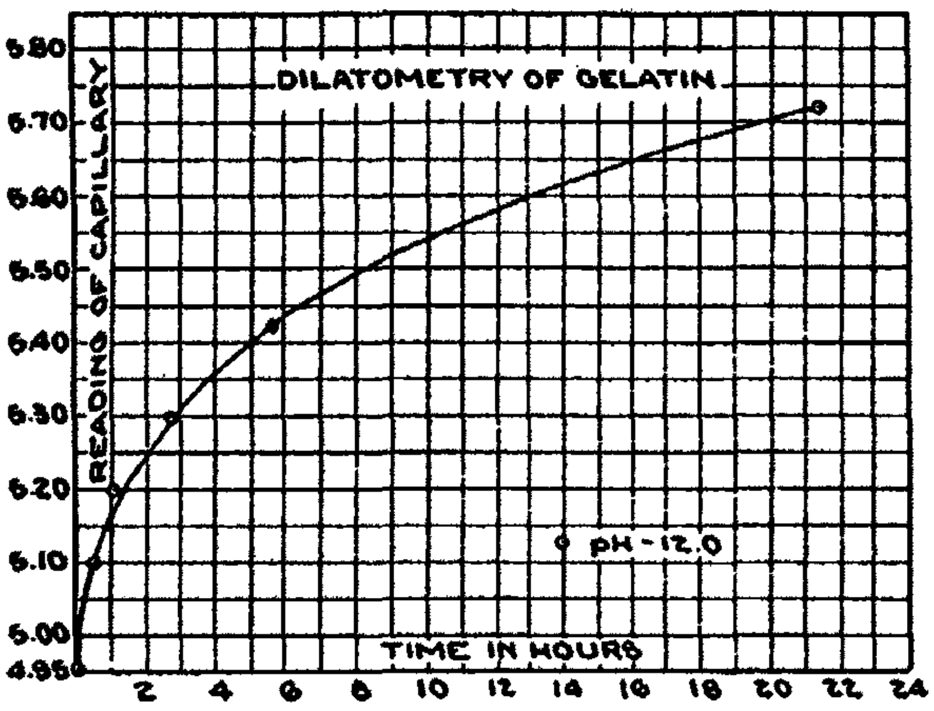

FIG. 6

of reaction, this points to the conclusion that the viscosity is due to the presence of large molecules (macromolecules in Staudinger's sense) and decreases with hydrolytic fission of these macromolecules. If there is any true solvation of these molecules, it must consist in a monomolecular layer of oriented water dipoles, the amount of which is not substantially altered by transection of the macromolecules. As pointed out in the second paper of this series, these appear to be relatively elongated, thin structures, in accordance with (a) spreading experiments giving a thickness of 7 Å.U., and (b) anisotropy of stretched and dried gelatin gels.

Summary

1. Log $\phi_k \sim 1/T$ curves were plotted for gelatin and fair straight line fits obtained. From the slopes of these lines heats of hydrolysis were calculated which varied from 19,900 to 26,500 calories, depending on the pH.

2. The heat of hydrolysis of gelatin obtained by calculation using the data of Greenberg and Burk was found to be 21,480 calories.

3. The general agreement, at least so far as order of magnitude is concerned, of our values with that of Greenberg and Burk, is considered further evidence that the fluidity changes are mainly due to hydrolysis of large molecules, rather than to disgregation of micelles.

4. Dilatometric experiments, establishing constancy of specific volume during hydrolysis and fluidity increase, show that the high viscosity of gelatin sols is not due to solvation.

References

[1] S. E. Sheppard and R. C. Houck: "The Structure of Gelatin Sols and Gels. Part I. The Viscosity of Gelatin Solutions," J. Phys. Chem., 34, 273 (1930).

[2] C. S. Hudson: J. Am. Chem. Soc., 29, 1571 (1907).

[3] J. H. Northrop: J. Gen. Physiol., 3, 715 (1921).

[4] D. M. Greenberg and N. F. Burk: J. Am. Chem. Soc., 49, 275 (1927).

[5] H. Dakin: J. Biol. Chem., 13, 357 (1912-13).

[6] H. Fikentscher and H. Mark: Kolloid-Z., 49, 135 (1929); S. E. Sheppard: J. Rheology, 1, 471 (1930).

[7] The Svedberg: J. Am. Chem. Soc., 46, 2673 (1924).

[8] H. A. Neville and H. C. Jones: Colloid Symposium Monograph, 6, 309 (1928).

Rochester, N.Y.,
May 14, 1932.

THE DECOMPOSITION OF ETHYL BROMIDE, ALKYL HALIDES, AND ACETAL IN THE GAS PHASE AT 300°-400°*

BY EDWARD T. LESSIG[1]

The object of this investigation was to find new unimolecular reactions with which to test theories of kinetics. To be of value in the study of kinetics, a reaction should proceed according to a simple stoichiometrical equation and it must be uninfluenced by the walls of the containing vessel. Of the thirteen compounds investigated here, the thermal decomposition of ethyl bromide into ethylene and hydrobromic acid is particularly significant; but the decomposition of propyl bromide, acetal and isobutyl chlorocarbonate are also interesting. Some of the other decompositions are worthless in the study of kinetics but they are described briefly as empirical facts. The data are to be regarded only as semi-quantitative, and suggestive of further investigations in kinetics.

Apparatus and Procedure

The decomposition of the organic vapors was followed by pressure measurements, using the all-glass apparatus and diaphragm[2] developed in this laboratory. The reaction chamber, made from a 250 cc flask of pyrex or quartz, and the thermostat are shown in Fig. 1. It was deemed essential in this work to keep every part of the reaction chamber up to the full temperature of the thermostat. In this way there was no opportunity for the vapor to condense in a tube leading to a manometer at room temperature. The pressure in the reaction chamber was balanced through a sensitive glass diaphragm against a measured air pressure. The point of balance was determined by electrical contact through platinum wires one of which was attached to the diaphragm. When quartz reaction chambers were used the technique was similar except that the platinum wires, used for the contacts, were anchored mechanically by melting into small capillaries of quartz which were then sealed into the diaphragm and into the chamber. It was necessary also, to hold the side wire tight with a spring. Otherwise the difference in thermal expansion caused the wire to sag away from the contact at the higher temperatures. Sparking with an induction coil usually served to rejuvenate the contacts when they became fouled. A loose packing of glass wool kept the wires separate and prevented circulation of cold air down to the diaphragm.

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*Contribution from the Laboratory of Physical Chemistry of the University of Wisconsin.

[1] This communication is based on a thesis submitted for the Ph.D. degree at the University of Wisconsin in 1929. The investigation was carried out under the direction of Farrington Daniels.

[2] Daniels: J. Am. Chem. Soc., 50, 1115 (1928).

The thermostat consisted of a rectangular iron box 30 × 20 × 20 cms filled with molten lead and well insulated with transite and 12 cms of loose asbestos. Heating units of nichrome wire on transite board were placed around the box. The lead was stirred with an iron stirrer driven by a motor. The temperature was determined with a Leeds and Northrup platinum resistance thermometer and precision bridge. The heating units in two separate circuits were controlled by hand. When the line voltage varied as indicated by a meter in the circuit, the necessary compensation was made by adjusting a reactance coil in series with the heating units. In this way it was possible to keep the temperature constant within 0.2°.

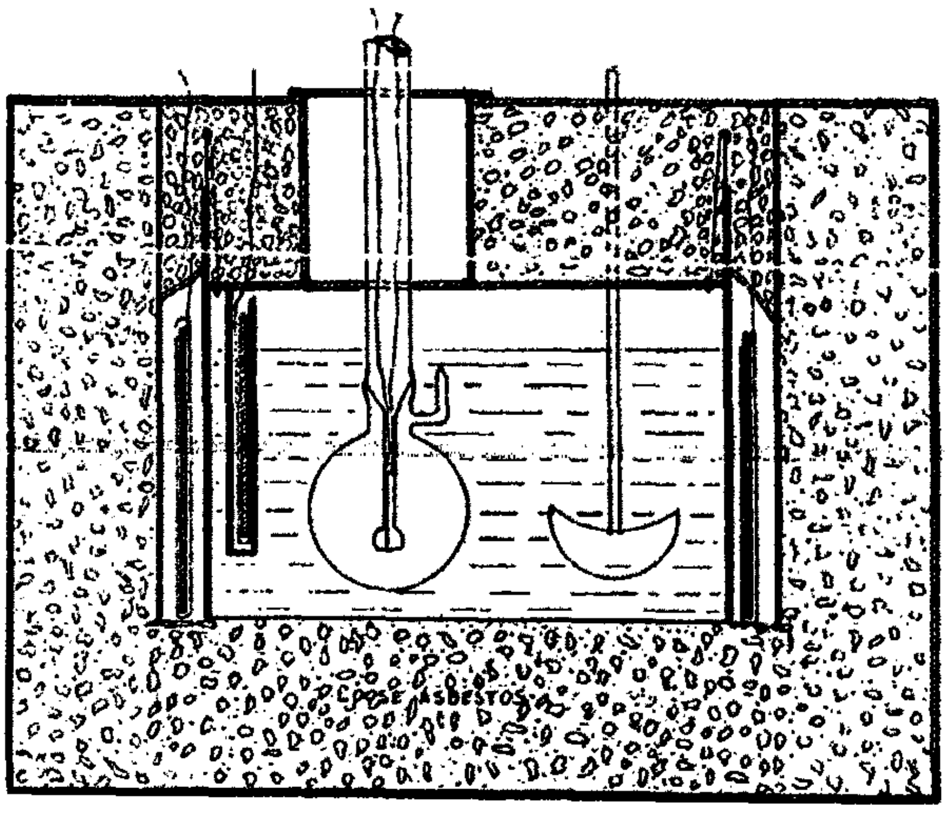

Fig. 1
Reaction vessel and thermostat

If the decomposition products (ethylene in the case of ethyl bromide) remained long in the reaction chamber a film of carbon was deposited on the walls. Such a film, if allowed to remain, gave erratic results in any subsequent experiments. Accordingly the chamber was cleaned each time with chromic acid, rinsed and dried; and then filled with oxygen and heated to redness.

In carrying out an experiment the zero point is first determined with the flask fully immersed in the thermostat and the side arm of the reaction chamber extending out to the air. The flask is then raised slightly and the side arm is drawn down to a capillary. A small glass bulb about 1 cm in diameter is made with a capillary tip. The bulb is filled with the liquid to be used, and sealed off while the liquid is boiling under reduced pressure. In this way air is excluded. After making a file scratch, the capillary is inserted through a stout rubber tube into the capillary of the side arm. The connections with the rubber tube are made still tighter with deKhotinsky cement. The whole flask is then evacuated with an oil pump through a tube fused onto the side arm. When all the air has been removed the line to the pump is fused off, the bulb is moved sideways so as to break the capillary and the liquid vaporizes to fill the reaction chamber. Since the capillary of the bulb extends well beyond the connection, the vapor does not come in contact with any rubber. No stopcocks are used.

The side arm of the flask is then sealed off and the flask is immediately lowered into the thermostat bath as shown in Fig. 1. Pressure readings are taken at frequent intervals by observing the outside pressure which is just necessary to permit contact of the platinum points. Typical pressure-time curves are given later.

The pressure-time data are used in different ways to calculate the specific reaction rates and to test for unimolecularity. When the pressure does not change any more the decomposition is assumed to be complete, and the difference between this final pressure P_f and the pressure at any time P_t, in the simplest cases, is a measure of the amount of undecomposed material. The initial pressure P_i may be obtained by extrapolating the curve to zero time. The accuracy of this extrapolation varies with the steepness of the slope. If one molecule decomposes into two the final pressure should be twice the initial pressure except for a recombination of the products. If three molecules are produced on decomposition, the final pressure should be three times the initial. If the reverse reaction is appreciable, however, an equilibrium will ensue and the final pressure will be less than the expected pressure. The simplest way of testing for unimolecularity is to determine the period of half and three-quarter life. If the reaction is of the first order and the reverse reaction is negligible the time taken for the value of $P_f - P_t/P_f - P_i$ to become 3/4 will be twice as great as the time for it to become 1/2. The value of the specific reaction rate k is $0.639/t_{1/2}$ where $t_{1/2}$ is the period of half life.

When the data justify it, they are treated more completely by plotting log $(P_f - P_t)$ against the time t. The straightness of the line indicates the extent to which the reaction follows the first order equation and the slope of the line multiplied by 2.303 gives the value of the specific reaction rate, k.

These methods do not allow for the reverse reaction and can not be considered exact unless the final pressure is exactly twice (or three times etc.) as great as the initial pressure. A more accurate method was used in some of the experiments on ethyl bromide where the reverse reaction is bimolecular. Representing the initial concentration of ethyl bromide by a, the amount decomposed by x, and the equilibrium constant K by the ratio k/k′ where k is the velocity constant of the dissociation reaction and k′ is the velocity of the recombination reaction,

$$dx/dt = k(a-x) - k'x^2 = k\,[(a-x) - (x/K^2)]. \qquad (1)$$

The integrated form was used as follows,

$$k = \frac{1}{t}\,\frac{2.303}{\sqrt{4a/K+1}}\log\frac{(+2x/K+1+\sqrt{4a/K+1})\,(-1+\sqrt{4a/K+1})}{(-2x/K-1+\sqrt{4a/K+1})\,(+1+\sqrt{4a/K+1})} \qquad (2)$$

Ethyl Bromide

The first 22 experiments were carried out with an impure preparation, synthesized in a student laboratory. In general there was an inflection in the early part of the pressure curve indicating some complication. Experiments with air alone under similar conditions showed that equilibrium was reached within five minutes. The large inflections noted can not be attributed to thermal lag alone.

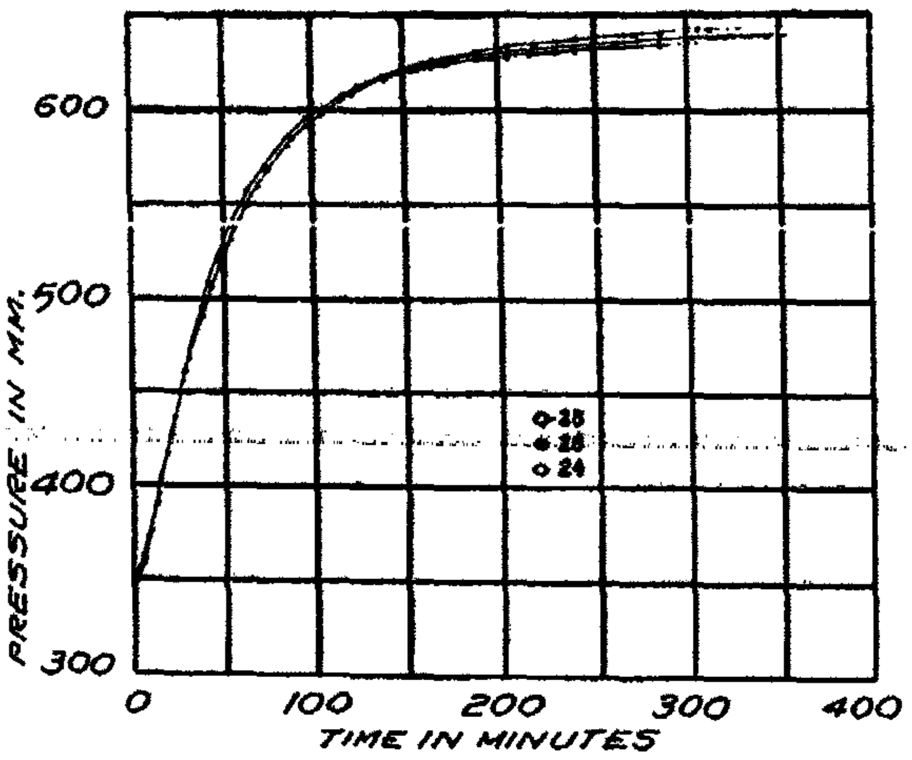

FIG. 2
Dissociation of Ethyl Bromide

Experiments 23-32 were made with preparation B, a high grade product from the Eastman Kodak Company which was further distilled several times. Fig. 2 is typical of this group. Three check experiments, at nearly the same initial pressures, are seen to agree closely.

In the last and most significant experiments, 33-48, preparation C was used. This was very pure material prepared in the laboratory of Professor Timmermans at Brussels under the auspices of the International Union of Pure and Applied Chemistry and distributed through the U. S. Bureau of Standards.[1] Figs. 3 and 4 give some of these results in detail. It will be noted that the inflections have nearly disappeared in these cases.

The final pressure was always a little less than twice the initial pressure. The reaction follows the equation

$$C_2H_5Br = C_2H_4 + HBr$$

but the reverse reaction becomes appreciable particularly at the end of the experiment. In some cases the products of the reaction remaining at the end of an experiment were analyzed, chemically. The flask was cooled and the

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[1] Several liquids are now available in small quantities. They are guaranteed to have the constants described by Timmermans and Martin in J. Chim. phys., 23, 733 (1926) and later communications. Investigators greatly appreciate this convenient means for getting samples of pure organic liquids.

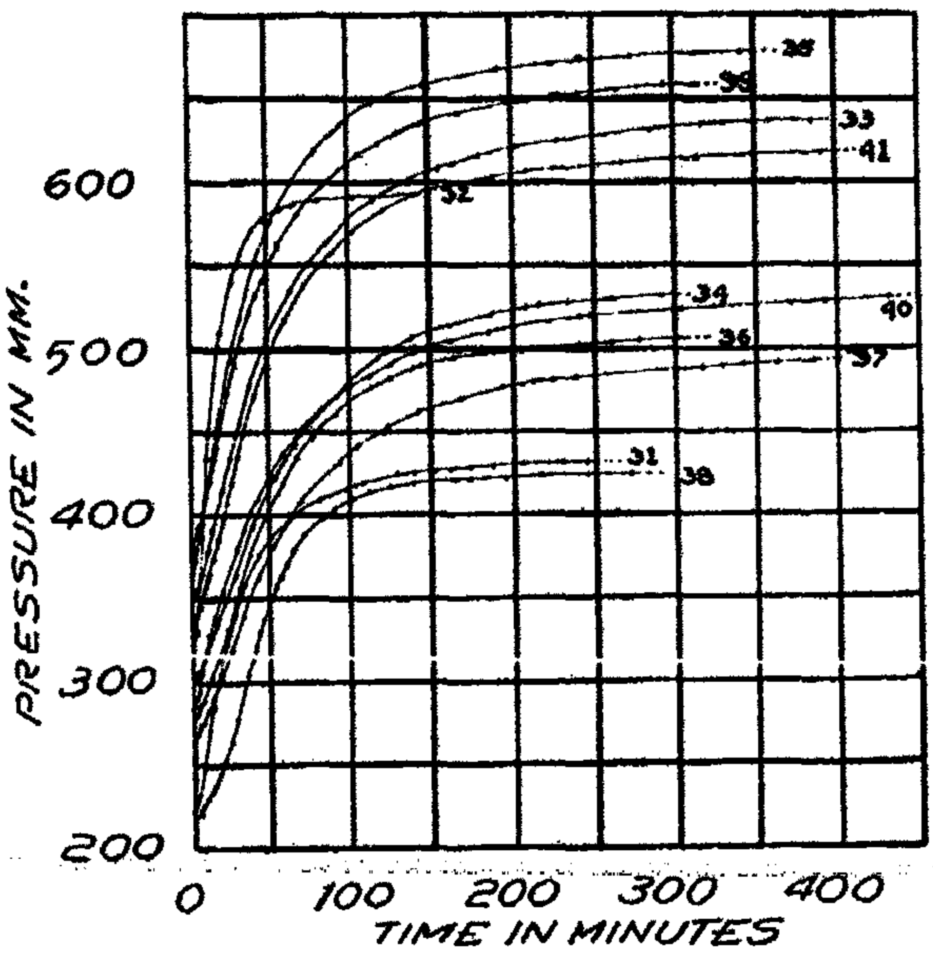

FIG. 3
Dissociation of Ethyl Bromide

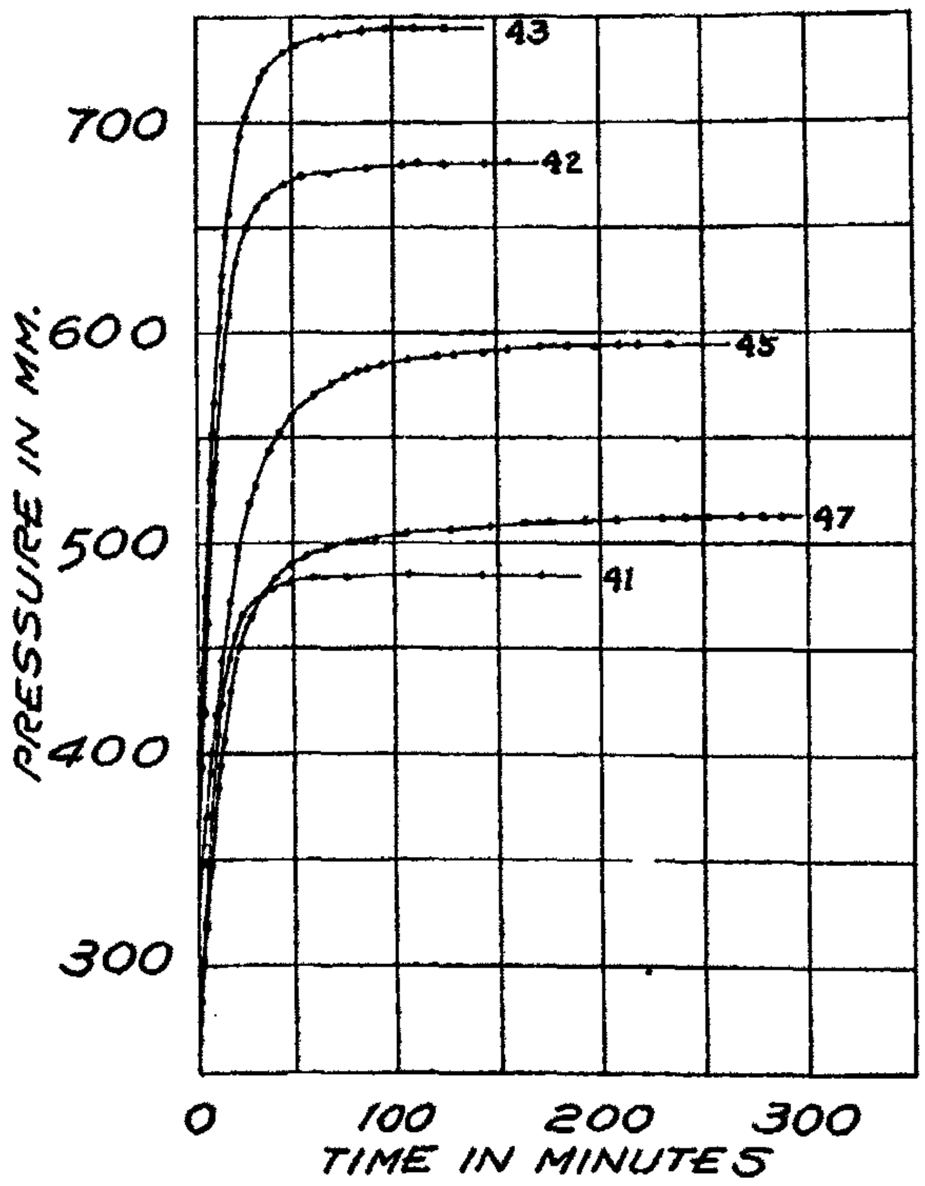

FIG. 4
Dissociation of Ethyl Bromide

tip broken off under air-free water. No free bromine was found in the solution as tested with starch-iodide solution. The reaction flask was never colored red, even when withdrawn quickly from the thermostat and it may be concluded that bromine is not formed under the conditions of these experiments. Even if hydrobromic acid did dissociate in the thermostat into bromine and hydrogen the pressure measurements would not be affected because such a dissociation involves no volume change.

The gas remaining after the absorption of hydrobromic acid in the water was found to be ethylene. It was completely absorbed in bromine water, a fact which indicated that it was composed of unsaturated hydrocarbons and that neither hydrogen nor saturated hydrocarbons were present. After explosion with oxygen the shrinkage due to water formation was 10.0 cc and the shrinkage due to absorption of the remaining carbon dioxide in sodium hydroxide solution was practically the same—9.8 cc. After removal of the hydrobromic acid in water, then, the gas must have contained twice as many hydrogen atoms as carbon atoms. Furthermore, a small amount of liquid ethyl bromide was sealed off in a small bulb in the absence of air and weighed. The bulb was broken in an evacuated flask of known volume and the observed pressure agreed with the pressure calculated from the simple gas laws, both before and after decomposition.

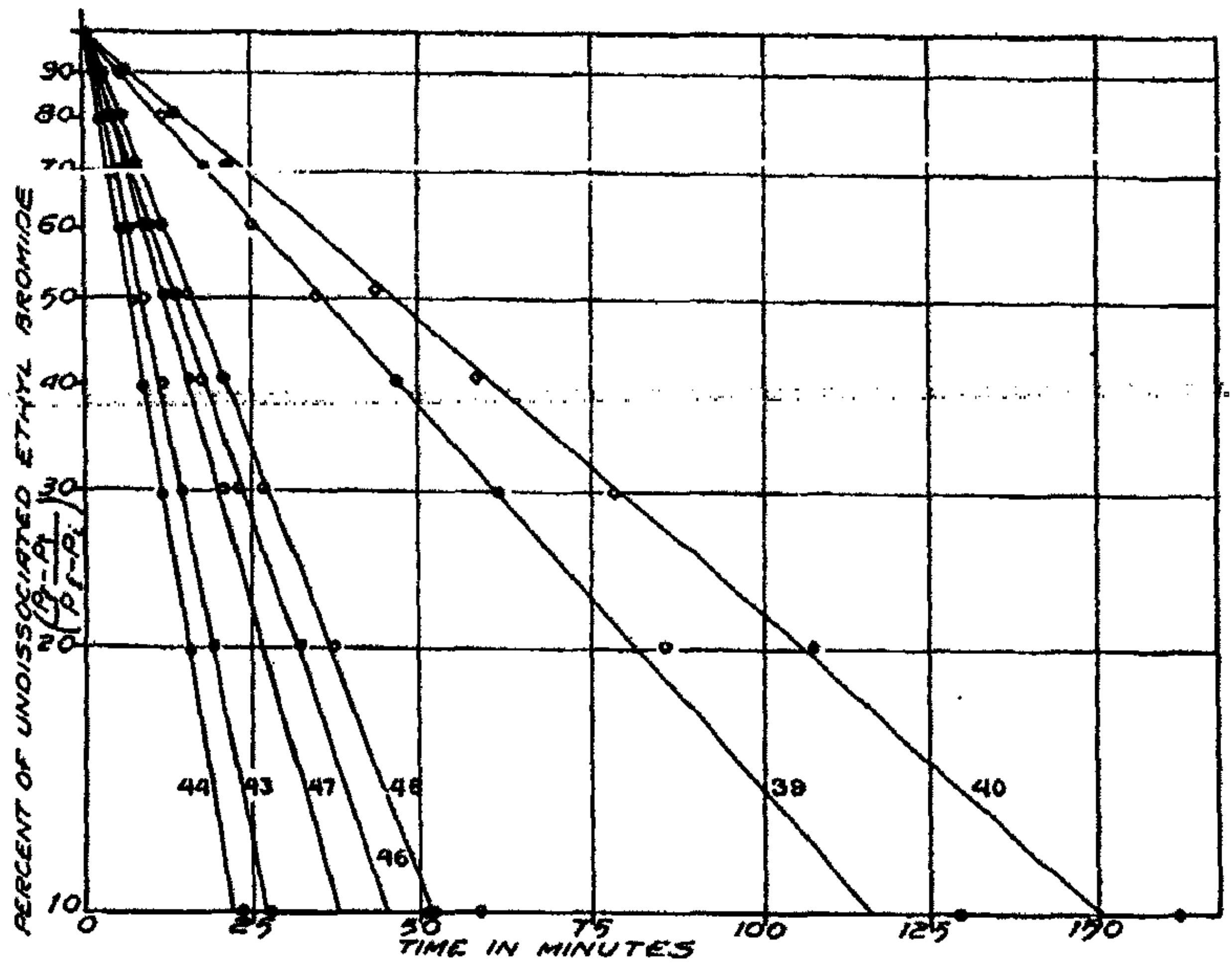

FIG. 5
Dissociation of Ethyl Bromide

The fact that this dissociation is essentially first order is shown by the straight lines of Fig. 5 in which log $(P_f - P_t)/(P_f - P_i)$ is plotted against time for a few typical experiments. In plotting these graphs the values of $P_f - P_t$

TABLE I

The Dissociation of Ethyl Bromide

Expt. No.	Temp. °C.	Material	Initial Press. mm.	k_1(min^{-1}) Slope	k_2(min^{-1}) Statis.	k_3(min^{-1}) Corr.	k_4(min^{-1}) Elim.
16	356.4	A		−0.031	0.0284	0.038	
17	358.5	A	343	.035	.0329	.043	
22	356.5	(A)	335	.013			
23	358.0	(A)	340	.005			
24	375.0	B	345	.019	.0194		
25	374.5	B	347	.022	.0212		
26	374.5	B	345	.021			
27	373.0	B	463	.027	.0281		
29	373.0	B	508	.029	.0288		
31	387.5	B	215	.034	.0303		
33	372.5	B	350	.017			
34	371.0	C	295	.016		.011	.010
35	369.3	C	277	.022	.0219		
36	369.5	C	277	.019		.011	.011
37	370.0	C	265	.016		.011	.010
38	375.5	C		.029	.0221		
39	375.5	C	358	.019	.0198	.017	.017
40	375.5	C	282	.015		.016	.016
41	401.7	C	263	.098		.072	.072
42	401.7	C	366	.095		.075	.064
43	401.7	C	390	.089		.070	.064
44	401.7	C	647	.107		.065	.064
45	388.0	C	331	.044		.033	.033
46	388.0	C	600	.056		.034	.034
47	388.0	C	281	.066		.040	.038
48	388.0	C	331			.038	.037

No. 22 Material A purified.
No. 23 Material A twice purified.
Nos. 41-48 and No. 31-32 in quartz vessel. All others in pyrex.
No. 17 Excess of glass surface.

were taken from the smooth pressure-time curves at intervals corresponding to 10, 20, 30 etc. per cent decomposition.

The experimental determinations on ethyl bromide are summarized in Table I. The specific reaction rates calculated from the slopes of the logarithmic graphs are given under k_1. The values of the rate-constants as calculated from the same data using a statistical method are given under k_2. The rate constants corrected for the reverse reaction by using equation (2) are given under k_3. In these calculations the equilibrium constant K was estimated from the difference between the final pressure and twice the initial pressure. In the calculation of k_4 the reverse reaction is practically eliminated by measuring the time required for the pressure to increase to 1¼ times its original value. This time is then divided into 0.289 (i.e. 2.303 log 1/¾). It will be noted that whereas k_1 and k_2 increase with pressure, k_3 and k_4 are nearly independent of pressure over the range studied here. k_3 and k_4 are more nearly correct than k_1 and k_2.

Only a few of the data on the impure material are given here. It is sufficient to state that this material decomposed much more rapidly than the pure material; that an induction period was often present at the beginning during which there was little decomposition; and that the constant k appeared to be distinctly larger at high pressures. The logarithmic graphs were less satisfactory than those shown in Fig. 5, and they often intersected the ordinate above 100 per cent. The influence of impurities on the reaction rate is shown by a comparison of experiments 17, 22 and 23—the refractive indices of which were respectively 1.4255, 1.4248 and 1.4240.

It was found that increasing the surface of glass five fold by inserting additional pieces caused no change in the decomposition rate. This fact combined with the large temperature coefficient showed that the decomposition is not a wall reaction. In two other experiments it was found that the addition of an excess of bromine caused a considerable increase in the rate of decomposition.

It will be noted that there is no marked difference in decomposition rate between the experiments in pyrex and those in quartz,—another fact which indicates that the reaction is not a wall-reaction.

When log k_4 is plotted against 1/T the best straight line through the somewhat scattered points leads to a value in the neighborhood of 50,000 calories for the energy of activation of ethyl bromide.

The study of ethyl bromide has been continued in this laboratory, particularly at low pressures, and additional material will be published shortly.

Propyl Bromide

Normal and isopropyl bromide were obtained from Professor Timmermans' laboratory. The results[1] were less satisfactory than those for ethyl bromide. The data on normal-propyl bromide are summarized in Table II.

It is evident from this table that the reaction is first order, but that there is a reverse reaction which prevents the final pressure from becoming twice as great as the initial pressure. The decrease in the constant with a decrease in pressure is striking. This phenomenon may be accepted as a qualitative fact but the quantitative interpretation must await further, more accurate experiments. As in the case of ethyl bromide *part* of this decrease is due to the reverse reaction which has not been allowed for in the calculations of Table II. The experiments with extra glass surface, having a five-fold increase, indicate that the decomposition is not a wall reaction. Two isolated experiments suggest that a trace of propyl alcohol retards the decomposition whereas a

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[1] The physical constants are given in J. Chim. phys., **23**, 733 (1926); **25**, 15 (1928).

Table II

Rate of Dissociation of n-Propyl Bromide

Temp. °C.	Initial Pressure	Final Pressure	Period of—		k	Remarks
			½ life	¾ life		
353.5	274 mm	504 mm	12 min	26 min	0.058 min^{-1}	
	237	451	13	29	.053	
	215	397	11	24	.063	
	168	316	12	27	.058	
	164	—	15	33	.046	
	150	—	17	38	.041	
	127	250	17	41	.041	Glass × 5
	119	222	12	25	.058	Glass × 5
	92	128	17	34	.041	
	54	106	26	52	.027	
364	301	537	8	18	.087	
	250	450	8	17	.087	Saturated with H_2O
	217	396	9	21	.077	
	201	388	14	24	.050	Trace n-C_3H_5OH
	168	319	9	21	.077	Trace Bromine
	165	323	10	20	.069	
	131	243	11	23	.063	
	100	188	12	26	.058	
	95	180	5	11	.14	10 mm. n-C_3H_5OH
	73	136	16	32	.043	
	61	118	15	29	.046	
	14	27	20	40	.035	
374	274	473	6.5		.11	
	168	309	6		.115	
	94	182	7.0		.10	
	77	146	7.0		.10	

larger amount accelerates it. It has been established that oxygen greatly accelerates the rate at which the pressure rises and some of the abnormal results may be explained by the presence of a little air. A small amount of water vapor had practically no influence on the decomposition.

The propyl alcohol itself decomposed slowly in an erratic manner. The addition of methyl propionate and propyl acetate did not cause any large change in the rate of decomposition of propyl bromide.

The data on iso-propyl bromide were still less satisfactory. All the decompositions were first order as shown by the fact that the period of three-quarter life was roughly twice the period of half life. However, six independent determinations at 346.5°C. ranging from 116 to 213 mms initial pressure gave constants which ranged from 0.05 to 0.17. Two determinations at 356.5 gave 0.10 and 0.17.

It has been established[1] before that n-propyl bromide decomposes on heating into propylene and hydrobromic acid. This fact was subjected to further test. No free bromine was obtained in the decomposition. After removal of hydrogen bromide the residual gas was completely absorbed in bromine water. Combustion of the gas indicated the formula C_3H_6.

The situation is further complicated by the conversion of one isomer into the other. Michael and Leupold[2] found that at 262°C. 30.9 per cent of n-propyl bromide is converted into iso-propyl bromide in one hour and starting with pure iso-propyl bromide 1.8 per cent passes into the normal form in one hour.

The iso-bromide decomposes more easily than the normal and the normal may change over in part to the iso form before decomposing.

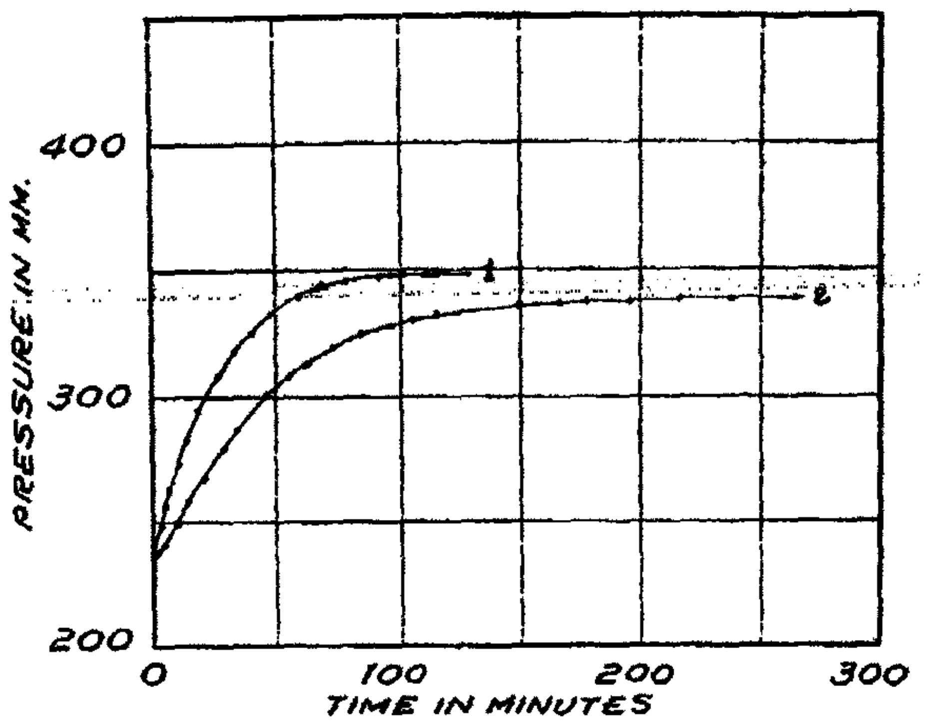

FIG. 6
Decomposition of Ethyl Iodide

Ethyl Iodide

Two isolated determinations were made on ethyl iodide from two different sources as shown in Fig. 6. In the first determination at 355° the initial pressure was 232 and the final pressure 350 mm giving a half life of 18.5 and a three-quarter life of 36 minutes. In the second determination at 345° $P_i = 235$ mm, $P_f = 340$, $t_{1/2} = 35$ mm and $t_{3/4} = 63.5$. The constants k, estimated from $t_{1/2}$, are respectively, 0.020 and 0.037. Although a graph of log $(P_f - P_t)$ gives a very satisfactory straight line when plotted against time the reaction is complicated by the fact that the pressure did not double and by the fact that some free iodine was produced.

Alkyl Chlorides

The alkyl chlorides studied did not give straight lines when log$(P_f - P_t)$ was plotted against time, although in some cases the pressure-time curves appeared to be smooth and normal as in Fig. 7. They are not simple first-order

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[1] Brunel: Ann., **384**, 245 (1911); Nef; **354**, 327 (1907).

[2] Michael and Leupold; Ann., **384**, 245 (1911).

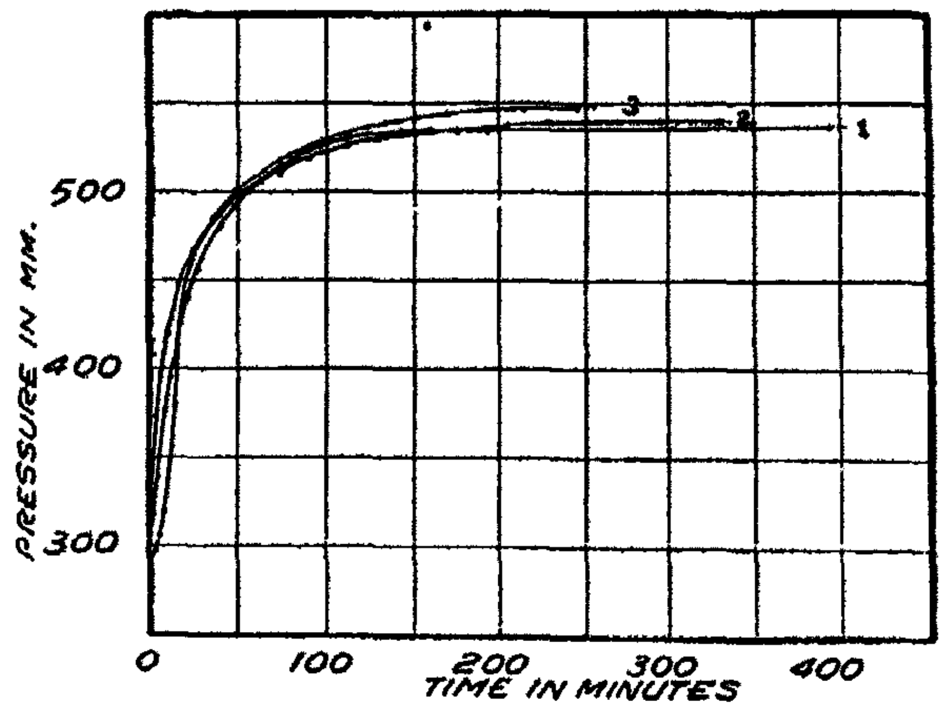

Fig. 7
Decomposition of tertiary Butyl Chloride

reactions. The empirical facts are summarized in Table III. The chloroform curve was very irregular. A yellow crystalline material together with a tar was produced.

TABLE III

Rate of Decomposition of Alkyl Chlorides

Compound	Temp.	P_i	P_f	Approx. ½ life
Ethylene Chloride	360°	355 mm	716 mm	(69) min.
Ethylene Bromide	328	175	355	(10)
Isopropyl Chloride	335	265	532	(85)
Tert-butyl Chloride	280	300	538	(17)
	300	294	542	(10)
	315	289	548	(18)
	350	Too fast to measure		
Ethylene Chlorohydrin	368	158	474	(141)
Chloroform	368	300	420	
	396	210	420	
	400	330	570	

Acetal and Methylal

Three experiments with acetal in pyrex vessels are summarized in Table IV.

TABLE IV

Decomposition of Acetal

Exp.	t°C.	P_i	P_f	$t_{1/2}$	$t_{3/4}$	k
1	370°	173	518	21 min	43 min	0.033 min^{-1}
2	360	227	680	34.5	68	.020
3	350	344	989	58	—	.012

The final pressure is nearly three times the initial pressure, a fact which indicates that the acetal molecule breaks up into three molecules.

The third experiment at the lowest temperature was so slow that complicating reactions resulted, and the logarithmic graph showed a sharp break when half of the material had decomposed.

Methylal decomposed in the gas phase at 410° in a quartz vessel, doubling its pressure in about 50 minutes and then changing slowly without reaching equilibrium even after seven hours. An approximate constant of 0.03 was calculated from the slope of the logarithmic graph for the first half.

Isobutyl Chlorocarbonate

Isobutyl chlorocarbonate was found to decompose in a unimolecular manner at a low temperature. The material was obtained from the Eastman Kodak Co. The final pressure is more than twice the initial pressure and decomposition into three molecules is indicated. Although the $\log(P_f - P_t)$ graphs are quite straight, the reaction appears to be complicated. The data are summarized in Table V.

TABLE V

Decomposition of Isobutyl Chlorocarbonate

	Temp.	P_i	P_f	$t_{1/2}$	$t_{3/4}$	k
1	267°	150 mm	504 mm	160 min	380 min	0.0043 min^{-1}
2	302	500	1107	16	35	0.043

Conclusions

Many organic compounds decompose in the gas phase at easily measurable rates in the temperature range 300-400°C. Some of these are reactions of the first order.

In some cases studied here there is good agreement with the first-order equation, as indicated by the straightness of the line produced when $\log(P_f - P_t)$ is plotted against temperature. The line is often straight even up to 90 per cent completion. It must be emphasized, however, that agreement with the first-order equation does not necessarily permit the calculation of correct unimolecular constants. Reverse reactions and other complicating reactions sometimes act in such a way as to make the resultant of all the reactions appear to be first-order.

It will be noted that among related compounds the complex molecules decompose more rapidly than the simple ones—i.e. they reach a given specific reaction rate (k) at lower temperatures. For example the decomposition rate for propyl bromide at 360° is about the same as that for ethyl bromide at 390°. Ethyl iodide also decomposes at 360° with approximately the same rate as ethyl bromide at 390°. Acetal decomposes at 360° with about the same rate as methylal at 410°. Tertiary butyl chloride and isobutyl chlorocarbonate, with more complicated molecules, have comparable reaction rates at 315° and 300°.

In some cases the specific decomposition rate (k) was found to decrease with pressure but the present data do not permit any theoretical interpretation of this fact. A considerable part of the decrease is due to the fact that two or more reactions are proceeding simultaneously.

Impurities often have a marked specific effect on the decomposition rate.

Caution must be used in the theoretical interpretation of reaction rates even if a smooth first-order equation is indicated.

The author wishes to express his indebtedness to Professor Farrington Daniels; and to the E. I. du Pont de Nemours Co. for a fellowship during a part of this work.

Summary

1. The rate of decomposition in the gas phase of thirteen organic compounds has been measured in the range 300-400°.

2. The decompositions were followed by measuring the pressure increases in all-glass and all-quartz vessels totally immersed in a thermostat.

3. The decomposition of ethyl bromide is an excellent unimolecular reaction.

4. Gaseous n-propyl bromide, iso-propyl bromide, ethyl iodide, acetal, and isobutyl chlorocarbonate appear to follow the first-order equation in their decomposition. Some of these decompositions are undoubtedly unimolecular.

5. The decomposition of gaseous ethylene chloride, ethylene bromide, isopropyl chloride, tert-butyl chloride, ethylene chlorohydrin, and methylal are roughly first-order reactions but they are complicated.

6. The decomposition of gaseous chloroform is seriously complicated.

7. Precautions necessary in the interpretation of data of this type are emphasized.

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THE DEPOSITION OF COPPER IN THE PRESENCE OF GUM ARABIC[1]

ROBERT TAFT AND OREN R. BINGHAM

In a previous paper[2] from this laboratory, an extensive study was made of the deposition of copper in the presence of gelatin. It was shown in this paper that the mass of the cathode deposit increased as the gelatin content of the plating bath became greater; that definite changes occurred in the form of the deposit as the gelatin content increased; and lastly, that gelatin produced a considerable increase in the cathode polarization as the current density was increased.

The experimental results obtained were interpreted to mean that gelatin is adsorbed upon the surfaces of the copper crystals as they are deposited, thus affecting the form of the deposit. Gelatin was chosen for the purposes of the original study, as it was a typical addition agent,[3] the primary purpose of the investigation being to secure evidence for a satisfactory theory of addition agent action.

It is the purpose of this paper to present additional evidence for the theory of addition agent action proposed in our first paper; the evidence being secured by a study of the deposition of copper in the presence of gum arabic.

Our reason for choosing gum arabic was as follows: It has been suggested that an addition agent in order to be effective must itself be charged and migrate toward the cathode.[4] If addition agent action is a question of adsorption only, its effectiveness might be more or less independent of its charge. With this in mind, we sought a material which could be used as an addition agent but which was known to migrate toward the anode. A study of the physico-chemical properties, including the electrical conductance, of gum arabic[5] had been made in this laboratory. The results of this study had convinced us that gum arabic was an organic electrolyte and should properly be considered as a mixture of two salts, calcium arabate and magnesium arabate.[6] If this be true, the large and complex anion, (i.e. the arabate), would upon electrolysis, migrate toward the anode. As it could scarcely be expected that

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[1] Presented at the New Orleans Meeting of the American Chemical Society, March 30, 1932.

[2] Taft and Messmore: J. Phys. Chem., 35, 3585 (1931).

[3] For a definition of addition agent consult Blum and Hogaboom: "Principles of Electroplating and Electroforming," 2nd ed., 102, (1930).

[4] Frolich: Trans. Am. Electrochem. Soc., 46, 67 (1924).

[5] Taft and Malm: J. Phys. Chem., 35, 874 (1931).

[6] In addition to this evidence, Thomas and Murray: J. Phys. Chem., 32, 677 (1928), have shown that gum arabic, freed from metals by electrodialysis, is an acid which is not amphoteric.

a negative ion would be adsorbed by the negatively charged cathode,[1] any adsorption of gum arabic upon copper, if shown, would presumably be that of the undissociated gum arabic.

For this reason, as well as the added reason that no systematic studies of gum arabic as an addition agent for copper plating baths were available in the literature, we decided to carry out an investigation somewhat similar in scope to the study reported for gelatin and copper deposition, replacing the gelatin with gum arabic.

The gum arabic used was purified according to the method described by Taft and Malm.[2] The material used had a moisture content of 10.5% as determined by drying to constant weight at 100°C. Its ash content was 3.1% on a moisture-free basis. The remaining materials, copper sulfate and sulfuric acid, were the c.p. grade of a well-known manufacturer.

The experimental procedure was, in the main, similar to that used by Taft and Messmore.[3] A number of electrolytic cells were connected in series with suitable coulometers, a variable resistance, and a source of direct current. The electrolytic cells consisted of 150 cc. pyrex beakers (containing 100 cc. of electrolyte); a platinum cathode and a copper anode, which had previously been given a heavy plate of copper electrolytically, were used to conduct the current to and from each cell.[4] The electrodes in all cells were cut to the same size and were approximately 2.5 cms. on an edge. Electrolysis in the test cells was carried out at constant temperature, the constancy of temperature being secured by placing the cells in a constant temperature bath whose temperature fluctuations were less than 0.1°C. The coulometer used as reference was a copper coulometer employing as electrolyte, copper sulfate, alcohol, and sulfuric acid in the proportions recommended by Oettel.[5] The coulometers, in duplicate or triplicate, were always run in an ice bath, it having been found[6] that the mass of copper deposited from such a bath gave results more consistent with the standard silver coulometer.

In most of our solutions, pH measurements were made. As has been previously pointed out (Taft and Messmore) these serve chiefly to indicate

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[1] In this connection, however, one should recall that the increased stability of negatively charged colloidal particles, which results in certain cases when electrolytes are added, is explained by the assumption that the negatively charged particle is increasing its negative potential. This increase in potential, it is assumed, results from the adsorption of negative ions by the negatively charged body. (cf. Bancroft: "Applied Colloid Chemistry," 2nd ed., 294 (1926).) If this assumption is correct, by analogy, it would be possible for a negatively charged surface to adsorb the negative gum arabic particles. Evidently in this case it would be the relative "negativeness" which would determine whether adsorption occurred or not.

[2] Loc cit.

[3] Loc. cit.

[4] The electrodes in each cell were equally spaced at approximately 3 1/2 cms. apart. A clearance of 2 cms. was left between the bottom of each electrode and the bottom of the beaker to allow complete settling of the anode mud.

[5] Chem. Ztg., 17, 543 (1893). Matthews and Wark, (J. Phys. Chem., 35, 2345 (1931)) have called attention to the doubtful value of alcohol in the copper coulometer bath. Extensive investigation of the effect of alcohol in such baths, now under way in this laboratory, confirms the work of Matthews and Wark. We have continued to use alcohol, however, as our early trials were made before this information was available.

[6] Taft and Messmore: unpublished data.

an additional characteristic of these baths, and in addition are of some value in interpreting our results, particularly with respect to the formation of copper oxides. The pH values were determined at 26°C by the use of the quinhydrone and saturated calomel electrodes, employing the equation:

$$\mathrm{pH} = \frac{0.7177 - 0.00074 \times t - 0.2458 - \mathrm{Ec}}{0.0001983\ \mathrm{T}}$$

where Ec was the observed potential of the cell, quinhydrone electrode—solution—calomel electrode, *t*, the temperature of determination on the Centigrade Scale, and *T*, the absolute temperature.

Data was obtained upon the mass, form and copper content of cathode deposits over a range of concentrations and temperatures. Analysis for copper of the cathode deposits was made according to the procedure described by Taft and Messmore.

After some preliminary trials, in which the mass of the cathode deposit was found to vary in an apparently erratic fashion with gum content, a series of cells was used at the same gum content, but of varying copper sulfate concentration, the remaining conditions being constant, i.e. 30°C and at a current density of 2 amperes per square decimeter.[1] The results of this run are given in Table I.

Table I

Mass of Cathode Deposits in Presence of Gum Arabic, Gum Content 0.25 gm/100 cc. solution

Concentration of copper sulfate	0.25 M		0.50 M	
	1	2	1	2
Mass of Deposit, grams	0.5197	0.5200	0.5206	0.5205
Excess Weight, grams	0.0117	0.0120	0.0126	0.0125

Concentration of copper sulfate	0.625 M		0.75 M		0.875 M	
	1	2	1	2	1	2
Mass of Deposit, grams	0.5170	0.5178	0.5143	0.5140	0.5115	0.5122
Excess Weight, grams	0.0090	0.0098	0.0063	0.0060	0.0035	0.0042

Concentration of copper sulfate	1.0 M		1.25 M	
	1	2	1	2
Mass of Deposit, grams	0.5090	0.5093	0.5088	0.5087
Excess Weight, grams	0.0010	0.0013	0.0008	0.0007

	Coulometer	
	1	2
Mass of Deposit	0.5078	0.5083

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[1] All current densities stated in this paper are calculated on the basis of one side of the cathode alone. Actually copper is deposited upon both sides, although not as extensively on the rear side as on the front. The current densities actually employed were, therefore, between 2/3 and 1/2 the values given.

The excess weights tabulated above were obtained by subtracting the average mass of the two coulometer deposits from the mass of the cathode deposit. This excess, as will be shown, is due to the inclusion of oxides of copper and of gum arabic or its hydrolysis products. The above results showed that the maximum mass effect was obtained in the cells having a copper sulfate concentration of 0.5 molar. As the effect was small at best, most of our subsequent studies were carried out at this concentration of copper sulfate.

In order to show that the gum arabic does affect the mass of the deposit, however, it was necessary to show the effects of varying the copper sulfate concentration upon the mass of the cathode deposit in the absence of gum arabic. With this object in view, the above run was duplicated with the exception of the addition of gum arabic. The results obtained for this run are shown in Table II.

Table II[1]

Mass of Cathode Deposits in Absence of Gum Arabic

Concentration of copper sulfate	0.25 M		0.50 M	
	1	2	1	2
Mass of Deposit, grams	0.5203	0.5206	0.5205	0.5217
Excess weight, grams	0.0028	0.0031	0.0030	0.0042

Concentration of copper sulfate	0.625 M		0.75 M	
	1	2	1	2
Mass of Deposit, grams	0.5213	0.5214	0.5214	0.5214
Excess weight, grams	0.0038	0.0039	0.0039	0.0039

Concentration of copper sulfate	0.875 M		1.0 M		1.25 M	
Mass of Deposit, grams	0.5208	0.5203	0.5216	0.5213	0.5194	0.5204
Excess weight, grams	0.0033	0.0028	0.0041	0.0038	0.0019	0.0029

	Coulometer	
	1	2
Mass of Deposit	0.5176	0.5174

The average excess weights are in all solutions, save the most concentrated, between three and four milligrams. Variations are undoubtedly due to two factors:

(1) The variation of hydrolysis with concentration, which, in the more dilute solutions, would produce relatively more copper oxide. Upon formation and adsorption such oxide (or hydroxide) would tend to increase the mass of the cathode deposit as already shown by Richards, Collins and Heimrod.[2] It should be noted, however, that while the percentage hydrolysis increases with dilution, the concentration of cupric oxide would be the product of the fractional hydrolysis by the concentration of the salt. Without doubt this product reaches a maximum, not in the most dilute solution, but in some concentration of salt intermediate between the values employed, i.e. between 0.25 M and 1.25 M.

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[1] Temp. 30°C; current density, 2 amperes per square decimeter.

[2] Proc. Am. Acad. Arts Sci., 35, 123 (1899).

(2) To the increased solvent action of the copper sulfate solution, as its concentration increased, upon metallic copper. Such solution takes place presumably (cf. Richards, Collins and Heimrod) according to the equation:[1]

$$(1)\quad Cu^{++} + Cu = 2Cu^{+}$$

The point of immediate concern, however, is the effect of gum arabic upon this excess weight. Comparison of the deposits at a copper sulfate concentration of 0.5 M from Tables I and II, shows that the excess weight is some three to four times as great in the presence of gum arabic as it is in its absence.[2]

The difference between the excess weights in the two sets of experiments (at 0.5 M) cannot immediately be said to be due to inclusion of gum arabic alone. It might be reasoned, and with some justification, that the gum arabic disturbs the ratio Cu^{+++}/Cu in favor of cuprous ion, thus producing more cuprous oxide which presumably could increase the mass of the deposit, as suggested above. Or possibly, the increased cuprous ion concentration would favor the discharge of the cuprous ion, thus producing a greater mass of copper than in the coulometer deposit. We have endeavored to determine in two ways if these factors are the prevailing ones:

(a) To determine the reducing action of the gum arabic used upon copper sulfate;

(b) To analyze the cathode deposits for copper, the results of which are discussed later in this paper.

To determine the visible extent of the reducing properties of gum arabic, 0.5 gm. were treated with Fehling's solution, according to the directions of Quisumbing and Thomas.[3] With our purified material no cuprous oxide was visible upon several trials after long standing, indicating complete absence of reducing action.

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[1] Solution may also take place as a result of the net reaction:

$$Cu + H_2SO_4 + O_2 = CuSO_4 + H_2O$$

(Cf. Mellor: "Treatise on Inorg. Chem.," 3, 87). We have found, as a result of a large number of trials, that deposits from "neutral" (see Table VII) copper sulfate, or from solutions deliberately acidified with sulfuric acid, are always heavier when deposited from an electrolyte which has been deoxygenated by bubbling an inert gas through the solution before electrolysis and protecting such cells from atmospheric oxygen during electrolysis. Comparison with similar cells, run under otherwise similar conditions but not so treated, shows that the differences are small, and further depend, as is to be expected, upon the concentration of sulfuric acid and copper sulfate. The differences between such deposits are rarely greater than two or three tenths of a milligram in a deposit of 0.5 gram, obtained as a result of approximately a four hour run. The increased weight (in the absence of oxygen) may also be due, in part, to the absence of oxidation of cuprous ion. In the presence of oxygen such oxidation would cause increased solution as indicated by equation (1). In any case the effect of oxygen (both in cells containing gum arabic and in those free from this substance) is small compared to the effect noted above, so that we have made all electrolyses reported in this paper in air.

[2] Strictly speaking, the two runs are not directly comparable, as the quantities of electricity passed through the two sets of solutions are not the same. Multiplying the excess weights by the ratio of the coulometer deposits reduces them to a more nearly comparable basis. From the standpoint of the above argument the deposits are comparable as the differences of the coulometer deposits in the two trials are slight.

[3] J. Am. Chem. Soc., 43, 1503 (1921).

We next determined the effect of varying the gum arabic content upon the mass of the cathode deposit, keeping the copper sulfate content of the solutions constant at 0.5 M for the reason stated previously. The results of this run are given in Table III.

TABLE III

Mass of Cathode Deposit as a Function of Gum Arabic Content, grams.
Temp. 30°C—Current Density 2 amps./dm²

Gum arabic/100 cc. solution	0.		0.010	
	1	2	1	2
Cathode Deposit	0.5004	0.4998	0.5059	0.5053
Excess Weight	0.0035	0.0029	0.0090	0.0084
Copper, upon analysis	0.4985	0.4986	0.5027	0.5023
Excess copper	0.0018	0.0019	0.0060	0.0056

Gum arabic/100 cc. solution	0.025		0.050	
	1	2	1	2
Cathode Deposit	0.5075	0.5075	0.5091	0.5091
Excess Weight	0.0106	0.0106	0.0122	0.0122
Copper, upon analysis	0.5032	0.5030	0.5021	0.5024
Excess copper	0.0065	0.0063	0.0054	0.0057

Gum arabic/100 cc. solution	0.100		0.150		0.200	
	1	2	1	2	1	2
Cathode Deposit	0.5128	0.5121	0.5126	0.5137	0.5126	0.5126
Excess Weight	0.0159	0.0152	0.0157	0.0168	0.0157	0.0157
Copper, upon analysis	0.5042	0.5039	0.5036	0.5044	0.5031	0.5035
Excess copper	0.0075	0.0072	0.0069	0.0077	0.0064	0.0068

	Coulometers	
	1	2
Cathode Deposit	0.4969	0.4969
Copper, upon analysis	0.4966	0.4968

The excess copper, tabulated above, is the difference between the copper found upon analysis of the cathode deposit in each test cell and the average of the two analyses for copper in the coulometer deposits, i.e. 0.4967 gm. As will be seen, the excess copper is sensibly constant around 6 mgm. for all cells containing gum arabic, with a slight tendency to increase in the cells containing the largest quantities of gum arabic.

In this connection, it might be mentioned that increasing the gum content greatly beyond a concentration of 0.25 grams per 100 cc. of solution led to erratic results, as will be seen by an examination of Table IV.

TABLE IV

Mass of Cathode Deposit as a Function of Gum Arabic Content, grams. Temp. 30°C; Current Density 2 amps./dm²

Gum Arabic/100 cc. solution	0.25		1.5	
	1	2	1	2
Mass Deposit	0.5502	0.5496	0.5480	0.5703
Excess Weight	0.0171	0.0165	0.0149	0.0372

	Coulometers	
	1	2
Cathode Deposits	0.5329	0.5333

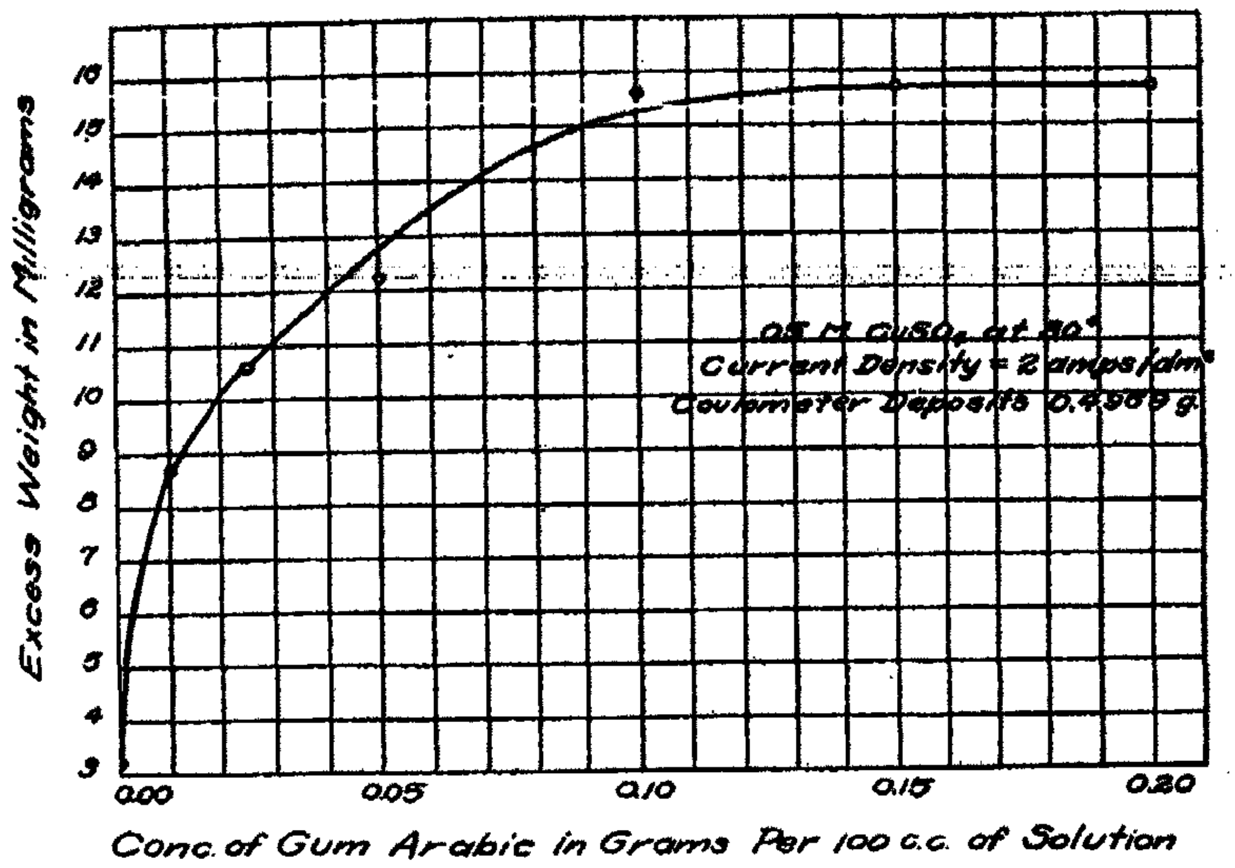

FIG. 1

The average of the two values obtained at 0.25 gm. agrees with the limiting value obtained in the data of Table III when multiplied by the ratio of the coulometer deposits. The two values obtained at 1.5 gm. (of gum arabic) show a very marked discrepancy. We finally traced this result to the fact that solutions containing 0.5 molar copper sulfate become saturated with calcium sulfate[1] when the concentration greatly exceeds 0.25 grams per 100 cc. of solution. The discrepancies are due then to the irregular mechanical inclusion or adsorption of the particles of calcium sulfate and its lack of adherence during the drying and weighing process.

To return to the data of Table III, however, it is apparent from considering the increase in excess weight that a limiting value is reached. This is seen more clearly in Fig. 1, where the excess weight is plotted as a function of gum concentration. The form of this curve resembles an adsorption curve

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[1] Calcium sulfate is formed as the result of reaction between the ionizable calcium of the gum arabic (Cf. Taft and Malm, loc. cit.) and the high concentration of sulfate ion from copper sulfate.

and we are, therefore, assuming that this excess weight has been adsorbed upon the surface of the depositing copper crystals. As has been pointed out by Taft and Messmore, the justification for such an assumption is this: the masses of copper in this series of trials are sensibly the same. Ordinates would, therefore, represent amount adsorbed per unit mass, the unit mass being taken as the mass of the coulometer deposit. The difference to be noted, as suggested by Taft and Messmore, between this series of trials and ordinary adsorption experiments lies in the fact that the specific surface becomes greater, the greater the concentration of addition agent is. It should be stated that the differences in form here are considerably less than those which occur when copper is deposited in the presence of gelatin, i.e. the copper deposits do not reduce their crystal size as rapidly as with increased concentration of gelatin. The situation is further complicated by the fact that the nature of the surface also changes, as an examination of Fig. 2 will show.

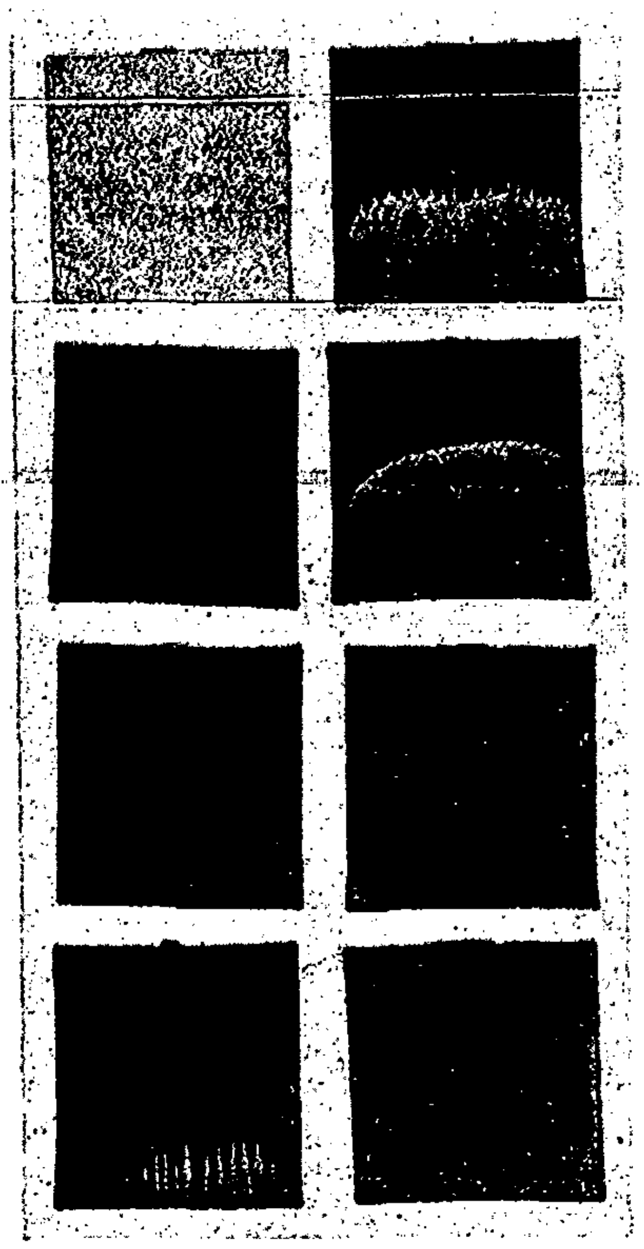

FIG. 2
Cathode deposits obtained from neutral copper sulfate in the presence of gum arabic. Concentrations of copper sulfate, left column, top to bottom, coulometer deposit, 0.25 M, 0.50 M, 0.625 M; right column, top to bottom, 0.75 M, 0.875 M, 1.00 M, 1.25 M. × 3/4.

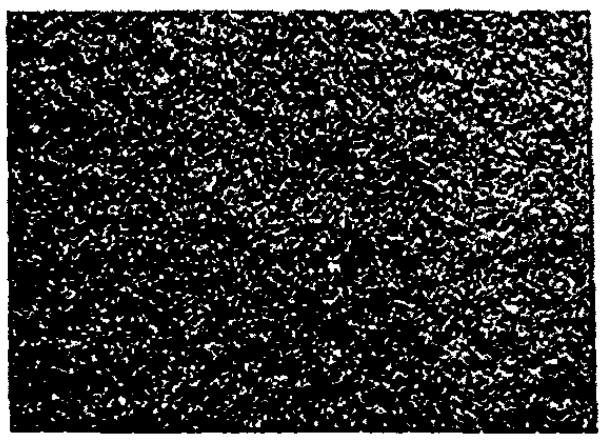

FIG. 2A
Photo-micrograph of *dark* area from electrode similar to those shown in Fig. 2. × 90. Notice that the deposit, which is chiefly copper, shows no crystalline structure at this magnification.

While we are thus assuming that the total excess weight arises as a result of adsorption upon the crystals of depositing copper, it will become evident, we hope, that the gum arabic is adsorbed in two ways.[1] In order to show this

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[1] That organic matter is actually present in such deposits we have shown qualitatively by heating such deposits in a stream of dry oxygen and collecting the issuing gas in a solution of barium hydroxide. The production of barium carbonate is evidence that organic matter is present. Controls give no appreciable deposit of the carbonate.

it will be necessary to examine our analytical data. Consider, for example, the data of the first four cells (Table III), i.e. those containing no gum and those containing 0.010 gm. per 100 cc. It will be noted that the addition of the gum produces approximately a threefold increase in the excess copper. This increased mass of copper in such deposits might arise from one or more of the following effects produced by the gum arabic:

(1) Increase in the concentration of Cu^+ and its subsequent discharge.

(2) Increasing adsorption of cupric oxide which may be formed as a result of hydrolysis of copper sulfate. This increased adsorption of cupric oxide might be due to an increase in the concentration of this oxide, or to an increase in the effectiveness of the adsorbent.

(3) Increase in the adsorption of cuprous oxide for reasons similar to those suggested under cupric oxide.

(4) Adsorption of copper arabate, which is undoubtedly present, as a result of the formation of calcium sulfate described previously.

(5) Inclusion of copper from the anode "mud". This "mud" always contains free copper in considerable proportion which is formed by mechanical disintegration of the anode. It is present in somewhat greater amounts in baths containing gum arabic than in those which do not. We do not believe that this source of copper is to be seriously considered as affecting the mass of copper in the cathode deposit. The "mud" falls very directly to the bottom of the cell beneath the anode and forms a deposit with fairly sharp edges, which indicates that the particles in the mud are nearly uniform in size; since the nearest edge of this deposit is some 4 cm. from the cathode, it is not likely that any appreciable amount of copper is taken up by the cathode from this source. Furthermore, this copper has little tendency to adhere to the cathode, i.e. if the cathode deposit be stirred in the anode mud and then washed, there is no appreciable gain in weight. Of course, the correct experimental procedure would be to enclose the anode in a porous membrane, which would retain any mud formed. We have not done this for two reasons: (a) enclosing the anode in parchment paper or filter paper would likely introduce deleterious material from the paper. At least it has been found to do so in the silver coulometer. (Rosa and Vinal);[1] (b) the use of a porous cup around the anode, we felt, was precluded because of the considerable difference in concentration of copper sulfate produced in the anolyte. As we were using solutions only 0.5 M originally, the concentration effect might be of greater magnitude than the effect of the gum arabic. It may be recalled, too, that the silver coulometer employing a glass dish beneath the anode to catch the "mud" gives the same results as the silver coulometer employing a porous cup. (Rosa and Vinal: loc. cit.). Evidently, in the case of silver, there are no finely divided particles of the anode mud which reach and adhere to the cathode. In the case of our cells, the anode mud settles very rapidly and leaves a deposit, as we have already pointed out, with *sharp* edges immediately below the anode.

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[1] Bureau Standards Bull., 13, 479 (1917).

Of the possibilities listed above to account for the increased copper, we are inclined to regard the second and third points as the probable ones, although the first and fourth may be concerned to a slight extent. Our reasons for discarding the first of the possibilities listed above are that the gum arabic used, as has been pointed out, has no visible reducing properties upon cupric ion in alkaline solution and would likely have a smaller reducing ability (if it possesses any at all) in the slightly acid solutions with which we worked. (See Table VII). More important than this, however, is the appearance of our deposits. An inspection of Figs. 2, 4 and 6 shows that the deposits are quite dissimilar. If the excess weight were copper from cuprous ion, it should still have the appearance of copper, which it does not. This variation of form we have considered in greater detail below.

On the other hand, deposits of copper obtained in the presence of considerable sulfuric acid and gum arabic have excess weights as is shown by the data of Table V.

TABLE V

Excess Weights in Presence of Sulfuric Acid (1 N), grams
0.5 M $CuSO_4$, 30°C and 2 amp./dm^2

Gum Arabic per 100 cc. solution	Coulometer		0.		0.01	
	1	2	3	4	5	6
Mass of deposit	0.4702	0.4704	0.4693	0.4692	0.4695	0.4693
Excess Weight	—	—	—	—	0.0003	0.0001

Gum Arabic per 100 cc. solution	0.025		0.050		0.10	
	7	8	9	10	11	12
Mass of deposit	0.4695	0.4695	0.4694	0.4700	0.4699	0.4700
Excess Weight	0.0003	0.0003	0.0002	0.0007	0.0007	0.0008

Gum Arabic per 100 cc. solution	0.150	
	13	14
Mass of Deposit	0.4699	0.4701
Excess Weight	0.0007	0.0009

In sulfuric acid of this concentration there is little or no possibility of oxide formation and we are, therefore, assuming that the excess weight is due to adsorption of gum arabic. It will be noted that the excess weights of Table V are very small. Due to the increased solvent action and the absence of any oxide in these acid solutions, the deposits of copper obtained in the absence of gum arabic are lighter than those obtained in the coulometers. For this reason the excess weights have been calculated by taking the difference between the mass of the deposits obtained in the presence of gum arabic and the control. That the effect of increasing the gum arabic content is to increase the amount of gum arabic adsorbed upon the copper is shown by plotting the data of Table V, which has been done in Fig. 3. The evidence here, we believe, is quite conclusive, as there seems to be no other way by which the gum arabic could be found in the deposit. We have demonstrated the presence of organic matter in deposits obtained from these acid solutions of copper sulfate in the same way as described in Footnote 1, p. 2345, i.e. by passing oxygen over the heated deposit and collecting the gases in barium hydroxide solution. Controls give no appreciable deposit of barium carbonate, while those deposits formed as above described give a measurable quantity. The possibility of the formation of a complex cation of gum arabic and copper can be dismissed for two reasons: (a) complex cations are not formed, as a rule, from complex anions and simple cations; (b) when one recalls the carbohydrate-like character of gum arabic, any complex ion formation would undoubtedly produce a complex *anion* rather than a cation.

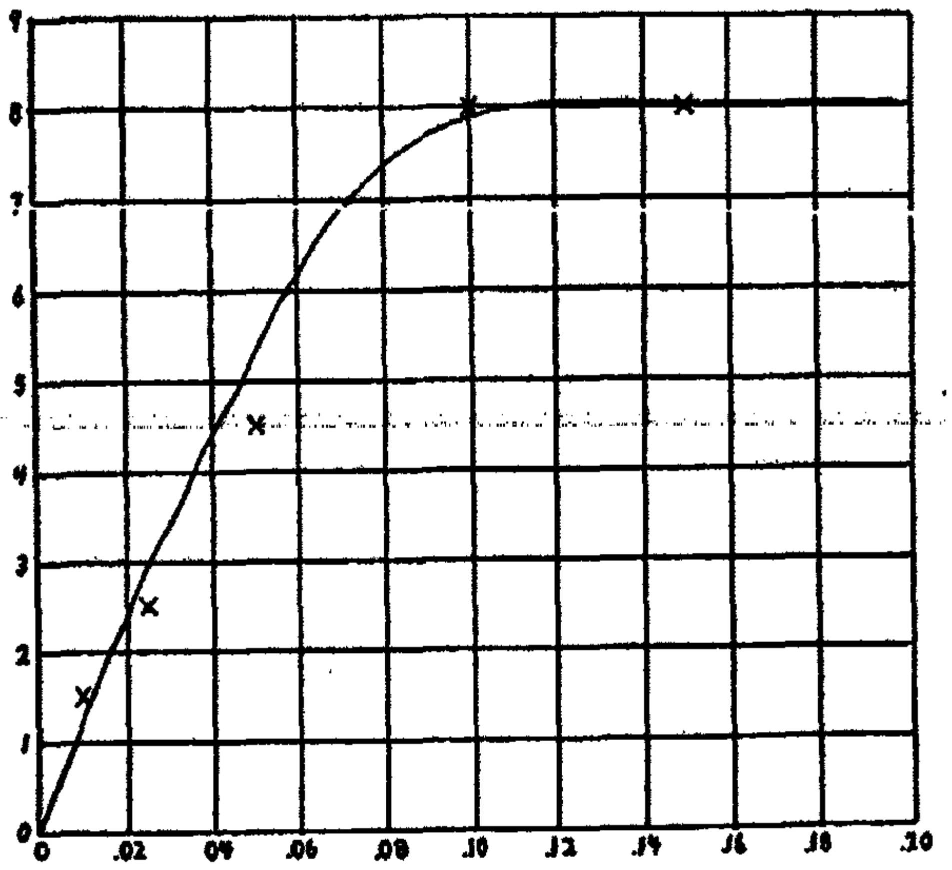

Fig. 3

Excess weights in presence of sulfuric acid and gum arabic. Ordinates, Excess Weight in Tenths of Milligrams; Abscissae, Grams of Gum Arabic per 100 cc. Solution.

The form of the deposits obtained from an acid bath in the presence of gum arabic is shown in Fig. 4 (deposit from cell No. 13, Table V). The micro-structure of these deposits shows that the adsorption of gum arabic produces a considerable distortion of the copper crystals, as is shown in Fig. 5.

Considerable information as to the nature of the excess weight can be obtained by comparing Fig. 4, the deposit of copper obtained in the presence of gum arabic in an acid bath, with the form of the deposit obtained from "neutral" copper sulfate in the absence of gum arabic (Figs. 6 and 7). It will be noted that the deposits are not greatly different in form (Figs. 4 and 6). Both are apparently crystalline and are copper colored. Both, however, show excess weight; the deposit from the acid bath showing an excess weight as a result of adsorption of gum arabic; that from the neutral bath being heavier due to inclusion of copper oxides. When both gum arabic and copper oxides are present, there is a marked increase in the excess weight, as has been

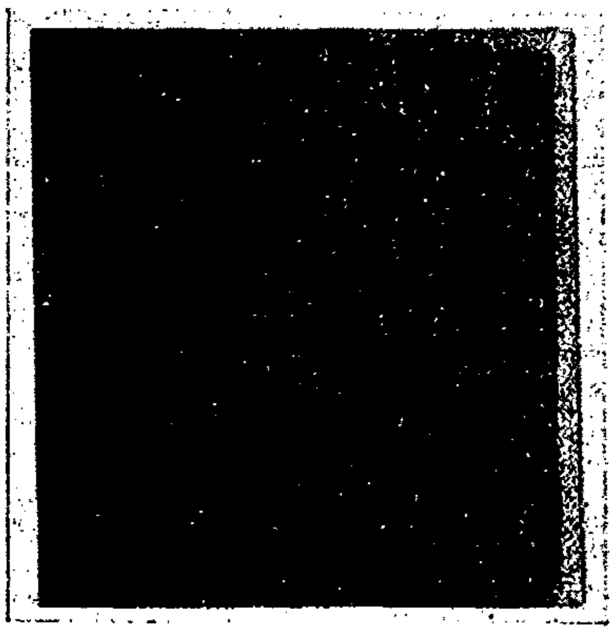

FIG. 4

Cathode deposit from solution containing 0.5 M $CuSO_4$, 1 NH_2SO_4, and 0.025 gm. of gum arabic per 100 cc. solution. Temperature 30°C; current density, two amperes per square decimeter. × 1.7.

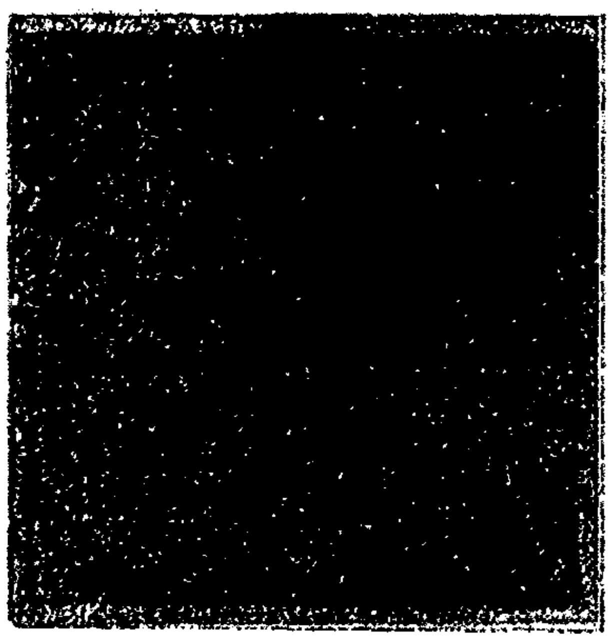

FIG. 6

Cathode deposit from neutral copper sulfate, absence of gum arabic. 0.5 M $CuSO_4$; 30°C; 2 amperes per square decimeter.

FIG. 5

Photo-micrograph of an area from electrode shown in Fig. 4. × 28. The "wrinkled" appearance of the copper crystals is due apparently to their displacement as they are deposited, *i.e.* the "wrinkles" in cross section appear as a series of steps.

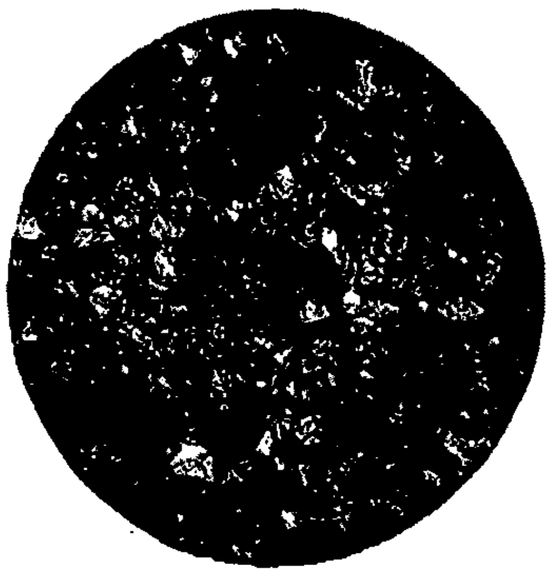

FIG. 7

Photo-micrograph of an area from electrode shown in Fig. 6. × 30.

pointed out, and further, a marked difference occurs in the form of the deposit, as can be seen by inspection of Fig. 2. Before we "explain" the form of these deposits (in Fig. 2), we must consider the evidence for the presence of the copper oxides. That such substances are present in small quantities is not open to question. Richards, Collins and Heimrod have established the evidence for the presence of cuprous oxide. This comes as a result of the reaction already formulated in equation (1) and the subsequent hydrolysis of cuprous sulfate.

These investigators apparently overlooked the possibility of the presence of cupric hydroxide (or oxide) in neutral copper sulfate solutions. As a result of our pH measurements, there can be little doubt that some cupric hydroxide is present. The data for the pH measurements is given in Table VI.[1] As can be seen, the gum arabic is with little effect upon the pH of the solution. If it be assumed that the sulfuric acid is completely dissociated, it is possible to calculate the approximate percentage hydrolysis of these solutions from the relation $\mathrm{pH} = \log 10^{2}/xC$, where x is the percentage hydrolysis and C the concentration of copper sulfate in gram-equivalents per liter. Such a calculation gives 0.03% hydrolysis for the first two solutions listed in Table VI and only slightly less for the remaining ones. This would represent about 1.5 milligrams of cupric hydroxide per 100 cc. of solution. This value seems reasonable, in spite of the likely error introduced by the high concentration of salt as mentioned above, as O'Sullivan[2] obtained a value of 0.07% for the hydrolysis of N/10 $CuSO_4$ at 18°.

Table VI

pH Measurements of 0.5 M $CuSO_4$ at 26°

Grams of Gum 100 cc. solution	pH	Grams of Gum 100 cc. solution	pH
0.0	3.52	0.10	3.53
0.01	3.52	0.15	3.53
0.025	3.53	0.20	3.53
0.05	3.53	0.25	3.53

Bearing more directly upon the inclusion of cupric oxide is the fact that the ratio excess copper/excess weight of the deposits obtained from "neutral" copper sulfate averages around 0.65. Thus, if these ratios are taken from the data of Tables III and VII, they are found to be 0.56, 0.66, 0.67, 0.62, 0.71 and 0.67. The only one left out of consideration is the data of the cell electrolyzed at 0° which obviously is in error. When the errors involved in determining a small quantity by the difference of two relatively large ones are considered, the agreement is surprising. The average of the above values is 0.65 which is that of the ratio $Cu/Cu(OH)_2$. Some caution should be observed in drawing the conclusion that the only compound included in such deposits is $Cu(OH)_2$, however, as we are not certain how much of the copper results from electrolysis; that is, how much is produced as a result of the reaction:

$$Cu^{++} + 2E = Cu$$

The uncertainty is produced, as has already been pointed out, as a result of a re-solution of part of the copper and of the possible discharge of cuprous ion.

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[1] These pH values are likely in error due to the salt effect for which no correction has been made. It is quite probable that the activity coefficients of quinone and hydroquinone will be appreciably different in our relatively concentrated solutions than in pure water. (Clark: "Det. of Hydrogen Ions," 3rd ed., 408.) However, we are more concerned with the relative effect in the copper sulfate solutions without and with the presence of gum arabic.

[2] Trans. Faraday Soc., 21, 319 (1025).

Likely then, both oxides of copper are present, the relative proportion of which will be determined by the concentration of the copper sulfate; the amount of cupric hydroxide increasing with dilution; the amount of cuprous oxide increasing with increasing concentration of copper ion, as inspection of the equilibrium equation for solution of metallic copper shows. Since both hydrolysis and rate of solution increase with rising temperature, the amounts of these oxides will increase at higher temperatures.[1]

We believe that the presence of these oxides accounts for the form of the deposits as illustrated in Fig. 2. In the more dilute solutions (0.25 and 0.50 M) hydrolysis is relatively extensive and there is thus considerable cupric oxide present. This, we are assuming, is present in sufficient proportion at these dilutions to allow its simultaneous adsorption with the gum arabic, giving rise to the dark colored deposits. In the more concentrated solutions (0.625 M and greater) the catholyte requires dilution (which results from the deposition of copper upon the face of the cathode) before sufficient oxide is formed. As the rising catholyte is depleted of its copper, a concentration is eventually reached at which the amount of cupric oxide formed is sufficient to be visibly adsorbed. As the concentration of copper sulfate is increased, the level at which hydrolysis will furnish sufficient oxide to give the dark colored deposit becomes higher and higher, as our photographs show.[2] It is not solely a question of hydrolysis, however. For, if such were the case, there would be a *gradual* darkening of the color of the deposit as it rises higher and higher on the cathode. An inspection of the deposits shows that the dividing line between the dark colored material and the lighter colored copper is quite sharp. Further, it has been found that for the same concentration of copper sulfate, an increase in the gum arabic content produces the dark colored area at a lower level. It appears as if a factor related to a solubility product is involved, i.e. when $C_{\text{gum}} \times C_{\text{oxide}}$ (C's representing concentrations) exceeds a certain value the dark colored material is produced. Possibly the colloidal cupric hydroxide reacts with gum arabic[3] at the surface of the cupric hydroxide micellae, forming copper arabate. This material, it might be assumed, is more powerfully adsorbed than either cupric hydroxide or gum arabic singly. It must be admitted that the possibility of inclusion of the gum arabic—cupric hydroxide complex might take place as the result of a charged colloidal

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[1] The remaining possibility of those listed on page 2346, i.e. that the excess weights in the presence of gum arabic in "neutral" solutions of copper sulfate may be due to adsorption of copper arabate *alone*, is eliminated for several reasons: The excess copper could not be accounted for on the basis of such a compound (and likely of any adsorption complex) as the copper content of such a compound is probably less than 3%. This figure is based on the approximate equivalent weight of gum arabic of 1200 and the monobasic character of the free acid, as established by Thomas and Murray (loc. cit.). The per cent of excess copper in the excess weights of such deposits is invariably many times higher than this. (Cf. Table III). Further, it is not constant at constant temperature and increases as the temperature rises. (Cf. Table VII).

[2] The dark-colored deposits grow from the bottom of the cathode up and not from the top down, as Fig. 2 might lead one to believe. We hope to publish shortly a study of the growth of such deposits.

[3] That gum arabic is taken up at a solid interface is shown by the rather marked protective ability of gum arabic. Zsigmondy (Z. anal. Chem., 40, 697 (1901)) has shown, for example, that gum arabic has a relatively small gold number.

particle. Undoubtedly colloidal cupric hydroxide formed in a solution containing a high concentration of cupric ion will be positively charged. The fact that there is no diminution in total copper after the formation of the dark areas, taken together with the form of our excess weight curve, is the argument against this view. Our original intention of showing adsorption by a neutral particle, however, is shown in the deposition of copper in the presence of gum arabic in *acid* solutions of copper sulfate. Here, we believe, there can be little question that the limiting value of excess weight is due to the adsorption of gum arabic.

TABLE VII

Mass of Cathode Deposit as a Function of Temperature, grams.
Current Density 2 amps./$dm.^2$
Copper Sulfate, 0.5 M

Temp. °C	0°	0°	0°	0°	0°	0°
Grams of gum/100cc.sol.	0	0	0.01	0.01	0.15	0.15
Mass of Deposit	0.5180	0.5181	0.5197	0.5194	0.5314	0.5314
Excess Weight	0.0004	0.0003	0.00130	.0010	0.0130	0.0130
Copper, upon analysis	0.5174	x	x	x	0.5209	0.5203
Excess copper	−0.0010	—	—	—	0.0025	0.0019

Temp. °C	40°	40°	40°	40°
Grams of gum/100cc. sol.	0	0	0.15	0.15
Mass of Deposit	0.5293	0.5291	0.5464	0.5479
Excess Weight	0.0109	0.0107	0.0280	0.0295
Copper, upon analysis	0.5258	0.5250	0.5348	0.5352
Excess Copper	0.0074	0.0066	0.0164	0.0168

Temp. °C	60°	60°	60°	60°
Grams of gum/100cc. sol.	0	0	0.15	0.15
Mass of Deposit	0.5482	0.5442	0.5578	0.5571
Excess Weight	0.0298	0.0258	0.0394	0.0387
Copper, upon analysis	0.5396	0.5358	0.5419	0.5411
Excess Copper	0.0212	0.0174	0.0235	0.0227

	Coulometers	
	1	2
Mass of Deposit	0.5182	0.5185
Copper, upon analysis	x	0.5184

x Analyses not made or lost.

That the composition of the adsorbed material varies with the temperature will be seen from the data of Table VII, which compares a series of cells, run under otherwise similar conditions at 0°, 40°, and 60°. As will be seen by a consideration of this data, the excess weight increases with rising temperature, but the excess copper increases more rapidly than the excess weight.

The inference to be drawn from this set of data is that the proportion of organic matter in the deposit increases as the temperature is lowered. That is, if one takes the difference between excess weights in baths containing gum arabic and those which do not (at the same temperature) these differences increase as the temperature is lowered. We feel, therefore, that our position with respect to the *adsorption* of both substances, i.e. copper oxides and gum arabic, is very securely fixed by this additional data.

The effect of temperature on the form of these deposits at various temperatures is worthy of note. These are illustrated in Fig. 8. The deposit obtained at 0° in the presence of gum arabic was one of the most striking of any of the hundreds of copper deposits made in this laboratory. In appearance it resembled a very highly polished bronze surface, but unfortunately, as far as any practical purpose goes, it was quite brittle. This deposit, it will be noted, was obtained when the proportion of organic substance in the deposit was the greatest. The deposit obtained at 40° (in the presence of gum arabic) was still smooth, but rather grainy. The deposit obtained at 60° (in the presence of gum arabic) was highly striated, the striae standing out as deep ridges, the area between the ridges being barely covered by a deposit of lighter colored "copper." This deposit contained the greatest proportion of copper oxides, both of which are very much poorer conductors of electricity than is copper itself. We plan, in another paper to be published shortly, to discuss the growth of such striated deposits in somewhat greater detail.

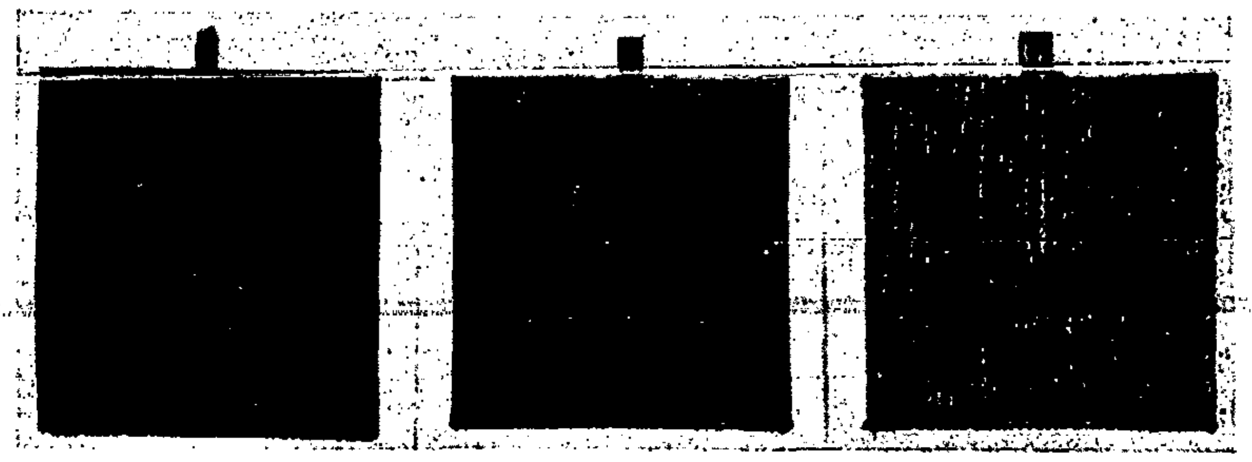


FIG. 8

Effect of temperature upon the form of the cathode deposit. Left to right, deposits obtained at 0°C, 40°C and 60°C. 0.5 M $CuSO_4$, 15 grams of gum arabic per 100 cc. solution, 2 amperes per square decimeter. The deposit at 0° has the appearance of highly burnished bronze. × 1.1.

Summary

1. The mass of cathode deposits in the presence of gum arabic, both in neutral and acid solutions of copper sulfate, increases with increasing concentration of gum arabic to a limiting value.

2. Cathode deposits in neutral copper sulfate solutions contain more copper than is obtained in a copper coulometer placed in series with such baths, the proportion of such "excess copper" increasing with rising temperature.

3. We interpret our results to indicate that copper oxides (both cuprous and cupric) and gum arabic are *adsorbed* simultaneously upon the surface of the newly deposited copper crystals obtained upon electrolysis of neutral copper sulfate solutions; from acid solutions gum arabic alone is adsorbed.

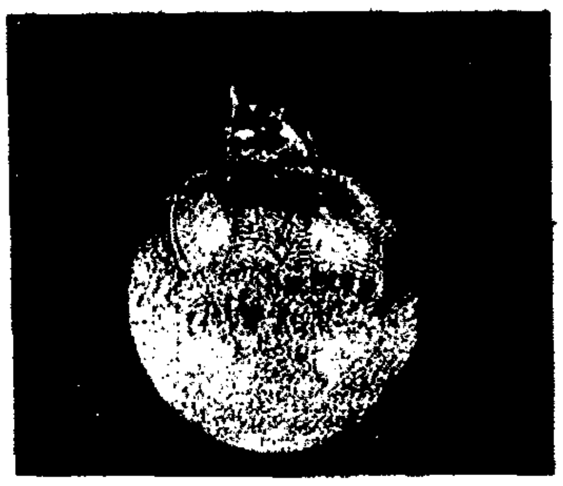
THE RHYTHMIC CRYSTALLISATION OF MELTS

Part. I. A Preliminary Investigation of the Factors influencing the Phenomenon

BY JOHN FREDERICK JAMES DIPPY

The phenomenon of rhythmic crystallisation of molten substances in thin films has been observed in the following instances: mannitol, and ammonium lithoxanthate;[1] ethyl tetracarbethoxylate, benzophenone and coumarin;[2] sulphur;[3] p-ethoxybenzylideneaminophenylpropionic acid;[4] salol, methyl salicylic acid, and p-toluonitrile;[5] myristic, lauric, undecoic and decoic acids;[6] antipyrine, sulphonal, malonamide, benzoin, benzonaphthol, santonin, m-diethylaminophenol, diaminonaphthalene, asparagine salts, benzoic acid, salicylic acid and hippuric acid;[7] benzil, menthol, acetanilide and m-dinitrobenzene.[8]

The author finds that the phenomenon is also exhibited by piperonal, terpin hydrate, vanillin, phenyl benzoate, phenanthrene, cinnamic acid, thymol and 3:5-dichloro-4-methyldiphenyl (the preparation of this compound will be described in a separate publication).



PHOTOGRAPH I

A preliminary investigation of the factors controlling the phenomenon has been made by the author. The most suitable substance for examination was found to be 3:5-dichloro-4-methyldiphenyl, since it crystallises rhythmically so readily and in such well defined fashion. This substance was noticed to exhibit the phenomenon, when in its preparation, a flask containing the molten compound upon its walls was allowed to cool. After considerable supercooling rhythmic crystallisation occurred (see photograph 1).

Rhythmic Crystallisation upon Slides

The crystallisations of the melts were performed upon glass microscope slides which had been specially cleaned by immersion in nitric-chromic acid

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[1] Brewster: Trans. Roy. Soc. Edinburgh, 20, 607 (1853).

[2] Alexéeff: J. Russ. Phys.-Chem. Soc., 38, 1120 (1906).

[3] Fischer-Treuenfeld: Kolloid-Z., 16, 109; Köhler: 17, 10 (1915); Hughes: Nature, 123, 603 (1929).

[4] Vorländer and Ernst: Z. physik. Chem., 93, 521 (1919).

[5] Schubert: Kolloid-Z., 35, 219 (1924).

[6] Garner and Randall: J. Chem. Soc., 125, 369 (1924).

[7] Bernauer: Neues Jahrb. Mineral. Geol., 56, 342 (1927).

[8] Hedges: Nature, 123, 837 (1929).

mixture for three months, then washed several times with distilled water and steamed. The slides were stored in a calcium-chloride desiccator until perfectly dry. A flat iron bar over a small Bunsen burner flame was used for heating the slides. In order to procure a melt of a substance upon a slide, the latter was quickly transferred to the bar, which recorded a temperature about 20°C above the melting point of the substance. A small quantity of the substance was then added to the slide and the melt so produced was spread in a thin film by use of a clean glass rod. The slide was then placed upon a sheet of asbestos in an empty desiccator and allowed to cool, the interference of impurities and dust particles being thus largely eliminated.

PHOTOGRAPH 2
(Actual size)

PHOTOGRAPH 3
(Actual size)

In this manner thirty different organic compounds were allowed to crystallise spontaneously from their melts. In the majority of cases crystallisation was continuous, but in the instances already cited the rhythmic phenomenon was manifested.

Rhythmic growth invariably begins with the appearance of one or more nuclei which gradually extend radially in all directions for some distance; then there follows an abrupt arrest in growth, after which crystallisation extends once more into the melt. This pulsation of crystallisation proceeds regularly until the melt is completely solidified. The result is a series of concentric bands of solid separated by what appear to be gaps (see photographs 1 to 5).

Phenanthrene and cinnamic acid yield minute bands of crystals best observed under a lens. Thymol crystallises in plates but gives evidence of definite pulsations of growth although not of the common banded form. Piperonal, terpin hydrate, vanillin, phenyl benzoate and 3:5-dichloro-4-methyldiphenyl all gave bands easily observed by the naked eye. The regular manner in which 3:5-dichloro-4-methyldiphenyl crystallises is depicted in photograph 2. The growth began from opposite corners; the junction of the two waves is well defined. Photograph 3 is a side view of the same slide, showing the bands approaching the centre from either side in "drift" formation. In all the following text the compound under investigation is 3:5-dichloro-4-methyldiphenyl, except where stated otherwise. The specimens used had been recrystallised two, three and four times from absolute alcohol, and stored for three months in a vacuum desiccator before being used. Identical results were achieved by employing any of the three specimens.

The Effect of Supercooling

It was noticed that where rhythmic crystallisation occurred, the film of melt had been allowed to crystallise spontaneously. Hence almost invariably the melt had supercooled considerably before crystallisation began. In order to discern if this were a factor contributing to the phenomenon, films which had spontaneously crystallised rhythmically were melted afresh and allowed to cool. At frequent intervals the melts were inoculated with some of the solid so as to prevent supercooling. In all cases continuous crystallisation resulted. Forty observations were made, yielding the same result.

Photograph 4
(1/2 actual size)

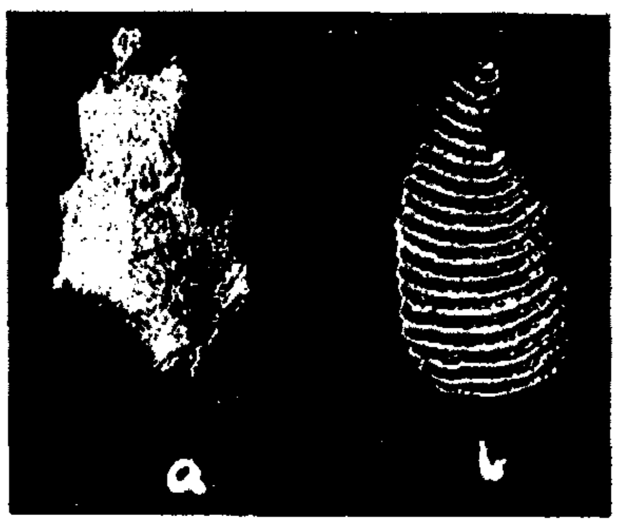
The different results obtained with and without supercooling are shown in photograph 4. Two films of melt were allowed to crystallise side by side on the same glass slip; film (a) was inoculated to prevent supercooling, and film (b) crystallised spontaneously. The experiment was repeated several times and the same result obtained.

When supercooling was small it was observed that the melts crystallised in a small number of unusually wide bands. Thus it would appear that the degree of supercooling is a factor essential to the production of rhythmic crystallisation in a molten substance. The relation between the degree of supercooling and the frequency of the crystal bands has not yet been ascertained. It is hoped later to study this further.

It was emphasised by Alexéeff[1] that supercooling is a factor upon which depends the rhythmic crystallisation of the substance he investigated.

The Effect of an Air Interface

The presence of an air interface is another factor controlling the appearance of rhythmic crystallisation. On a large slide two independent films of 3:5-dichloro-4-methyldiphenyl were, in the one case (6), left exposed to the air, and in the other case (a), covered by a clean glass cover-slip. Upon cooling, both films crystallised spontaneously, (a) did so in continuous fashion, and (b) in rhythms, (see photograph 5). This experiment was repeated a large number of times and always proved reproducible.



Photograph 5
(1/2 actual size)

Further evidence for the air interface factor is supplied by the following experiment. A film of the melt was partly covered with a glass slip and al-

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[1] Alexéeff: loc. cit.

lowed to supercool. When the air exposed portion of the film crystallised first it did so rhythmically, but upon extending into the region contained between the two glass interfaces, the growth immediately became continuous.

The dependence of rhythmic crystallisation upon the presence of an air-interface was also noticed by Alexéeff.[1]

The Effect of the Thickness of the Film

It was often found impossible to obtain a film of the melt of reasonably uniform thickness. This difficulty arose from the fact that upon cooling the slide, the surface tension of the melt increased and so caused the area occupied to diminish, but, on occasions, leaving behind an extremely thin film. Upon crystallising, these melts did so rhythmically in the portions of normal thickness, but the abnormally thin films crystallised continuously, even when inoculated by a growth of crystals from the rhythmic region.

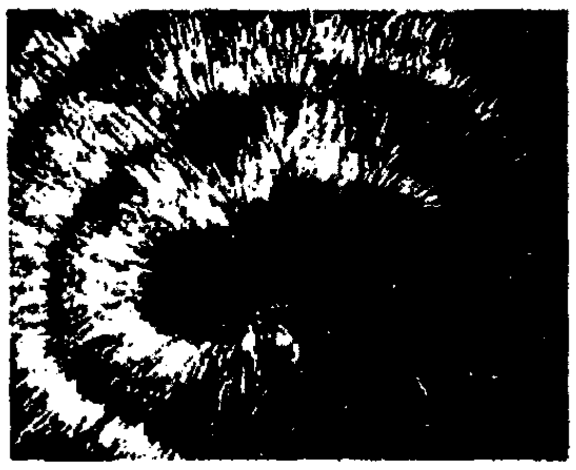
It has also been observed that where rhythmic crystallisation occurs, the thinner the film the more rapid are the pulsations of crystal growth, that is, the narrower and more frequent are the bands; whilst on the same slide thicker portions of film crystallise with slower pulsations and consequent production of wider bands.

Repeated attempts were made at bringing about rhythmic crystallisation in melts contained in glass tubes of 5 mm. diameter (previously cleaned and dried in a manner similar to that employed for the slides) met with no success. In all cases crystallisation was continuous. Variations of degree and rate of supercooling appeared not to influence the mode of crystallisation. This result agrees with the behaviour of some unusually thick films of melt which crystallise spontaneously in continuous form.

It seems, therefore, that film thickness is a factor influencing rhythmic crystallisation. Measurements already made point to there being definite limits of thickness of film within which rhythmic crystallisation can occur. However, the author proposes to investigate this factor in more detail.

The Nature of Rhythmic Growth

The pulsations of crystal growth in melts of 3:5-dichloro-4-methyldiphenyl have been closely examined. As seen from photograph 3, each band increases in height in the direction of its growth. This maximum height of growth is followed by what appears to be a gap, then begins the growth of the subsequent band.



PHOTOMICROGRAPH I
(X 30)

The so-called gap when examined under a hand lens or a microscope, appears to be constituted of a very thin layer of crystals. This is depicted in photomicrograph 1 (taken with transmitted light). The bands of crystals appear dark, since they are comparatively dense,

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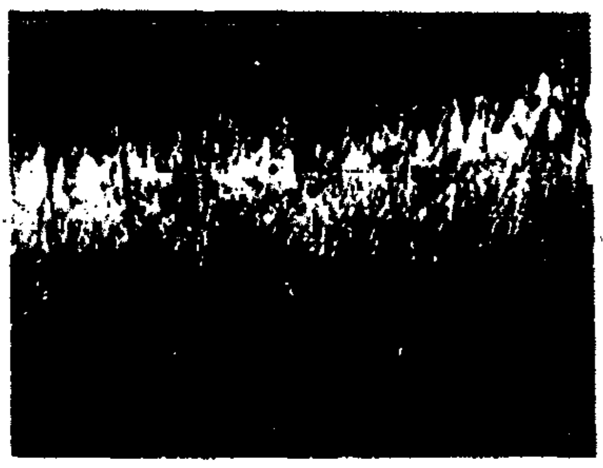
[1] Alexéeff: loc. cit.

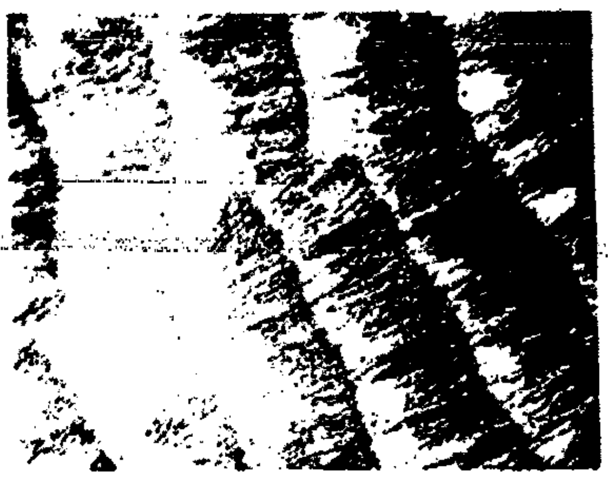
whereas the interim space between the consecutive bands stands out bright and shows the needle-like crystals aligned in the direction of radial growth.

Photomicrographs 2 and 3 illustrate the abrupt manner in which the growth of the bands begins and ends. Moreover, the peculiar "fan-like" growth of the crystals (noted also in certain observations made with the epidiascope) is well shown here. This "fan-like" growth extends with widening front in the direction of crystallisation.

The actual growth of crystals in a melt was followed upon a lantern screen with the aid of an epidiascope. This apparatus was fitted with a horizontal stage upon which was placed a slide containing a melt of 3:5-dichloro-4-methyldiphenyl. The image of the slide, obtained with reflected light, was focussed upon the screen; this afforded a magnified view of the entire field of the melt. It was observed that when, after supercooling, a crystal nucleus formed, and had extended some distance, the melt rapidly flowed away in a wave, there followed a very short arrest and then the wave returned towards the ridge of crystals.



PHOTOMICROGRAPH 2
(X 25)



PHOTOMICROGRAPH 3
(X 25)

The rapid crystallisation of 3:5-dichloro-4-methyldiphenyl made it somewhat difficult to follow the features of the growth. More satisfactory results were achieved with piperonal and salol. The slow rate of crystallisation of these substances made them eminently suitable for the epidiascope investigation. Using these substances, the details of the growth have been more closely observed. In the supercooled melt a nucleus first forms, this extends radially thrusting out "fan-like" growths of crystals into the melt. Some of the melt becomes entangled in this network of crystals. While this crystallisation proceeds, the surrounding liquid recedes in a wave and then returns to the crystals bordering the first band, thus crystal growth begins once more in a very thin layer gradually increasing in thickness until the second band is complete. In some cases this thrusting out of "fan-like" growths causes the front of the crystallising band to be most irregular, whereas on the other hand, particularly in thick films, the growth is remarkably even (c.f. photomicrographs 2 and 3).

Rhythmic Crystallisation upon Evaporation of a Solution

Rhythmic crystallisation of 3:5-dichloro-4-methyldiphenyl has been effected by allowing thin layers of an ethereal solution of the substance to evaporate from a glass slide at room temperature. The appearance of rhythmic crystallisation after evaporation of solutions of various organic compounds has been previously observed by Kägi,[1] and by E. C. H. Davies and his co-workers.[2]

Discussion

A number of attempts have been made to explain the phenomenon of the rhythmic crystallisation of melts.[3] The majority involve the operation of capillary forces. The view put forward by Alexéeff is that upon the formation of a crystal nucleus in a supercooled melt, the heat produced by the crystallisation is adsorbed by the melt in the immediate vicinity of the nucleus and hence the surface tension between the melt and the crystals diminishes. The liquid consequently moves from the solid until, after cooling, the surface tension has increased sufficiently to allow the liquid to become attached once more to the solid. This theory involves only the capillary force exerted between the melt and the crystals. The capillary force existing between the melt and the slide is also a factor to be considered. In virtue of this force, the melt should tend to spread itself out more upon increase of temperature, and so ensure better contact with the solid. This factor appears, therefore, to militate against the theory advanced by Alexéeff. The explanation of rhythmic crystallisation given by Hughes is essentially the same as that of Alexéeff.

Vorländer and Ernst put forward a theory in which the capillary forces between melt and slide, and melt and crystals, are both taken into account, although no mention is made of the variation of these forces with changes of temperature. These workers state that the nucleus exerts capillary attraction upon the surrounding melt whereupon the latter rises in the crystal network and subsequently solidifies. When the height of the ridge has become so great that the adhesion of the melt to the slide overcomes its attraction to the crystal network there follows an inductive period. This theory is in agreement with observations made in this paper, but does not provide a complete explanation. It is true that solidification of the melt proceeds until an optimum height is reached; this it does in "drift" formation. Moreover, minute observation of the edge of a "drift" reveals that it consists of a bristling mass of needles protruding into the air; this constitutes the end of the crystal network. Crystallisation observed on the screen by means of the epidiascope evidenced the intrusion of a network of crystals into the melt, and also the moving away of a wave of the latter from the solid, which doubtless begins at that point when the "drift" of crystals reaches its optimum height. Again,

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[1] Kägi: Helv. Chim. Acta. 6, 264; Kolloid-Z., 33, 284 (1923).

[2] Davies: J. Am. Chem. Soc., 44, 2705 (1922); Davies, Taylor and Riblett: J. Phys. Chem., 34, 842 (1930).

[3] Alexéeff: loc cit.; Fischer-Treuenfeld: loc. cit.; Köhler: loc cit.; Vorländer and Ernst: loc. cit.; Hughes: loc. cit.; Schubnikov and Lämmlein: Z. Krist., 67, 329 (1928).

the necessity of an air interface is understood on this theory, since this factor permits of the free movement of the melt, which is so vital a condition.

The theory of Vorländer and Ernst is insufficient, however, for it does not take into account the effect of the latent heat of crystallisation, and hence supplies no explanation of the influence of supercooling.

It would be anticipated that the crystallisation of a nucleus would continue with increasing height until the capillary force between the crystals and the melt had been balanced by the opposing capillary force exerted between the slide and the melt, whereupon crystallisation would proceed in continuous fashion at that limiting height. If, however, the melt in the close vicinity of the crystals increased in temperature, in virtue of the latent heat of crystallisation, the surface tension between the crystals and the melt would diminish and so disturb the balance between the two capillary forces in equilibrium. The melt would consequently descend from the crystal network. This would conclude the growth of the first "drift," and the second "drift" would begin its growth from the base of the first.

This effect of the latent heat of crystallisation would be possible only in a supercooled melt, since this condition permits of crystallisation with increasing temperature of the melt. If the melt were not supercooled, crystallisation would proceed without any fluctuation of temperature. Therefore, it follows that non-supercooled melts should crystallise in continuous fashion, whilst in the supercooled state melts may crystallise rhythmically.

It is interesting to note that the apparent rhythmic crystallisation of myristic, lauric, undecoic and decoic acids investigated by Garner and Randall[1] was ascribed to the formation of a solid skin which wrinkled and gave a waved effect upon the surface of the melt. This feature is distinct from the phenomenon discussed in this paper.

The general equation, $\log N = a \log r + \log K$, suggested by Hughes,[2] relating the number of bands (N) with the distance from the nucleus (r), has been borne out reasonably well in a number of instances of measurements made upon rhythmic bands of 3:5-dichloro-4-methyldiphenyl.

It is remarkable that rhythmic crystallisation of melts is confined to certain particular substances which have nothing in common with regard to their molecular structures. They are representative of many classes of compounds, and generally possess more or less powerful polar groups. Some have symmetrical formulae, others have not. Furthermore, only a few possess particularly long molecular structures.

The physical factors contributing to the phenomenon have still to be more fully understood. Doubtless, they include all the factors considered in this paper, and it is hoped to carry out soon a more quantitative study of them.

Summary

1. Rhythmic crystallisation of thin films of molten piperonal, terpin hydrate, vanillin, phenyl benzoate, phenanthrene, cinnamic acid, thymol and 3:5-dichloro-4-methyldiphenyl has been observed.

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[1] Garner and Randall: loc. cit.

[2] Hughes: loc. cit.

2. Investigations upon the effects of supercooling, the presence of an air-interface and the thickness of film have been made upon 3:5-dichloro-4-methyldiphenyl. It has been shown that these factors control the production of rhythmic crystallisation.

3. The details of rhythmic growth have been observed upon a lantern screen by means of an epidiascope, using melts of 3:5-dichloro-4-methyldiphenyl, salol and piperonal.

4. By modifying and amplifying the theory of Vorländer and Ernst, it is possible to supply a satisfactory explanation of rhythmic crystallisation and the factors governing it.

The author wishes to express his thanks to Mr. G. J. Strickson, A.R.P.S., of this College, for the help he rendered in procuring the photographs and photomicrographs, and also to Messrs Imperial Chemical Industries for a grant made to this Department.

Chemistry Department,
The Technical College,
Cardiff.
March 24, 1932.

NOTE

BY STUART MUDD AND R. L. NUGENT

Reiner and Fischer[1] in 1929 developed a formula for the change in free energy incident to altered dispersion of a microheterogeneous system. Mudd, Nugent and Bullock[2] subsequently reached a similar formula from somewhat different considerations. The two formulae are essentially equivalent except for differences in notation. However, we criticized adversely (p. 243) the derivation of the formula of Reiner and Fischer on the ground that they introduced expressions for the free surface energies of the disperse phase and of the dispersing medium whereas the only free energies actually in question are the interfacial energies. We did not understand at the time that the two first-mentioned free surface energies were introduced as factors in a reversible step in the derivation of the total free energy change. This fact has since been brought to our attention by Dr. Reiner. We regret that this misunderstanding should have occurred on our part, and wish to emphasize that we fully realize that the treatment of Reiner and Fischer involves the understanding that, in the ideal reversible case, the total free energy change involved in an increase in interface in a microheterogeneous system is given by the product of the increase in interfacial area multiplied by the free interfacial energy per unit area.

We further stated that certain measurements of Harkins, Clark and Roberts show that the difference between the work of cohesion of a substance and its work of adhesion with a second substance is not equal to the interfacial tension between the two. This statement is correct, but does not concern the treatment of Reiner and Fischer, because their derivation involves the sum of the works of cohesion of the particles and of the dispersion medium rather than the work of cohesion of the particles alone.

University of Pennsylvania.

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[1] Z. Immunitätsforschung, 61, 320 (1929).

[2] J. Phys. Chem., 36, 239 (1932).

NEW BOOKS

Vision and Colour Vision. *By R. A. Houston. 22 × 14 cm; pp. iv + 238. London: Longmans, Green and Co., 1932. Price: 15 shillings.* Dr. Houston's valuable researches on vision presaged a volume on the subject of more than common interest, and those who, knowing his flair for exposition, looked forward to a clear, orderly and fully documented account of the subject, have found their expectations realised, although on occasion they could wish that he had made more critical use of the information collected. To give in detail the subjects handled by Dr. Houston would reduce this review to a catalogue; stated as briefly as may be, they concern the discrimination of intensity, dark adaptation, acuity, the visibility of the spectrum, colour mixing, recurrent vision and flicker, fatigue, and simultaneous contrast and spatial induction. These topics account for three-quarters of the book; the remaining sixty pages give a detailed discussion of theories of colour vision and of the results of the examination of some two dozen colour blind subjects, collected from a student population of about a thousand. As was to be expected, Dr. Houston has not been content, apart from his own experiments, to take his knowledge at second hand; and much of the value of the work lies in its careful analyses of, and references to the original sources.

To the reader whose interests are not over-specialised there are two outstanding topics of special interest handled by the author. The first refers to the much discussed question of the Weber-Fechner law. Stated bluntly and without certain necessary reservations, sensation is proportional to the logarithm of the stimulus. Now, stimuli are physical quantities measured in terms of physical magnitudes. A pressure, a brightness (measured in millilamberts) the intensity of a sound (measured in micro-watts per square centimetre) are all definite objective physical stimuli. And if sensations are proportional (within a certain region) to the logarithms of these stimuli, we have at hand an algorithm which makes it possible to calculate the magnitude of a sensation. "Can't be done," say some physicists, some physiologists, and a great many psychologists. Why not? The answers vary in value and in clearness, but the fundamental fact on which most of them are based is that the process of measurement consists in laying alongside the magnitude to be measured another magnitude of the same kind (termed the unit) and finding how many times the unit can be stepped off along the magnitude to be measured. "Where is your unit of sensation?" ask some critics. "Is it ever possible to regard a sensation as built up of elementary magnitude?" ask others. Attempts to answer these queries were made by formulating a scheme of measurement which concerned itself with the determination of the *interval* between two sensation-magnitudes rather than with that of the magnitudes themselves. Titchener, among the greatest of the experimental psychologists, puts the matter perfectly clearly, though he is not to be regarded as the originator of the doctrine. He shews that a *scale* of sensation can be laid off—as a particular instance he describes a well-known experiment in which, by appeal to visual sensations alone, a series of grey papers of different shades are arranged in equal steps of increasing brightness. A photometric comparison of the objective brightnesses of these papers then shews that the brightnesses increase in a geometrical progression. The Weber-Fechner law may then be deduced in the form

$$S_1 - S_2 = k \log (I_1)/(I_2) \qquad (1),$$

where $S_1 - S_2$ is interpreted as a sense-interval. Hence, just as the height of a vertical pole may be determined in terms of the foot, so may the *interval* between two sensations be measured. But any one sensation is a point on a scale, and can no more be measured, in *itself*, than can the top of the pole, which, in itself, is merely a point on a scale of heights.

Thus for Titchener; Dr. Houston adopts a method which may be interpreted in similar terms. He shews, for example, that a scale of brightness sensations may be built up by means of a simple experiment with a wedge photometer. Two lamps, A and B, are adjusted in position until the two faces of the photometer are equally bright. Readings of the positions of A and B are taken, and A is moved in until one face of the wedge is just noticeably brighter than the other. B is moved in until balance is just restored, then A is again moved in, and so on. Taking these steps as measures of unit sensation distance, experiments are described which shew how steps of different magnitude may be taken along this scale. He adopts, also, another method of description, and it is a matter for discussion whether the two methods are, or are not, fundamentally identical.

Consider, for a moment, the ordinary statement of *Weber's law* (*not* the Weber-Fechner law) which, we must remember, is an experimental law, and is concerned purely with objective stimuli. If the magnitude of any stimulus is I, then the least perceptible increase (δI) of the stimulus, is proportional to that stimulus. Thus, if an observer can *just* distinguish between the weight of 29 and of 30 *drams*, he will just be able to distinguish between 29 and 30 *ounces*. As usually stated,

$$\delta I/I = k.$$

The method of statement is unfortunate, and a certain amount of confusion has arisen from the occasional non-recognition of the fact that δI is not a differential, but is a differential coefficient. It is the rate of increase of stimulus with sensation, and should be written ($\delta I/\delta S$). The statement of the law is now ($\delta I/\delta S$) $= kI$, and in this form may be taken as unexceptionable. But if we integrate to obtain

$$S = k \log I + C, \qquad (2)$$

we are tacitly assuming that $\Sigma\delta S = S$, that is, that a sensation may be regarded as built up from a number of elements of sensation—a conclusion which is hotly contested in many quarters.

In spite of Titchener's distinction between "distance" measurements and absolute determinations of sensation-magnitudes, it is questionable whether his argument (which is the argument of most psychologists since Delboeuf) does more than evade the point; equation (1) is of course a direct deduction from equation (2), and *any* formulation of the Weber-Fechner law involves, tacitly or overtly, an integration of the Weber equation and the consequent assumption that $\Sigma\delta S = S$. The fact is, that experimental psychologists in the main have been obsessed by the picture afforded of length-magnitudes built up by the direct opposition of unit-lengths, and that of sensations as points on a scale of "distances." Stumpf's observation "Jede Empfindung präsentirt sich als Unteilbares" has been the theme of volumes of criticism all tending to shew that it is the "sensation-interval and not the sensation itself that is measured, all based on the length-analogy just described. And yet, if we break away from the dominating length-analogy, a magnitude such as the surface-tension (T) of water at 15°C "präsentirt sich als Unteilbares," a fact which does not in the least dismay us, when, faced with an equation such as $dT/d\Theta = f(\Theta)$, we integrate and obtain a consistent and correct delineation of the variation of surface tension with temperature.

Again, a certain weight of criticism has been brought to bear on the assumption, commonly made, that the just noticeable differences on which a scale of sensation has been built up (compare Dr. Houston's wedge-photometer experiment, just cited) are *equal* unit-steps on the scale of sensation. Many of the criticisms are of very doubtful validity; thus, Fechner maintained that the just noticeable difference of sensation obtained when one dram is added to twenty-nine drams is equal to that obtained when one ounce is added to twenty-nine ounces. It has been seriously advanced as a criticism of this attitude that, were this so, an ounce and a dram would produce an equal sensation—as remarkable an *ignoratio elenchi* as has ever come before the writer's notice.

Dr. Houston does not spend much time in considering critically the dicta of adverse commentation in this field; he remarks, in effect, *solvitur ambulando*, and proceeds, unperturbed, with his investigations—an attitude towards which the present reviewer confesses a certain amount of sympathy. Adopting, then, the possibility of putting $\Sigma\delta S$ equal to S, Dr. Houston, in the matter of visual intensities, has made a very notable contribution to knowledge by plotting $I \times (\delta I/\delta S)$ as ordinate against $\log I$ as abscissa. It will be seen that an element of area $y\,dx$ under the resulting curve is

$$(I\delta S/\delta I) \times \delta(\log I) = \delta S,$$

so that "the sensation at any point on the axis of abscissae is proportional to the area to the left of that point. This holds no matter what the shape of the curve is."

Further, the experimental points fit, with considerable accuracy, a Gaussian probability curve, so that for any value x (= *log* I) of the abscissa, the sensation corresponding to the intensity I is given by

$$S = \int_{-\infty}^{x} l^{-\frac{1}{2}x^2} - dx.$$

One minor point may be noted. In a work making great use of a measure of sensation the very existence of which is in dispute, it is necessary to be meticulously careful in matters of nomenclature. Dr. Houston (p.2) discusses a "unit of the sensation of brightness" which "is wholly subjective." This is the quantity which we have been discussing at some length. A little later (pp. 8 and 9) he writes of the measurement of "subjective brightness, the brightness of the image on the retina," and points out that "when the brightness of the object is *m* milli-lamberts and the area of the pupil is *a* square millimetres, the brightness of the image on the retina is said to be *m a*" units. This last-named unit is obviously purely objective, and the double use of the term *subjective* is unfortunate.

Dr. Houston's book, whether regarded as a compendium of standard knowledge, or as a comprehensive account of recent investigations, is an important contribution to existing literature. Beginners in the subject may have to tread warily when reading certain sections, but the advanced student will find the book everywhere stimulating and suggestive.

Allan Ferguson

Das ultrarote Spektrum. *By Clemens Schaefer and Frank Matossi. 22 × 14 cm. pp. vi + 400. Berlin: Julius Springer, 1930.* This is the tenth volume of the "Struktur der Materie" series of monographs edited by Born and Franck. The experience of the authors, gained by original work in the field of infra red radiation, has enabled them to produce a book which should be of value to two classes of readers; those who wish only a general survey of the field, for which purpose the book is complete in itself, and the research workers in this field for whom the very complete list of references will be useful in seeking the details of the experiments in which they may be interested.

The authors have, for the most part, treated only those phenomena in which infra red radiation plays the main rôle. They have, accordingly, left out all accounts of phenomena in which electronic transitions occur, either alone or in conjunction with other energy changes in the molecule. There is a very good interweaving of theoretical discussions and descriptions of the experimental work which makes the book very readable. Although the main part of the book is taken up with the more modern aspects of research in the field, a brief account of the older work is included to make the book a fairly complete account of the subject to date.

After a brief historical introduction, the first chapter is devoted to a discussion of the various experimental methods employed in the investigations. The second chapter is a very brief discussion of the theoretical and experimental work on thermal radiation. The third chapter is an account of the Maxwell theory of radiation and its application to the optical properties of insulators and metals.

The fourth and fifth chapters form the main part of the book and, indeed, are the justification for the appearance of the volume. The fourth chapter contains a discussion of the modern theory of band spectra due to transitions in molecular states in which there is no electronic transition. The application of the theory to the problems of molecular structure and dissociation energies is pointed out. In addition to this discussion of problems associated with spectra from free molecules some space is given to the absorption spectra of liquids. The fifth chapter contains a treatment of the Born theory of crystal vibration and its application to the infra red spectrum of crystals. A great deal of experimental work in this field is described and the bearing of the theory on the results pointed out. These last two chapters contain a very good résumé of the recent work and on this account the book will be indispensable in the research laboratory.

J. R. Collins

Colloid Chemistry. *Edited by Jerome Alexander. Vol. IV. 23 × 16 cm; pp. 734. Chemical Catalog Company, 1932. Price: $11.50.* This volume is the second covering technological applications. The subjects discussed are: carbohydrates, including cellulose, wood, paper, explosives, sugar, starch products, sizing; dyeing; rubber, including latex and carbon black; plastics; tanning; photography; coatings, including paints, color lakes, and electrodeposition; foods; laundry and dry-cleaning; solidified alcohol and fire extinguishers; water supply and sewage disposal.

The papers and authors are: colloid chemistry of cellulose, Max Samec; colloid chemistry of wood and wood-formation, H. Wislicenus; colloid chemistry in the paper industry, R. Lorenz; cellulose esters, E. W. J. Mardles; smokeless powder, C. G. Storm; structural variations in smokeless powders, A. J. Phillips; colloid chemistry in the sugar industry, R. I. Balch and H. S. Paine; applied colloid chemistry in confectionery manufacture, Stroud Jordan; a summary of the colloid chemistry of starches, Max Samec; starch and some of its derivatives, V. G. Bloede; sizing and finishing of textile materials, L. A. Olney; the process of dyeing, Georg Georgievics; dyeing, William Harrison; theory of dyeing, W. D. Bancroft; the colloid chemistry of rubber latex and its industrial applications, A. van Rossem; the structure of rubber, E. B. Spear; physico-chemical aspects of Hevea rubber, R. P. Dinsmore; carbon black in the rubber industry, N. A. Shepard; synthetic resins, H. L. Bender; dispergation and aggregation of natural silk in aqueous solutions of neutral salts, P. P. von Weimarn; technologically useful properties of casein, F. L. Browne; tanning, and the modern theory of colloidal swelling, H. R. Procter; tanning, E. Stiasny, tanning, G. D. McLaughlin; colloid chemistry and photography, Lüppo-Cramer; colloids and photochemistry, S. E. Sheppard; color photography, H. Mouquin; notes on colloidal phenomena in paint and varnish products, H. A. Gardner; colloidal aspects of paint and varnish removers, Norris Boehmer; water-Japan, W. P. Dewey; synthetic mother-of-pearl, L. Clément and C. Rivière; color lakes, H. B. Weiser; addition agents in electrodeposition, William Blum; colloidal aspects of baking chemistry, C. N. Frey and Quick Landis; butter and margarine from the standpoint of colloid chemistry, William Clayton; colloidal chemistry and the art of brewing, Fritz Emslander; the pectic substances, Ruth Johnstin and Mary A. Griggs; "solidified" alcohol, P. C. L. Thorne and C. G. Smith; alkaline and other detergents, H. G. Elledge; the colloid chemistry of washing, L. Zakarias; the foam method of extinguishing fire, C. B. White; colloidal aspects of waste treatment, A. M. Buswell.

"Sugar is adsorbed by cellulose from alcoholic solution, a circumstance which can cause large errors in the determination of sugar in beets by alcoholic digestion," p. 14. The salts of organic bases are adsorbed by cellulose both in neutral solution and in a solution containing soda; in some cases the addition has a favorable influence, in other cases an arresting influence, on the adsorption. The strong adsorption of diamine salts (except o-phenylene diamine), benzidine, and the hydrazines is remarkable," p. 18. "Schwalbe attained the maximum swelling of cellulose by beating in a 0.1 percent solution of lactic acid; cellulose fibers impregnated with such a liquor retain five times their own weight of water after being centrifuged, whereas cellulose swelled in water alone does not bind more than one and a half times its own weight of water," p. 78.

"Traube found that latex will cream at a temperature of 50° after the addition of mucilaginous substances, such as a two percent sol of Irish moss. It has long been known that creaming of ordinary cow's milk is accelerated considerably by the addition of such substances; but this process is carried out in the milk industry at a low temperature, about 10°. Some experiments carried out at the Netherlands Government Rubber Institute with an ammoniated latex showed that the creaming of rubber latex is successful only at higher temperatures, e.g. 50°. Preliminary experiments proved albumin, casein, and gelatin to be ineffective; but, besides carragheen (Irish moss), tragacanth, saleb, agar-agar, and pectinous substances gave positive results," p. 257.

"When calcium carbonate is formed by diffusion into a colloidal mass, it automatically forms itself into an alveolar net-work, which optically, produces a pearly effect. Pearliness is not a specific property of calcium carbonate; in fact we can produce a more or less beautiful pearly effect with other salts—barium, lead, silver, copper. The superior beauty of calcium carbonate pearl is due to its fineness of grain. . . . We believe that our experiments represent a true synthesis," p. 504. Unfortunately Clément and Rivière did not determine whether the calcium carbonate was precipitated as aragonite.

Some of the more important emulsifying agents and their uses as employed in the baking industry are: gelatin for icings; egg albumen for cakes and frostings; egg yolks for cakes and custards; Indian tragacanth (Karaya) for icings; stearines and oxidized vegetable oils for caramels; and lecithin for cream fillings, p. 560.

"A garment or other textile article ready for the laundry or for dry cleaning is said to be soiled, a term really including dirty and stained. Loosely the three expressions are used synonymously. There is some precedent in the limited writings on cleansing to use the word stain to designate the more refractory localized discolorations, and dirt the more common soiling bodies. In these senses they are used here. Dirt is simply adsorbed particles, discolorants left on a surface by contact or by evaporation of a dispersing fluid. A stain usually requires treatment other than that accorded in the regular cleansing procedure. Thus in ordinary water washing, chewing gum is a stain, because it is most readily removed by a special solvent, namely carbon tetrachloride. In dry cleaning, maple syrup is a stain, because waterborne stains are not removed by the usual petroleum solvent," p. 636.

Wilder D. Bancroft

Introduction to Agricultural Biochemistry. *By R. A. Dutcher and D. E. Haley. 23 × 15 cm; pp. ix + 484. New York: John Wiley and Sons, 1932. Price: $4.50.* "The present volume is an outgrowth of lectures presented to agricultural students over a period of nearly twenty years. The book is designed for those students who have had preliminary training in inorganic and organic chemistry," p. *v*. It represents a well-written, interesting, and teachable survey of a large number of fields related to the interests of agricultural students. The book is divided into three parts.

Part one deals with the general applications of chemistry to these fields, and includes chapters on the development of agricultural chemistry, the chemistry of living matter, the carbohydrates, fats and related compounds, proteins, enzymes, and a chapter on the physical state of matter which includes a brief discussion of certain phases of colloid chemistry which are recognized as of dominant importance.

The second part is concerned with the plant, with especial emphasis on the plant food. This includes chapters on seed germination, the soil, soil acidity, farm manure, fertilizers, the atmosphere, insecticide and fungicides and related materials, absorption of mineral nutriments by plants, assimilation of mineral nutriments by plants, the plant carbohydrates, plant lipoids, vegetable proteins and related compounds, and respiration.

In the third part the animal is discussed in chapters entitled: foods and feeding stuffs, digestion of food, body tissues, metabolic changes in tissues, energy metabolism, biological response to foods, protein quality, vitamin A, vitamin B complex (B and G), vitamin C, vitamin D and ultraviolet light, and vitamin E. The chapters on nutrition and on the vitamins are particularly interesting and include much of the work done by the senior author in that field.

Throughout the book the writing is done in such a manner as to stimulate the reader to refer to some of the general references given at the end of each chapter. The impression is conveyed that the application of chemistry to many of these biochemical problems is but well begun and frequent are the points which are still in doubt. For these, condensed statements are given of the evidence now in and a basis laid for the correlation of the evidence yet to come.

The general philosophy which appears to underlie the book is refreshing. In the first chapter, after describing the experiment of van Helmont in which he believed he had grown one hundred sixty-four pounds of wood, bark, and roots of his willow tree from water alone, the authors comment; "This experiment, however, is thoroughly typical of much of the early investigational work in agricultural chemistry, as well as of other sciences. In this, as in other branches of science, it is very easy to fail to consider a vital factor and as a result, draw, from perfectly good experiments, a conclusion which appears to be correct but which is, in reality, entirely wrong. In the work cited above, van Helmont failed to take into consideration two most important factors, namely, the rôle played by the constituents of the atmosphere and the two ounces of soil which had disappeared. Hopkins has very truthfully said that an experiment is a question put to Nature, and Nature always answers every question truthfully, but the question that Nature answers and that the experimenter asks is not always the question that he thinks he asks," p. 7.

This book has many features to commend it and should prove an effective textbook for courses in agricultural biochemistry. *Herbert L. Davis*

Das periodische System in neuer Anordnung. *By Darwin O. Lyon. Second edition. 26 × 18 cm; pp. 40. Leipzig and Wien: Franz Deuticke, 1931. Price: 8 marks.* This book is essentially a work of reference on the physical properties of the chemical elements. These are presented to the reader in many tables, spirals and charts, some of which are in the form of those slight departures from the conventional, best representations of the periodic classification, which every writer on the subject feels actuated to make. These novel features were described and discussed, and, on the whole, commended in these pages (**32**, 1891 (1928)), at the time of publication of the original edition. The merit of the present work is that the great mass of information on many physical properties of the elements has been brought up to date. To those who did not see the first edition it may be said that Dr. Lyon's book is a breakaway from a survey of the periodic classification to which chemists are accustomed: from the chemical or physical-chemical points associated with such names as Mendeléef, Bohr and Aston. The author is concerned almost exclusively with the periodicity of such physical properties as magnetism (of which he has evidently made a special study, and on which he is good), resistance, entropy, thermal expansion, and sound conductivity, as well as the more usual properties which the textbooks describe. Nothing very novel has emerged in these compilations, but the information has been carefully collected and is critically as well as strikingly represented. The book is not in any bad sense 'viewy'. It is a work of learning which might well be included in a physical chemist's library. *A. S. Russell*

Kapillarchemie. *Eine Darstellung der Chemie der Kolloide und verwandter Gebiete. By Herbert Freundlich. Fourth Edition, revised with the assistance of J. Bikerman. Vol. I. 24 × 18 cm; pp. viii + 566. Leipzig: Akademische Verlagsgesellschaft, 1930. Price: 36 marks, bound 39 marks.* The fourth edition of this standard work is issued in two volumes. The first volume includes a discussion of the fundamental physical-chemical principles of colloid chemistry which the author groups under the term Kapillarchemie.

The book is divided into three portions, the first of these filling about 90% of the book under the general title Kapillarchemie. Discussion of the phenomena at various types of interfaces is the outline. These include liquid-vapor, liquid-liquid, solid-vapor, and solid-liquid. The first division also includes chapters on electrical phenomena and the properties of interfacial layers. The second division of the book treats of the kinetics of the formation of a new phase, particularly of a new solid phase. In the third division is found a discussion of Brownian movement and its mathematical formulation and significance.

From the standpoint of economy as well as that of convenience of use, it seems that a single volume edition might have been preferable even if it meant some omissions or abbreviations of discussion. The new edition is, like the previous ones, fitted to take a high place as one of the best reference books for workers in colloid chemistry. Revision has been extensive and the book represents a valuable survey of the phenomena illumined by the interpretations of a master of this fast-growing field. *Herbert L. Davis*

SEDIMENTATION OF CLAYS[1]

BY E. W. KANNING, R. J. HARTMAN AND FLOYD CHILDS

Introduction

The rate of sedimentation of particles from aqueous suspensions is a measure of the particle size. This was first shown by Stokes[2] in his classical discussion in the year 1846.

The combined forces which start any motion in suspended particles are due either to the buoyant force of the liquid or to the force of gravity. The force of gravity is always downward and is constant at a given location under similar conditions. As soon as the suspended particles start to fall, the retarding force of the liquid becomes active. This force is due to the viscosity of the liquid and is equal to $6\pi nrv$ where n is the viscosity coefficient of the liquid, r is the radius of the particles, and v is the velocity of settling in centimeters per second (constant rate of fall). This retarding force acts in opposition to gravity which is equal to $4/3\pi r^3(d_1-d_2)g$. Where d_1 is the specific gravity of the particles, d_2 is the specific gravity of the liquid, and g is the gravitational constant expressed in dynes. If the retarding force due to the viscosity of the liquid is equal to the force of gravity, the rate of settling of the particles would be constant. This may be shown by

$$6\pi nrv = 4/3\pi r_2(d_1-d_2)g.$$

From this equation is derived Stokes' law

$$v = \frac{2r^2(d_1-d_2)g}{9n}.^3$$

In any specific instance where the same material is suspended, d_1, d_2, g, and n are constant, and, therefore, the equation may be written

$$v = Kr^2 \quad \text{or} \quad r^2 = v/K.$$

Where particles are so small that sedimentation does not take place Stokes' law does not apply, since other forces such as Brownian movements act to keep the particles in suspension.

In this investigation Stokes' law has been applied to dilute aqueous clay suspensions for the measurement of the size and the velocity of fall of the particles. The clays studied are representative samples[4] from nine entirely different clay deposits in the state of Indiana.

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[1] Contribution from the Laboratory of Colloid Chemistry, Indiana University, Bloomington.

[2] Phil. Mag., 29, 60-62 (1846); Camb. Phil. Soc. Trans., 8, 287-319 (1846); 9, 8 (1856).

[3] "Mathematical and Physical Papers," 3, 1 (1910). For modifications and limitations see Cunningham: Proc. Roy. Soc., 83R, 357 (1910); J. Am. Chem. Soc., 41, 319 (1919); Millikan: Physik. Z., 11, 1097 (1910); Phys. Rev., (2) 22, 1 (1923); Ishida: Phys. Rev., (2) 21, 550 (1923).

[4] These samples were collected and classified by George I. Whitlatch under the direction of Dr. W. N. Logan, state geologist and professor of geology, Indiana University.

Experimental

Clays studied: The various clays studied, their geologic classification and location from which they were collected are cited in Table I.

TABLE I

Clay No.	Geologic Classification	Geographic Location
1	Borden Shale	Brooklyn, Indiana
2	Pennsylvanian Under Clay	Ashboro, Indiana South Pit of Big Ben Coal Co.
3	Pennsylvanian Shale (Ruby Shale)	Evansville, Indiana Standard Brick Co.
4	Chester Shale	Huron, Indiana
5	New Albany Clay	Wolcottville, Indiana
6	Alluvial Clay	Evansville, Indiana Standard Brick Co.
7	Kaolin	Lawrence County, Indiana
8	Mahogany Clay	Willow Valley Lawrence County, Indiana
9	Glacial Residual	Fort Wayne, Indiana Fort Wayne Brick Co.

The clays were dried in air at room temperature for four months, and ground in a mortar until the entire sample passed through a 40 mesh sieve. The ground clays were quartered down to 50 gram samples from which an aliquot part was weighed for the study of sedimentation. The clay suspensions consisted of known weights of approximately five grams of dry clay dispersed in 200 cubic centimeters of pure distilled water.

Apparatus and Procedure: An apparatus for the determination of sedimentation such as that of Calbeck and Harner[1] was not available, therefore a modification of this apparatus was improvised. Fig. 1 illustrates the construction of the apparatus used for determining sedimentation in this investigation.

A—Beam of analytical balance.

B—Glass cylinder, 10.16 cm. tall and 6.98 cm. diameter (inside measurements), resting on the bridge D.

C—Balance pan.

D—Wooden bridge over balance pan clearing same 2 cm.

E—Thin copper disc, 4.2 cm. in diameter.

F—Copper wires soldered to the disc E at three equidistant points.

G—Cork stopper.

H—Aqueous clay suspension.

I—Floor of balance.

J—Thermometer suspended from balance case.

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[1] J. C. Ware: "Chemistry of the Colloidal State," 36 (1930).

Into the glass cylinder B was placed 200 cm. of pure distilled water at 20°C. measured accurately with a pipette. This volume covered the copper disc E with 5.1 cm. of water. Approximately 35.32% of the total volume of the liquid was above the copper disc. The disc was tared by placing sufficient weights on the opposite pan. Approximately five grams of dry clay accurately weighed was added to the water and the mixture vigorously agitated by means of the copper disc E, temporarily disengaged from the balance hook. When the clay particles were thoroughly dispersed in the water the agitation was stopped, the copper plate replaced and a stop watch started. The balance arrest was adjusted so that the beam could swing only through a very small angle, causing a deflection of the pointer on the scale of but one division in either direction. As the clay particles settled on the disc E the pointer began to swing to the right. During the period of sedimentation it was necessary to add weights to the right pan and adjust the rider on the balance beam so that when a definite time period expired, the exact weight of the clay particles on the disc could be recorded.

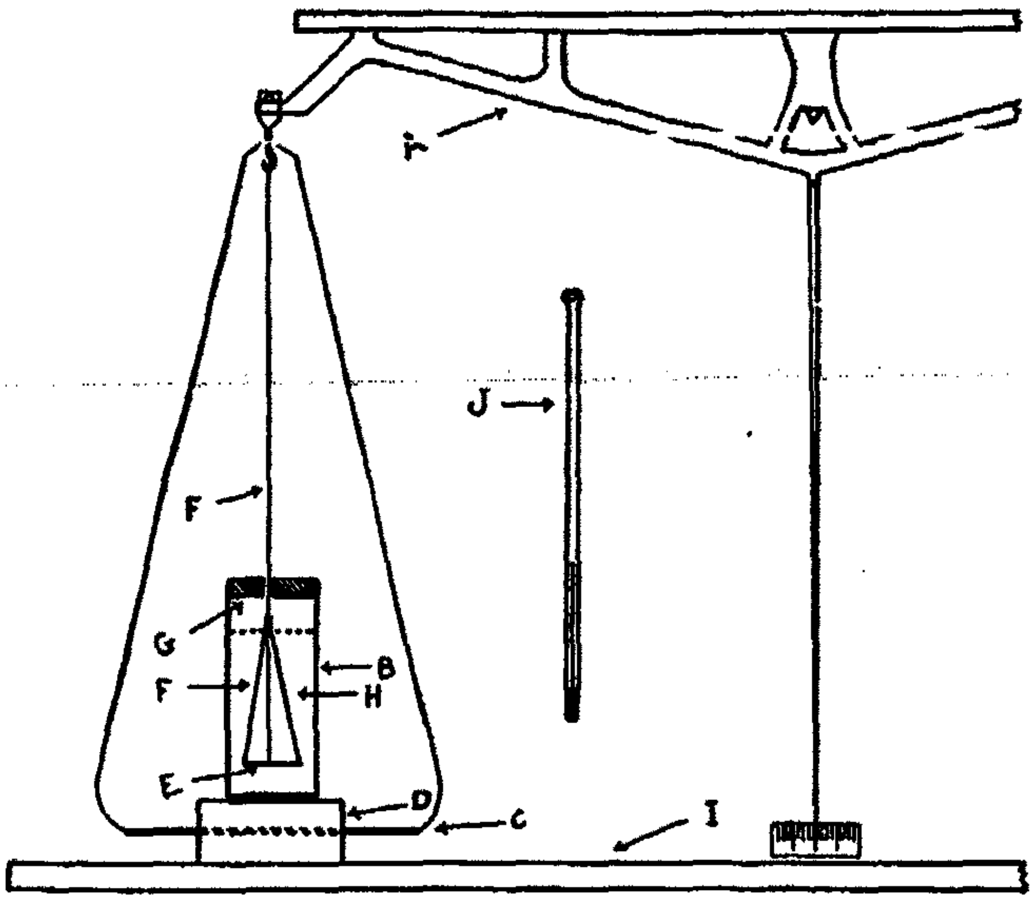


FIG. 1

The same apparatus was applied to the determination of the specific gravity of the dry clays. The specific gravity was found by dividing the weight of the dry clay by the loss of weight in water. In order to determine the weight of the clay in water, a small porcelain crucible was placed on the disc E, immersed in 200 cc. of distilled water in the glass cylinder B, and weighed. The disc was lifted and nearly all of the water poured out of the crucible back into the vessel and a known weight of clay placed in the crucible. Sufficient time was allowed for the clay to be thoroughly wetted by the water in the crucible. The crucible was then very slowly submerged in the water to prevent washing any of the clay sample out of the crucible. (This operation required several minutes). The weight in water of the crucible and clay was taken and the weight of the clay in water calculated by difference. The loss of weight in water was obtained by subtracting the weight of the clay in water from the weight in air.

Data and Results: Table II gives the specific gravity of each clay as determined in the above described manner.

TABLE II

Specific Gravity of Clay Samples

Clay No.	1	2	3	4	5	6	7	8	9
Specific Gravity*	2.55	2.40	2.53	2.51	2.43	2.00	2.26	2.45	2.41

* Each clay sample contained particles of various specific gravities; therefore, the specific gravity as determined is a mean value for all particles in that sample.

In order to determine the radius of the particles of clay samples it was necessary to determine by calculation the velocity of fall of particles (v in Stokes' law) settling at the definite experimental time intervals. The velocity in cm. per second was determined by dividing the distance of fall (5.1 cm.) by the total time elapsed in seconds for each time interval. Table III shows the velocity of fall of the clay particles settled out at definite indicated time intervals from aqueous suspension.

TABLE III

Velocity of Fall of Clay Suspensions in Water

Time in min. to fall 5.1 cm.	Time in sec. to fall 1 cm.	Velocity in cm. per second	Time in min. to fall 5.1 cm.	Time in sec. to fall 1 cm.	Velocity in cm. per second
2	23.53	.042500000	45	529.38	.001888888
5	58.82	.017000000	60	705.84	.001416666
10	117.64	.008500000	75	872.30	.001133333
15	176.46	.005666666	90	1058.76	.000944444
30	352.92	.002833333	120	1411.68	.000708333

Stokes' law was applied in determining the radii of the various clay particles by using the specific gravities of the various clays given in Table II, the velocities in centimeters per second for the various time intervals employed in the experimentation (Table III), the specific gravity and the viscosity coefficient of water at 20°C., and the gravitational constant. Table IV shows the results, mathematically calculated from Stokes' law, of the radii of the particles of the various clays studied. The radii of the clay particles, having settled at the definite indicated times, are equal to or greater than the values given in the table. At the expiration of two minutes the radii of the particles are equal to or greater than that indicated in Table IV for that time and not greater than that which would pass through a 40 mesh sieve. At any definite time thereafter the radii of the particles are equal to or greater than that indicated in Table IV for that time but not greater than the value indicated for the preceding time. For example, the particles in Clay No. 1 which settled out in 2 minutes had radii equal to or greater than .0011315 cm. Since the sample had passed through a 40 mesh sieve, no particle larger than the apertures of the sieve could be present. There are unquestionably many particles whose radii will vary between these two limits and it is possible that during this first time period some particles even smaller than .0011315 cm. could have settled. These smaller particles may have settled from only a short distance above the disc. The radii of the particles of Clay No. 1 which settled out during the next 3 minutes (time = 5 min.) will be equal to or greater than .0007156 cm. and not greater than .0011315 cm. The same is true between any of the time intervals in Table IV.

TABLE IV

Radii in Cm. of Clay Particles*

Time in min. to fall 5.1 cm.	Number of Clay 1	2	3	4	5
2	.0011315	.0011821	.0011315	.0011523	.0011703
5	.0007156	.0007481	.0007156	.0007205	.0007402
10	.0005060	.0005290	.0005060	.0005093	.0005234
15	.0004131	.0004319	.0004131	.0004159	.0004273
30	.0002921	.0003054	.0002921	.0002940	.0003021
45	.0002385	.0002493	.0002385	.0002408	.0002467
60	.0002065	.0002159	.0002065	.0002079	.0002136
75	.0001832	.0001932	.0001832	.0001859	.0001911
90	.0001686	.0001763	.0001686	.0001702	.0001744
120	.0001460	.0001527	.0001460	.0001470	.0001510

Time in min. to fall 5.1 cm.	Number of Clay 6	7	8	9
2	.0010154	.0012467	.0011664	.0011731
5	.0006422	.0007885	.0007377	.0007419
10	.0004541	.0005566	.0005217	.0005246
15	.0003708	.0004552	.0004259	.0004283
30	.0002622	.0003219	.0003011	.0003028
45	.0002140	.0002628	.0002459	.0002473
60	.0001854	.0002276	.0002124	.0002141
75	.0001658	.0002036	.0001904	.0001915
90	.0001513	.0001858	.0001739	.0001748
120	.0001311	.0001609	.0001505	.0001514

* The radii of the various clay particles are equal to or greater than the value indicated for the various time intervals.

In order to determine the sedimentation curves for the clays with the procedure and apparatus previously described, it was necessary to obtain the data shown in Table V which includes the following: total time in minutes at intervals, total grams of clay particles settled at the indicated time intervals, the increase in grams over the previous period which is the actual weight settled during each interval, the per cent settled of the total weight in suspension and the per cent settled between each interval. The per cent settled of the total weight in suspension was calculated with the total grams settled within the maximum time indicated at 100%. The per cent settled during each interval was calculated on the same basis.

TABLE V

Sedimentation of Clay Particles

Time in Minutes	Total Grams settled	Increase in Grams over Previous Period	Per Cent settled of Total in Suspension	Per cent settled between each Interval
		Clay No. 1		
2	.4278	.4728	62.4	62.40
5	.5367	.0639	70.9	8.45
10	.5834	.0467	77.0	6.16
15	.6099	.0265	80.5	3.50
30	.6446	.0347	85.1	4.58
45	.6651	.0205	87.8	2.71
60	.6746	.0095	89.2	1.25
75	.6833	.0085	90.9	1.12
90	.6894	.0061	91.7	0.81
120	.6988	.0091	92.9	1.20
1440	.7476	.0488	99.5	6.44
2880*	.7568	.0092	100.0	1.21
				Total 99.83
		Clay No. 2		
2	.2500	.2500	43.3	43.3
5	.3282	.0782	56.9	13.5
10	.3802	.0520	65.9	9.0
15	.4113	.0311	71.3	5.4
30	.4605	.0492	79.8	8.8
45	.4831	.0226	83.7	3.9
60	.4912	.0081	84.6	1.4
75	.5008	.0096	86.8	1.6
90	.5092	.0084	88.2	1.4
120	.5201	.0109	90.1	1.9
150	.5283	.0082	91.1	1.4
1440	.5769	.0486	100.0	8.4
				Total 100.0

* When the time indicated had elapsed the liquid above the disc was still very slightly turbid.

Table V (Continued)

Sedimentation of Clay Particles

Time in Minutes	Total Grams settled	Increase in Grams over Previous Period	Per Cent settled of Total in Suspension	Per Cent settled between each Interval
		Clay No. 3		
2	.1493	.1493	32.1	32.1
5	.2294	.0801	49.3	17.2
10	.2900	.0606	62.3	13.0
15	.3100	.0200	66.6	4.3
30	.3618	.0518	77.2	11.1
45	.3772	.0154	81.1	3.3
60	.3890	.0118	83.6	2.7
75	.3980	.0090	85.5	1.9
90	.4042	.0062	86.6	1.3
120	.4100	.0058	88.1	1.2
150	.4151	.0051	89.2	1.1
1440*	.4653	.0502	100.0	10.8
				Total 99.9
		Clay No. 4		
2	.7699	.7699	94.7	94.700
5	.7977	.0278	98.0	3.410
10	.8017	.0040	98.4	0.490
15	.8053	.0036	98.9	0.440
30	.8054	.0001	99.0	0.001
45	.8055	.0001	99.0	0.001
60	.8063	.0008	99.1	0.009
75	.8071	.0008	99.1	0.009
90	.8080	.0009	99.2	0.011
120	.8097	.0007	99.3	0.008
150	.8106	.0009	99.5	0.011
1440	.8145	.0039	100.0	0.480
				Total 99.570
		Clay No. 5		
2	.4136	.4136	64.1	64.10
5	.4627	.0491	71.3	7.64
10	.4958	.0331	77.2	5.15
15	.5114	.0156	79.5	2.42
30	.5315	.0201	82.6	3.12
45	.5575	.0260	86.7	4.05
60	.5688	.0113	88.3	1.75
75	.5741	.0053	89.2	0.82
90	.5819	.0078	90.5	1.21
120	.5903	.0084	91.6	1.30
1440*	.6443	.0540	100.0	8.40
				Total 99.96

* When the time indicated had elapsed the liquid above the disc was still very slightly turbid.

TABLE V (Continued)

Sedimentation of Clay Particles

Time in Minutes	Total Grams settled	Increase in Grams over Previous Period	Per Cent settled of Total in Suspension	Per Cent settled between each Interval
		Clay No. 6		
2	.6443	.6443	64.8	64.80
5	.7655	.1212	77.1	11.32
10	.8359	.0704	84.1	7.13
15	.8581	.0222	86.5	2.21
30	.8993	.0412	89.6	4.15
45	.9184	.0211	92.4	2.11
60	.9293	.0109	93.6	1.15
75	.9350	.0057	94.3	0.57
90	.9429	.0079	95.0	0.79
120	.9517	.0108	95.9	1.14
2880*	.9945	.0428	100.0	4.33
				Total 99.80
		Clay No. 7		
2	.3838	.3838	98.3	98.3
5	.3878	.0040	99.3	1.0
10	.3901	.0023	99.9	0.6
15	.3902	.0001	100.0	0.1
30	No gain	No gain		Total 100.0
45	No gain	No gain		
		Clay No. 8		
2	.6600	.6600	96.9	96.90
5	.6749	.0149	99.1	2.20
10	.6793	.0044	99.7	0.64
15	.6795	.0002	99.8	0.01
30	.6804	.0009	99.9	0.02
45	.6806	.0002	100.0	0.01
60	No gain	No gain		Total 99.78
75	No gain	No gain		
		Clay No. 9		
2	.5928	.5928	68.1	68.10
5	.6951	.1023	77.8	11.80
10	.7710	.0759	88.5	8.71
15	.7821	.0111	89.8	1.16
30	.8220	.0399	94.4	4.58
45	.8378	.0158	95.5	1.81
60	.8476	.0102	97.3	1.17
75	.8518	.0042	97.7	0.48
90	.8543	.0025	98.0	0.28
120	.8612	.0069	99.0	0.79
1440	.8712	.0100	100.0	1.15
				Total 100.03

* When the time indicated had elapsed the liquid above the disc was still very slightly turbid.

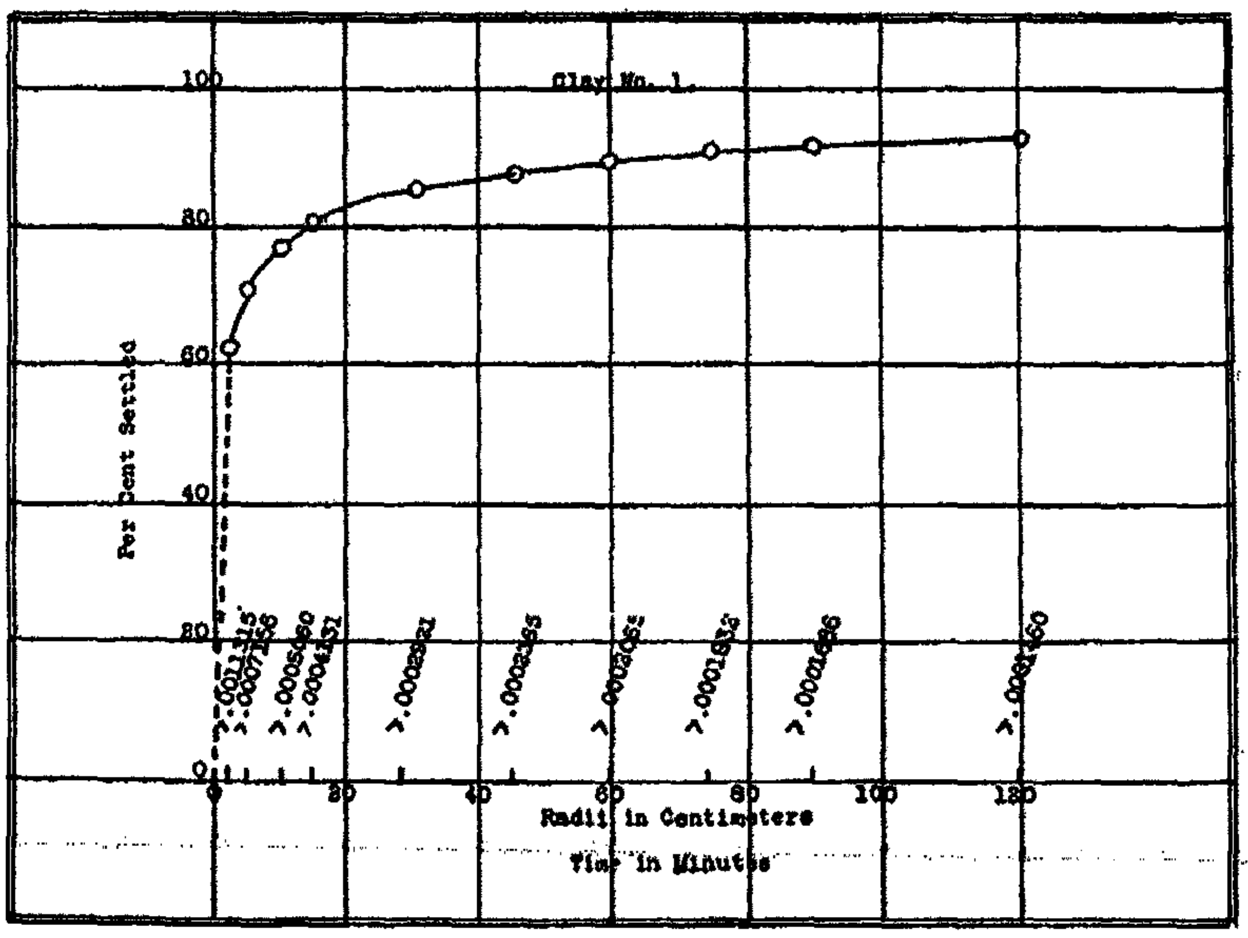

Clay No. 1.
Per Cent Settled
100
80
60
40
20
0
>.0011315
>.0007156
>.0005060
>.0004151
>.0002921
>.0002385
>.0002065
>.0001852
>.0001686
>.0001460
0
20
40
60
80
100
120
Radii in Centimeters
Time in Minutes

FIG. 2

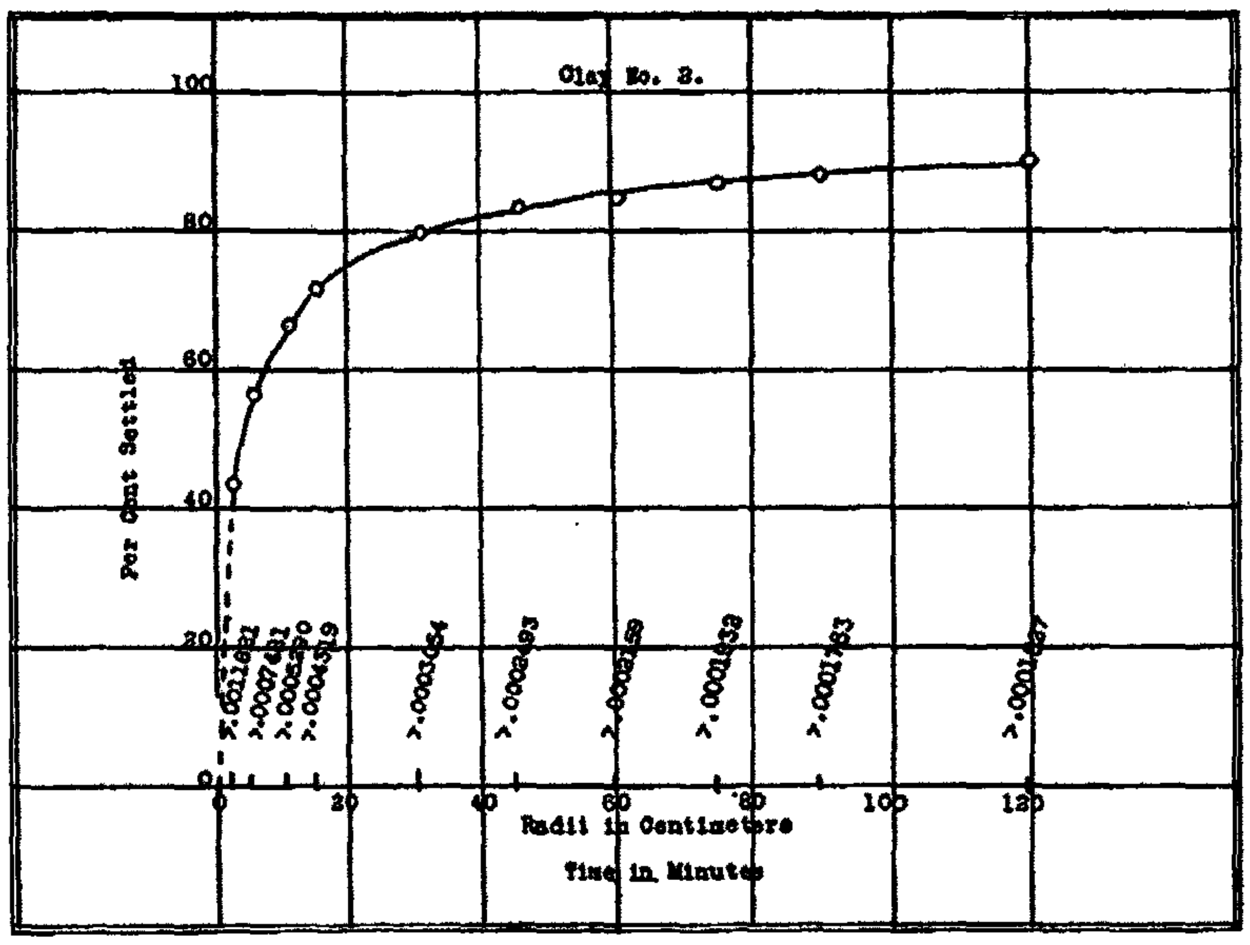

Clay No. 2.
Per Cent Settled
100
80
60
40
20
0
>.0011621
>.0007431
>.0005370
>.0004519
>.0003054
>.0002493
>.0002158
>.0001933
>.0001763
>.0001527
0
20
40
60
80
100
120
Radii in Centimeters
Time in Minutes

FIG. 3

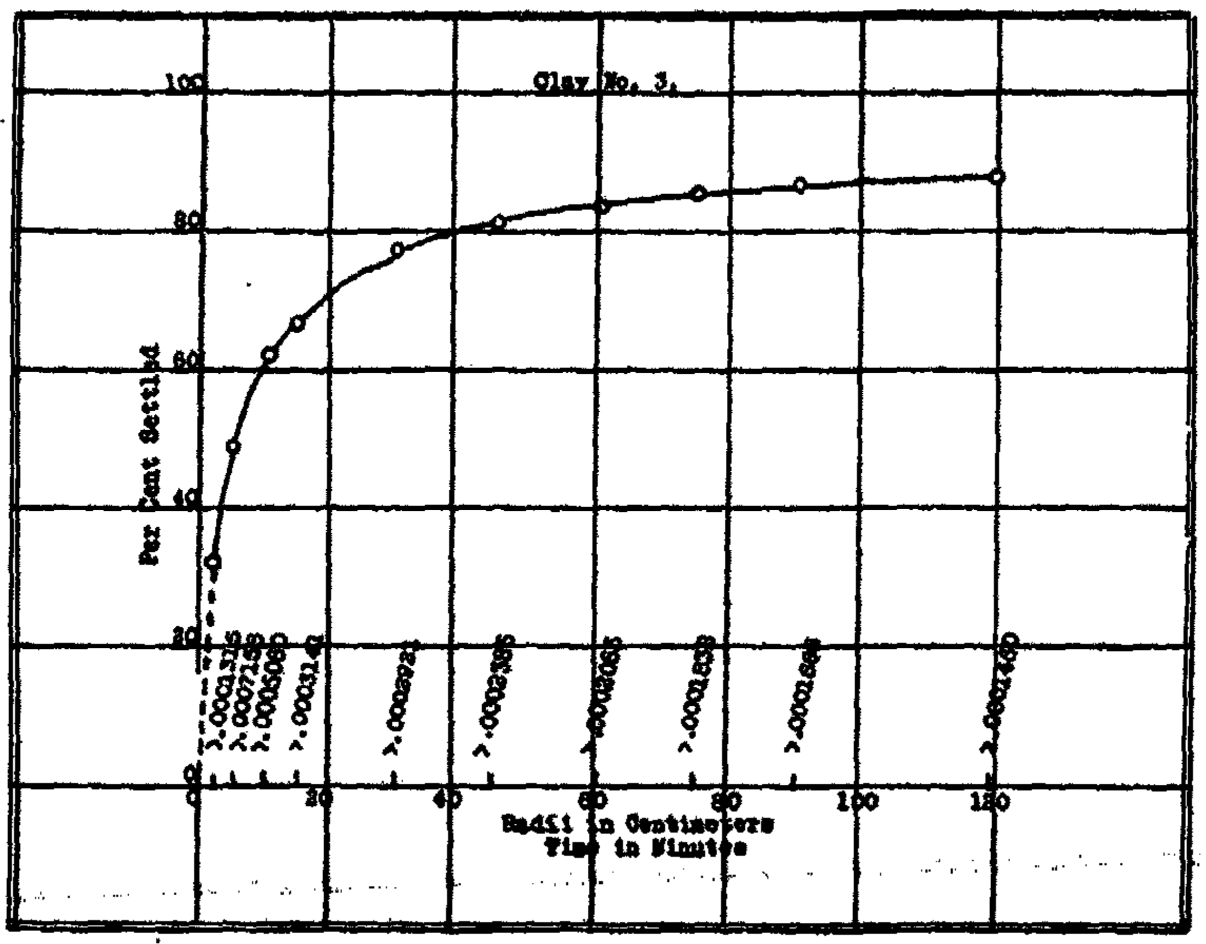

Clay No. 3.
Per Cent Settled
100
80
60
40
20
0
>.0001315
>.0007159
>.0005080
>.0003142
>.0002921
>.0002385
>.0002065
>.0001833
>.0001684
>.0001460
0
20
40
60
80
100
120
Radii in Centimeters
Time in Minutes

FIG. 4

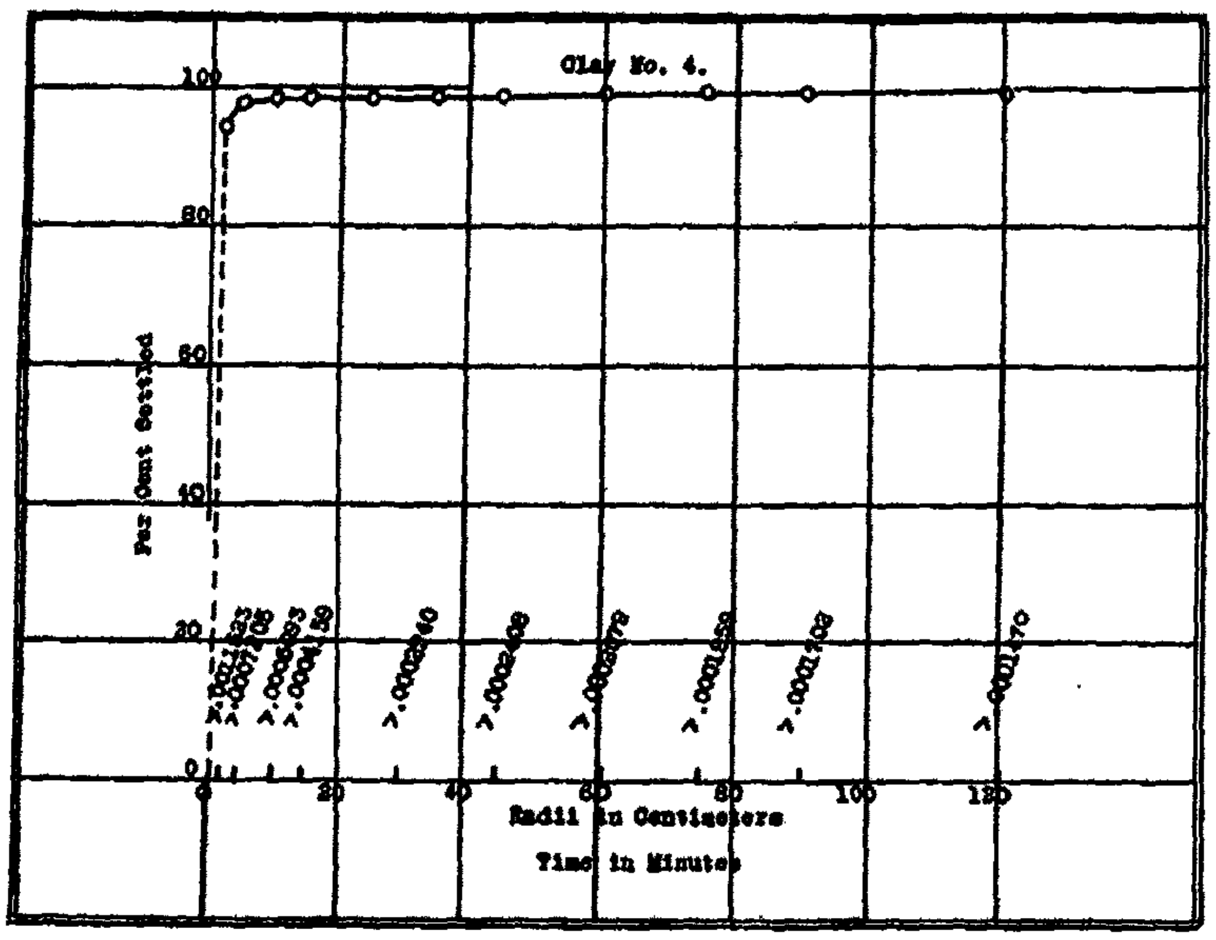

Clay No. 4.
Per Cent Settled
100
80
60
40
20
0
>.0011323
>.0007105
>.0005593
>.0004159
>.0002940
>.0002408
>.0002072
>.0001659
>.0001702
>.0001170
0
20
40
60
80
100
120
Radii in Centimeters
Time in Minutes

FIG. 5

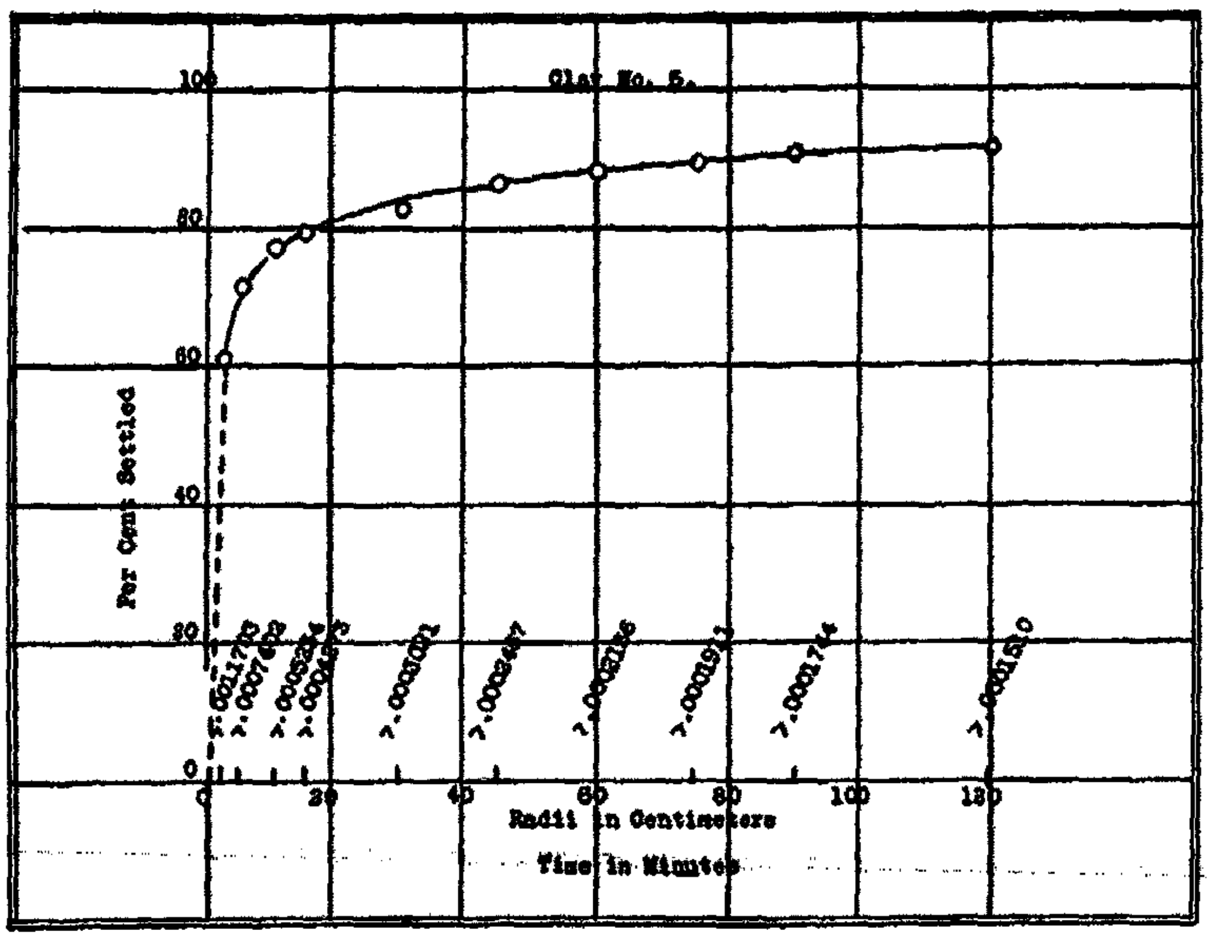

Clay No. 5.
100
80
60
40
20
0
Per Cent Settled
>.0011700
>.0007602
>.0005264
>.0004175
>.0003001
>.0002467
>.0002136
>.0001911
>.0001744
>.0001510
0
20
40
60
80
100
120
Radii in Centimeters
Time in Minutes

FIG. 6

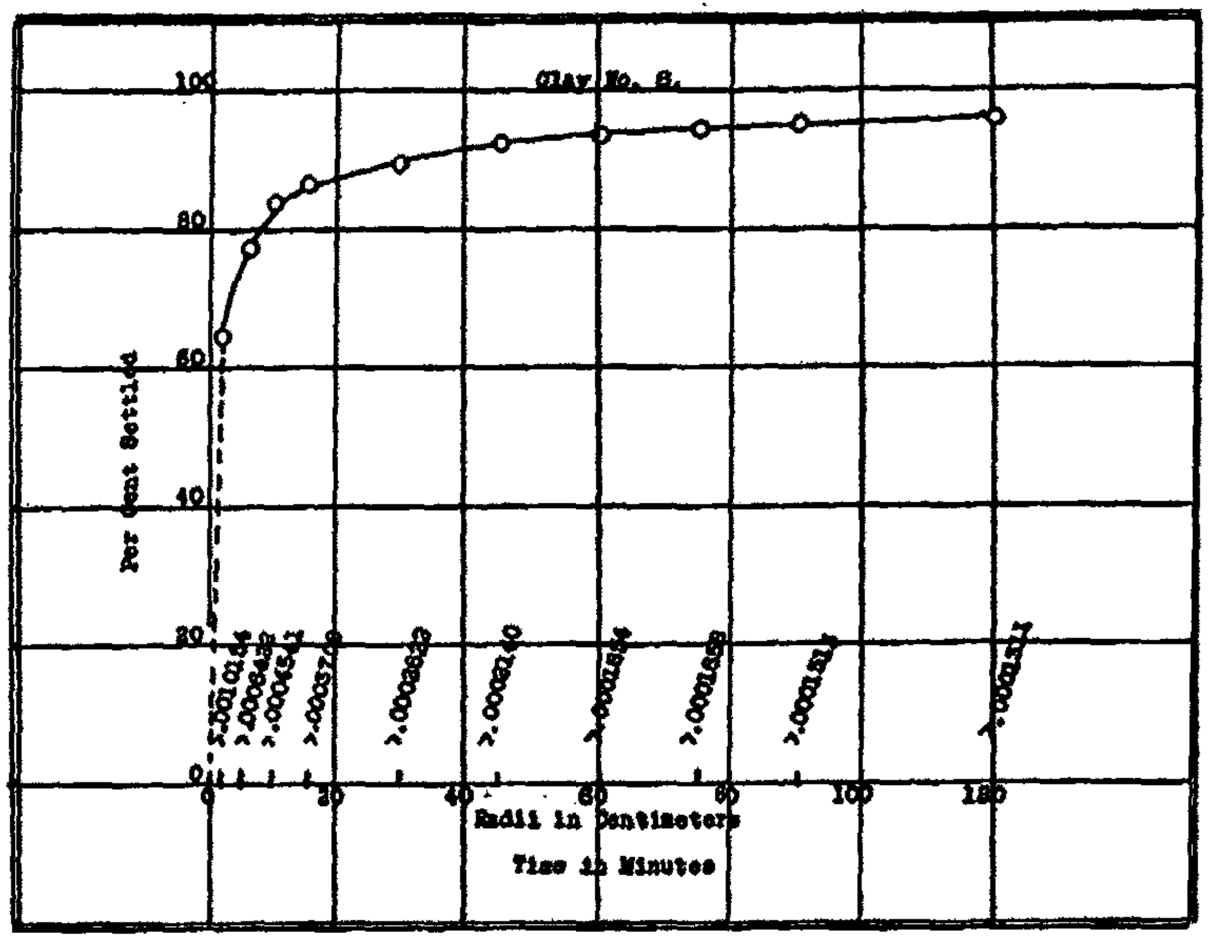

Clay No. 6.
100
80
60
40
20
0
Per Cent Settled
>.0010144
>.0008452
>.0004541
>.0003776
>.0002652
>.0002140
>.0001854
>.0001656
>.0001514
>.0001314
0
20
40
60
80
100
120
Radii in Centimeters
Time in Minutes

FIG. 7

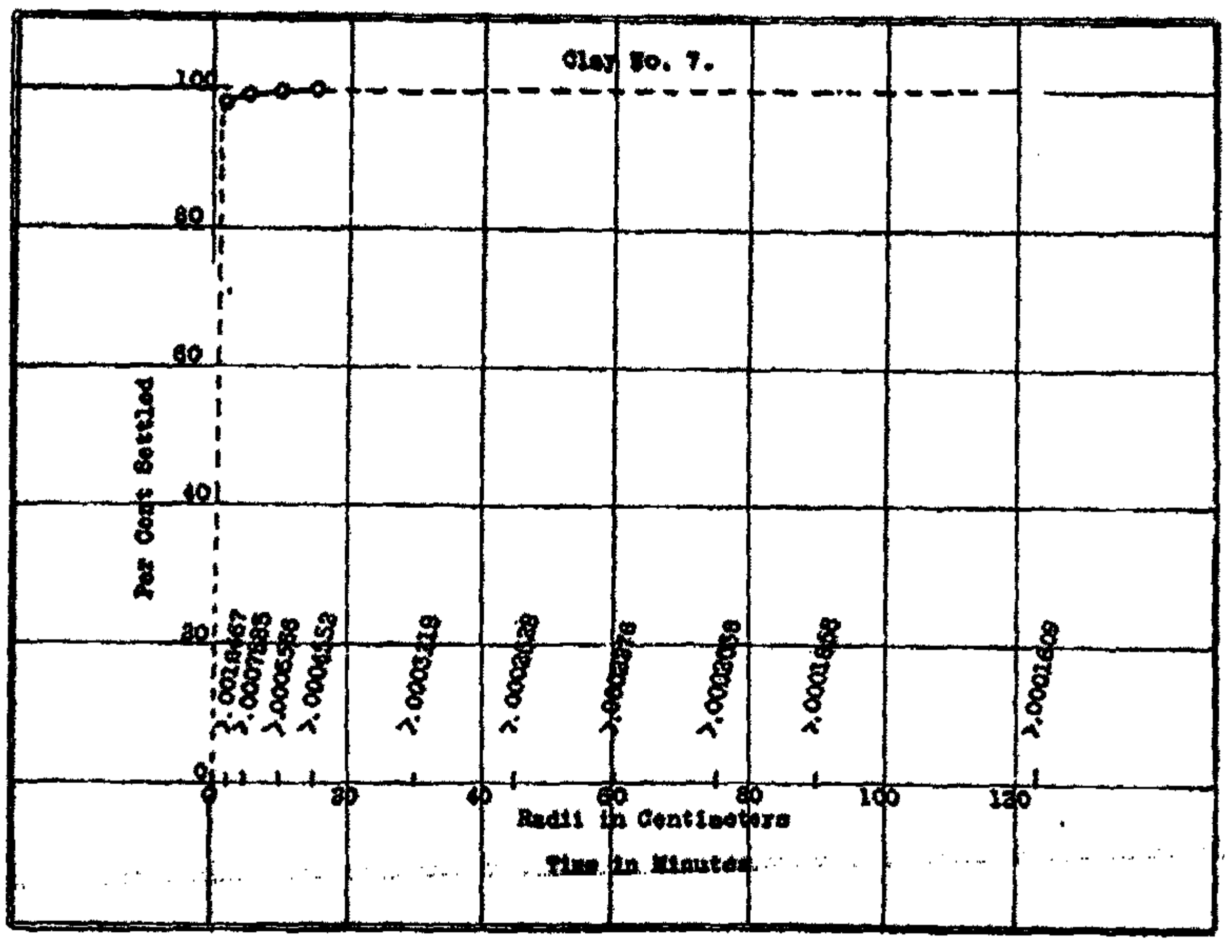

Clay No. 7.
Per Cent Settled
100
80
60
40
20
0
λ.0018467
λ.0007885
λ.0005586
λ.0004452
λ.0003219
λ.0002428
λ.0002276
λ.0002058
λ.0001858
λ.0001609
0
20
40
60
80
100
120
Radii in Centimeters
Time in Minutes

Fig. 8

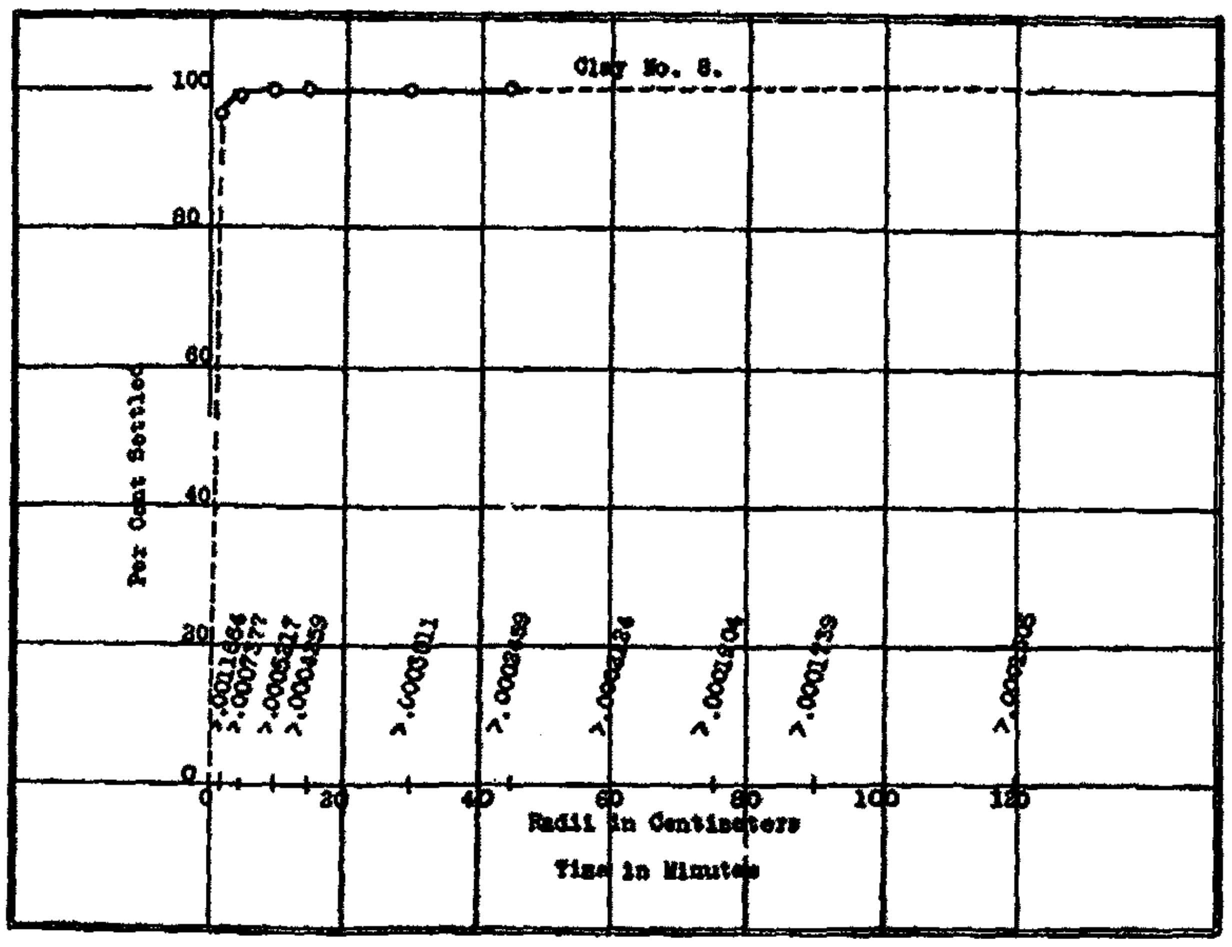

Clay No. 8.
Per Cent Settled
100
80
60
40
20
0
λ.0011664
λ.0007377
λ.0005217
λ.0004259
λ.0003011
λ.0002459
λ.0002134
λ.0001904
λ.0001739
0
20
40
60
80
100
120
Radii in Centimeters
Time in Minutes

Fig. 9

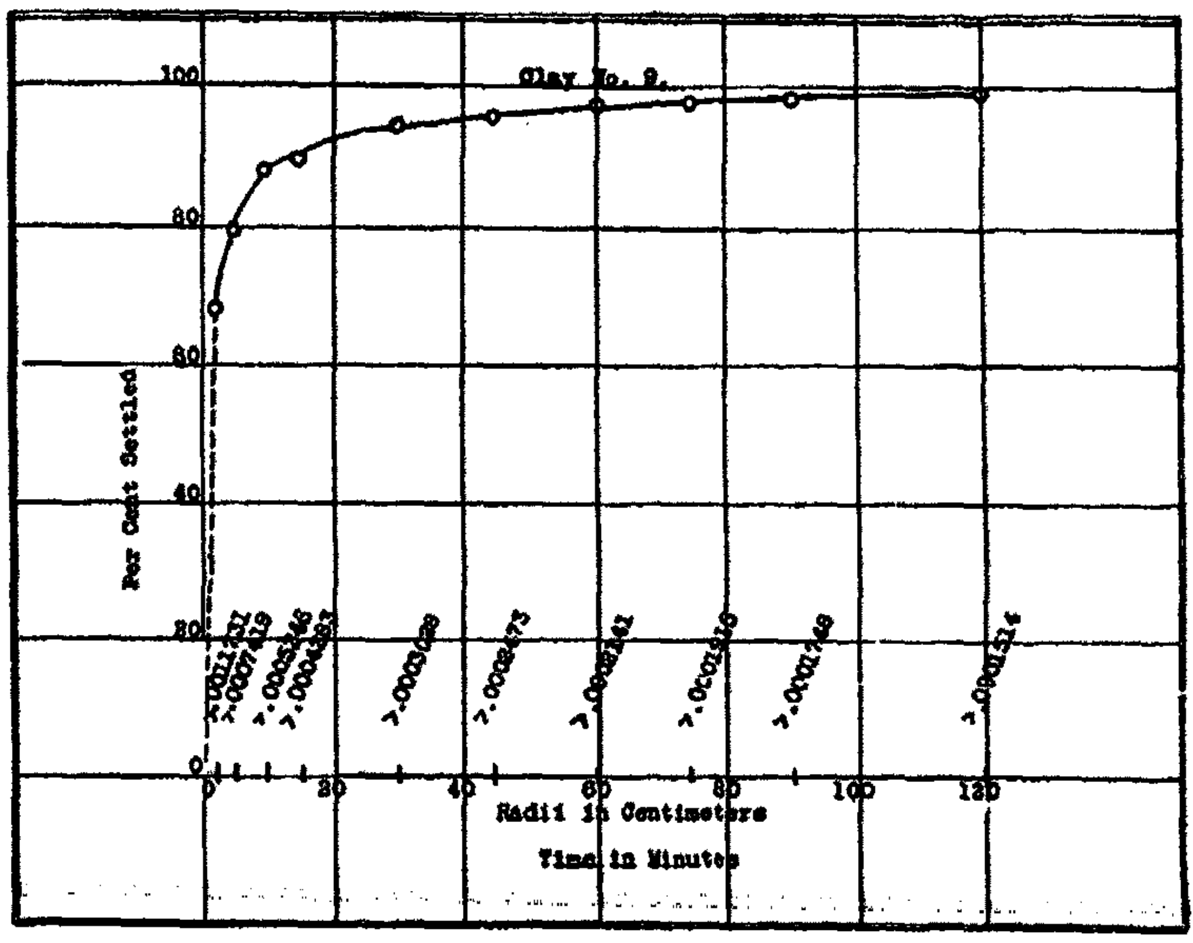


FIG. 10

From the data given in Table V, the sedimentation curves as shown in Figs. 2-10 inclusive were constructed for each clay over a period of 120 minutes. In these curves the per cent settled of total in suspension is plotted as ordinate and the time in minutes together with the radii in centimeters of the particles for each time interval as abscissa. From these curves in conjunction with Table V it is possible to determine the approximate per cent of various sized particles in each clay which indicates the distribution of the various sized particles.

Discussion

The data obtained from experimentation and calculation permit the determination of particle size, the per cent settled out at different time intervals and the per cent of a definite range of particle size existing in each sample. The sedimentation curves (Figs. 2-10 inc.) are graphic representations of the data. A rough comparison of the distribution of the various sized particles can be made by comparing the general shapes which the sedimentation curves assume. Careful examination of these sedimentation curves reveals the fact that the clays may be arranged in the following descending order with respect to the per cent of the large particles in the samples: No. 8 > 7 > 4 > 9 > 6 > 1 > 5 > 2 > 3. This arrangement was obtained by determining the time required for 75% and 90% of all the suspended particles to settle in each sample. The one requiring the shortest time for 75 or 90% of all the suspended particles to settle out is the first in the above order.

The rate of settling of particles from aqueous suspension depends upon two factors, specific gravity and the size of the particles. Clay No. 6, having the greatest mean specific gravity of any used in this investigation, did not settle out as rapidly as some of the others. This is evidently due to either one or both of two factors, first, the per cent of the smaller sized particles was greater and, second, the per cent of the particles having the lesser specific gravity was greater in comparison to the other clays studied.

It was also noted that sample No. 6 showed the presence of colloidal material which failed to settle out after standing a period of eleven days. Clearness was not even obtained then after centrifugation at 2000 R. P. M. for a period of one hour.

It is noticed from Table IV that the radii of the particles of Clays Nos. 1 and 3 for the definite time intervals indicated are the same. This is due to the fact that the specific gravities of these two samples (Table II) are the same. The sedimentation curves for these two samples are different as seen in Figs. 2 and 4, due to the fact that there exists a difference in the per cent of the various sized particles in the two samples.

The data presented in this investigation are intended to apply to the specific clay samples studied and treated in the manner herein specified; however, the generalisations pointed out may be applied to any aqueous clay suspension.

THE ELECTROLYTIC PREPARATION OF THE ISOINDOLINES

BY E. W. COOK AND W. G. FRANCE

The isoindolines have usually been prepared by laborious methods[1,2,3,4,5] which give rather poor yields.

The reduction of the phthalimide or the phthalimidine suggests itself as a likely possibility. However, attempts to carry out this reduction by the usual chemical methods have thus far been unsuccessful. Graebe[6] using tin and hydrochloric acid was able to reduce the imide only to the imidine, the second carbonyl group being unattacked.

Hope and Lankshear[7] in a preliminary report state that the preparation of isoindoline and methylisoindoline in high yields is possible by the electrolytic reduction of the corresponding phthalimidines, but nothing further has been published by them relating to this subject. Späth and Breusch[8] describe the successful preparation of isoindoline by the electrolytic reduction of phthalimide.

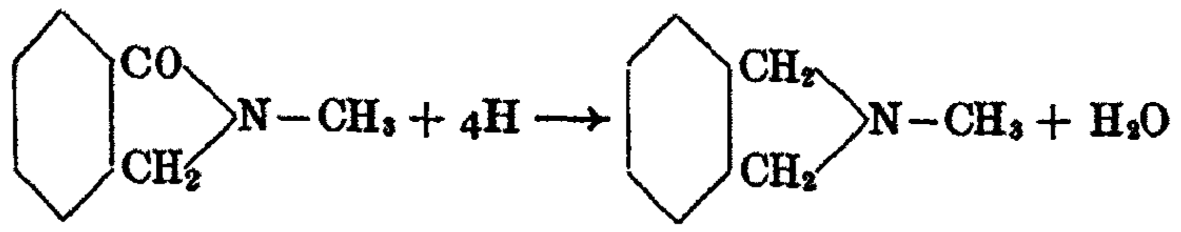
Sakurai[9] prepared a hydroxy compound and phthalimidine from phthalimide in an alcoholic sulfuric acid solution at lead and copper cathodes, but not the further reduction product, the isoindoline.

The work of these investigators indicated the desirability of carrying on a further investigation of the electrolytic preparation of the isoindolines, and it was with this object in view that the present work was undertaken.

Experimental

PREPARATION OF METHYLISOINDOLINE

1. *Reduction of Methylphthalimidine*



The cathode materials used were mercury, lead, tin, and cadmium. A layer of freshly redistilled mercury of about 2 mm. thickness at the bottom of the vessel served as the mercury cathode. Connection was made with the

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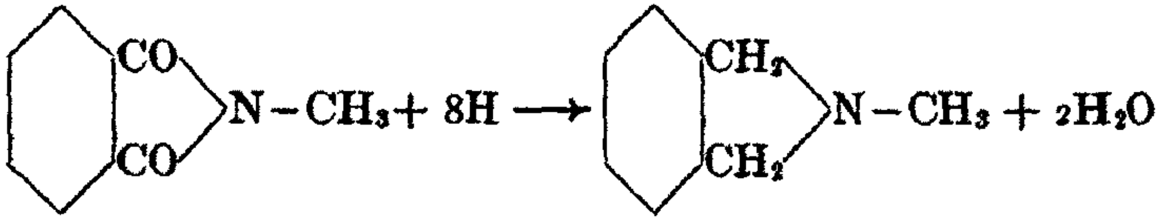
[1] Gabriel and Neumann: Ber. **26**, 525 (1893).
[2] Gabriel and Pinkus: Ber., **26**, 2210 (1893).
[3] Scholtz: Ber., **31**, 414, 627, 1154, 1700 (1898).
[4] Frankel: Ber., **33**, 2808 (1900).
[5] Braun and Kohler: Ber., **51**, 100 (1918).
[6] Graebe: Ann., **247**, 302 (1888).
[7] Hope and Lankshear: Proc. Chem. Soc., **29**, 224 (1913).
[8] Späth and Breusch: Monatshefte, **50**, 349 (1928).
[9] Sakurai: Bull. Chem. Soc. Japan, **5**, 184 (1930).

mercury cathode by means of a stout platinum wire sealed into a piece of glass tubing which was also filled with mercury. The rest of the cathodes were sheets of the pure metal 4.5 × 5 cm. bent into a semi-circular shape of about 6 cm. diameter and 4.5 cm. height. The lead cathode was cut from commercial sheet lead and prepared according to the directions of Tafel.[10] A platinum spiral anode was inclosed in a small porous clay cup and placed at the center of the semi-circular cathode. In the case of the mercury cathode the anode was placed about 2 cm. directly above the center of the mercury layer. For the catholyte 5 grams of methylphthalimidine was dissolved in a solution of 6 cc. of concentrated sulfuric acid in 102 cc. of water. During electrolysis the catholyte was vigorously stirred by means of an air driven stirrer. The anolyte contained 2 cc. of concentrated sulfuric acid in 20 cc. of water. The accompanying table indicates the other experimental conditions such as temperature and duration of electrolysis, as they were varied in the different experiments.

At the end of the electrolysis the catholyte was made alkaline with caustic soda and steam distilled until no more oily drops came over or until about 100 cc. of the distillate had been collected. A crystalline hydrate of methylisoindoline separated out in the distillate. This was filtered off and carefully dried in a dessicator. The hydrate melted at 45-45.5° which agrees well with the value 45-46° given by Braun.[11] The hydrate was readily dehydrated in a vacuum desiccator over sulfuric acid to give the free base which was a colorless oil having a strong basic odor. Upon standing in a closed vessel the base gradually assumed a darker color.

To further identify the compound the methiodide was prepared, which was identical with that prepared by Frankel[12] from isoindoline. The methiodide melted at 245-246°, turning to a dark color. This agrees with the value 244-245°, given by Frankel.

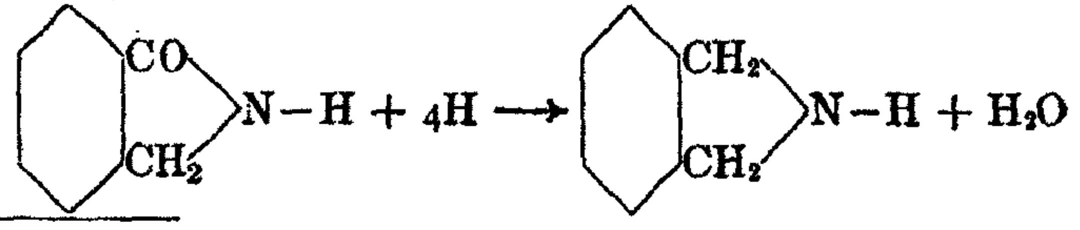
2. *Reduction of Methyl Phtalimide*



The procedure followed was similar to that for the imidine except that in this instance a suspension of the imide was used; the imide was quite insoluble, however, as the reduction progressed it gradually went into solution until at the end of about 7 ampere hours it had completely dissolved.

PREPARATION OF ISOINDOLINE

1. *Reduction of Phthalimidine*



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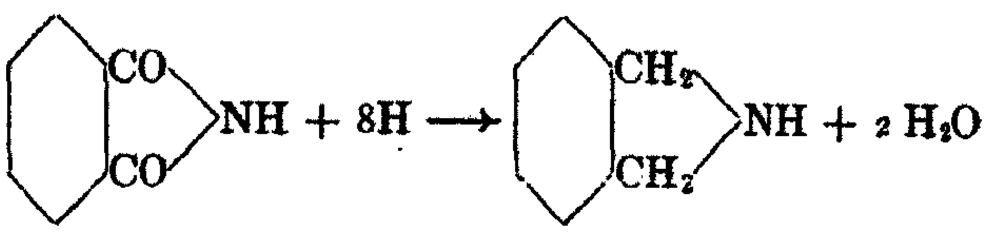
[10] Tafel: Ber., 33, 2215 (1900).

[11] Loc. cit.

[12] Loc. cit.

Not all of the 5 grams of the imidine used in the catholyte was dissolved and a small portion was left in suspension. This readily passed into solution early in the electrolysis. At the end of the electrolysis the catholyte was made strongly alkaline with solid sodium hydroxide and was steam distilled, the distillate being run into hydrochloric acid solution. Upon evaporation of the distillate the hydrogen chloride salt of isoindoline remained. For identification the nitroso derivative was prepared which melted at 96.5-97.5° as compared to the recorded[13] value of 96-97°.

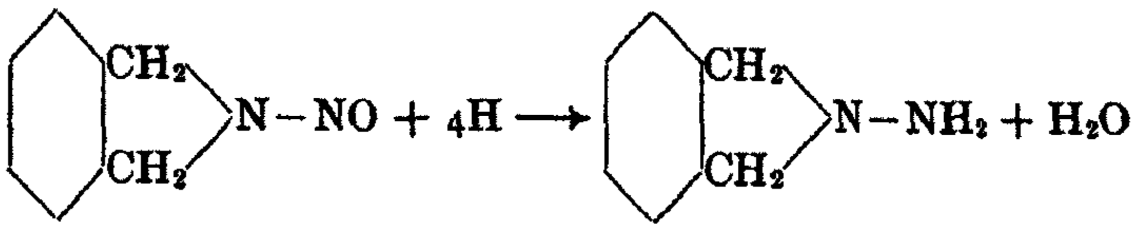
2. *Reduction of Phthalimide*



A suspension of 6 grams of phthalimide purified by sublimation was used in the catholyte. At the beginning of the electrolysis the catholyte was colored a greenish yellow, but at the completion was colorless.

Preparation of N-Amidoisoindoline

Reduction of Nitrosoisoindoline



About 5 grams of nitrosoisoindoline recrystallized from dilute alcohol was used in the catholyte. After the electrolysis an ether extraction was made on the catholyte to remove any possible nitrosoisoindoline that had escaped reduction. Then the catholyte was made strongly alkaline with solid sodium hydroxide and steam distilled into hydrochloric acid. This solution was evaporated almost to dryness when the hydrazine hydrochloride separated out. The hydrochloride was purified by recrystallizing from absolute alcohol. The yield of hydrazine was determined by oxidizing an aliquot portion of the catholyte with hot Fehling's solution and measuring the volume of nitrogen evolved. For identification the benzal hydrazone was prepared which gave a melting point of 127-129° which agrees with that given by Frankel.[14] With picric acid the hydrazine gives a picrate which melts at 96-98°.

Discussion of Results

It is remarkable that while no methylisoindoline was obtained from methylphthalimidine at a tin cathode, a small yield was obtained from methylphthalimide. This is apparently analogous to the reduction of cam-

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[13] Gabriel and Neumann: Loc. cit.

[14] Frankel: Ber., 33, 2812 (1900).

phoric-acid imide and camphidone reported by Tafel and Eckstein.[15] They obtained the α and β camphidones and camphidine as reduction products of camphoric acid imide, but were unable to reduce camphidone itself to camphidine.

Tabulation of Results

Cathode	Time Hrs.	Temp.	Amp.	Volts	Current Density amp/dm²	Yield Efficiency	
						Material	Current
		Reduction of Methylphthalimidine				%	%
Hg	6	11°	1	6	2.97	38.0	23.0
Pb	3	12°	3	5	4.66	57.1	23.1
Pb	5	46-49°	3	5.5	4.45	68.6	16.7
Sn	5.33	51°	3	5.2	4.45	00.0	00.0
Cd	5.33	53°	3	5	4.45	4.4	2.0
		Reduction of Methylphthalimide					
Sn	10.67	49-51°	3	5.6	4.45	7.7	1.9
Hg	32.00	41°	1	5	2.97	31.1	7.8
Cd	10.67	46°	3	5.4	4.45	57.1	14.3
Pb	10.67	50°	3	5	4.45	57.7	14.4
		Reduction of Phthalimidine					
Cd	5.33	49°	3	4.5-5	4.45	71.6	18.0
Pb	5.67	45°	3	5-6.5	4.45	64.3	15.3
Sn	8.67	52°	3	5.5	4.45	00.0	00.0
		Reduction of Phthalimide					
Pb	10.67	50°	3	5.5-6	4.45	73.2	16.7
		Reduction of N-nitrosoisoindoline					
Pb	3.75	43°	3	5-5.2	4.45	72.0	21.1
Cd	3.75	44°	3	5-5.3	4.45	91.7	29.5

In accounting for their results they assume the camphidones to be extremely resistant towards further reduction and not to be intermediate products in the formation of camphidine. Furthermore they believe either that camphidine is formed only when both carbonyl groups of the acid imide are by accident simultaneously attacked by the reducing agent, or, that a carbinol-like intermediate product in which the second carbonyl group is electrolytically attackable, is already formed during the transformation of camphoric acid imide to camphidone.

The extension of this explanation to the analogous reductions of methylphthalimidine and methylphthalimide with tin cathodes leads one to conclude that no methylisoindoline was obtained from methylphthalimidine for the following reasons:

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[15] Tafel and Eckstein: Ber., 34, 3274 (1901).

(1) Methylphthalimidine is incapable of undergoing further reduction;

(2) In view of this great resistance to reducing action it is unlikely that the imidine would be an intermediate product in the electrolytic reduction of the imide to the isoindoline. This is given some support by the fact that no imidine was isolated when a reduction of the imide was carried out for the theoretical length of time;

(3) Since the isoindoline is assumed to be formed only by the accidental simultaneous attack of two carbonyl groups by the reducing agent, it is obviously impossible for this to occur with the imidine which contains but one carbonyl group;

(4) Likewise the possibility of the formation of a carbinol-like intermediate product is excluded since this also is assumed to be formed from the imide.

The successful reduction of methylphthalimide with tin cathodes would therefore be explained on the basis of either the accidental simultaneous attack of both of its carbonyl groups or the formation of a readily reducible carbinol-like intermediate product.

However plausible this explanation may be it loses most of its force when considered in the light of the results obtained with mercury, lead and cadmium cathodes. Thus for example, good yields of the corresponding isoindolines were obtained from methylphthalimidine at mercury and lead cathodes, and from phthalimidine at cadmium and lead cathodes. Evidently the imidines are not "resistant enough to further reduction" to avoid being reduced when mercury, lead and cadmium cathodes are substituted for tin.

Reference to the data for the reduction of methylphthalimide shows that the yields of isoindoline were from four to seven times greater when lead, cadmium or mercury cathodes were substituted for the tin cathode. Therefore, according to the suggested explanation of Tafel and Eckstein it would appear either, that the chances for the simultaneous attack of the two carbonyl groups of the imide are very much less at tin than at lead, cadmium or mercury cathodes, or that the hypothetical carbinol-like intermediate product is less readily formed at a tin cathode than at the lead, cadmium or mercury cathodes. Since direct experimental evidence is lacking in support of either possibility and especially in view of the fact that the imidines were reduced a more satisfactory explanation is needed.

In the absence of catalytic effects, a stronger reducing action is obtained at a cathode having a high hydrogen overvoltage than at one having a low hydrogen over-voltage. The order of decreasing hydrogen over-voltages in N.H_2SO_4 for the various cathodes used in this work is given by Caspari[16] as mercury, lead, tin and cadmium. From this one would expect a weaker reducing action with tin than with lead or mercury cathodes. The differences in reducing energies as expressed by the hydrogen over-voltages of the metals, would reasonably account, on the one hand, for the failure to reduce the imidine and for the low yields obtained from the imide, when tin cathodes

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[16] Caspari: Z. physik. Chem., 30, 89 (1899).

were used; and on the other, for the successful reduction of the imidine and the higher yields from the imide when mercury, lead and cadmium cathodes were used. In the case of methylphthalimide the fact that the yields obtained at mercury having the highest over-voltage are lower than those obtained at cadmium having the lowest over-voltage may be the result of the catalytic activity of the metals.

Similar variations in results predicted on the basis of over-voltages have been frequently observed. Löb and Moore[17] found that the reduction of nitrobenzene to aniline in a caustic soda solution proceeded better at a copper cathode than at metals of higher over-voltage.

Fichter and Stocker[18] studying the reduction of phenol to cyclohexanol were able to effect the reduction at platinum and unable to at a lead cathode.

Bancroft and George[19] have more recently investigated the electrolytic reduction of phenol and the catalytic hydrogenation of phenol vapor in the presence of platinum and nickel catalysts. They state: "The experiments of Fichter have been confirmed, that phenol is hydrogenated at a platinum cathode and practically not at all at a lead cathode, in spite of the high over-voltage of the latter. The effect of platinum in activating phenol is evidently more important than the reducing power of the hydrogen. . . . Platinum has a specific effect on the hydrogenation of phenol both when used as a cathode and as a catalyst."

In view of the influence of the over-voltage and catalytic activity of the metal cathodes in determining the course of a reaction, it seems that the results obtained in this work on the preparation of isoindolines can be more satisfactorily and reasonably accounted for on the basis of the hydrogen over-voltages and probable differences in the selective activation of the depolarizer by the various cathodes, than by the explanation offered by Tafel and Eckstein in connection with the reduction of camphoric acid imide.

If as suggested in the work of Bancroft and George[20] there is a probability that the oriented adsorption of the depolarizer is different at different metals, it is also probable that a relation may be found to exist between the lattice constants of the cathodes and the polar properties of the depolarizer. This point together with the factors such as, nature of surface, current density, duration of polarization, and previous treatment, which influence the over-voltage of the metals is being considered in connection with other electrolytic reductions now in progress in this laboratory.

Summary

1. Isoindolines have been prepared by the electrolytic reduction of methylphthalimidine, phthalimidine, methylphthalimide, and phthalimide.

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[17] Rideal and Taylor: "Catalysis in Theory and Practice," 2nd Ed., 428 (1926).

[18] Fichter and Stocker: Ber., 47, 2015 (1914).

[19] Bancroft and George: Trans. Am. Electrochem. Soc., 57, 399 (1930).

[20] Loc. cit.

2. N-amidoisoindoline has been prepared by the electrolytic reduction of N-nitrosoisoindoline.

3. Variations in the yields obtained with different electrodes have been attributed to the hydrogen over-voltages and probable differences in selective activation of the depolarizer by the metals.

The authors express their gratefulness to Dr. C. E. Boord of this Department for his continued interest and advice throughout the course of this investigation.

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THE ATOMIC MASS OF POTASSIUM

I. The End-point of The Potassium Chloride-Silver Titration[*]

BY CLYDE R. JOHNSON[**] AND GEORGE W. LOW, JR.

This article describes a method by which the potentiometer may be substituted for the nephelometer in finding the end-point of certain precise titrations. The method is a general one for a type of titration widely applicable in atomic mass measurements. The technique required is simple, yet it completely avoids "liquid junction" and "activity" difficulties which have hitherto offered an obstacle to the use of the potentiometer in analyzing the systems obtained in work of this nature. The use and scope of the new method may be inferred from the following record of potentiometric and nephelometric analyses of potassium nitrate-nitric acid solutions saturated with silver chloride. The liquids analyzed were similar in every respect to the solution in equilibrium with the precipitated silver chloride at the end-point of the potassium chloride-silver titration. The equilibrium point of this system at 0°C. is to be used as a reference end-point in a determination of the potassium chloride-silver ratio.

Experimental

The experiments consisted in analyzing the unknown saturated solutions for silver and chloride by comparison with standard solutions having almost the same composition. The standard and test systems were prepared from carefully purified reagents with all of the necessary precautions[1] to obtain solutions containing equivalent amounts of silver and chloride.

Typical Analytical Systems. Each of the two test systems was 0.600 molar in potassium nitrate, 0.308 molar in nitric acid, and contained 13.5 grams of fine-grained silver chloride. Before making up the systems, silver chloride No. 1 was allowed to stand in contact with dilute nitric acid containing a small amount of silver nitrate; silver chloride No. 2 in contact with dilute nitric acid containing a small amount of potassium chloride. These solutions were later washed out with portions of the nitric acid-potassium nitrate mixture.

The supernatant liquids of the typical analytical systems were brought to equilibrium at 0°C. and analyzed for silver and chloride. While still in contact with the respective precipitates, they were next titrated away from the end-point in opposite directions by known additions of silver nitrate and potassium chloride, and again analyzed.

Standard Solutions. Each standard solution was also 0.600 molar in potassium nitrate, and 0.308 molar in nitric acid, but contained chloride and silver equivalent to 0.600 milligrams of silver per liter. Suitable correction was

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[*] Contribution from the Frick Chemical Laboratory, Princeton University.

[**] National Research Fellow in Chemistry.

[1] J. Phys. Chem., 36, 1942 (1932).

made for the nitrate and potassium added to the standards with the silver and chloride. For the sake of uniformity standard solutions of the same composition were used in all of the nephelometric and potentiometric analyses. It was recognized that this procedure would decrease to some extent the accuracy of the nephelometric analyses of the solutions not at the end-point.

The Analyses. The 4-liter glass-stoppered Pyrex bottles containing the test systems were packed in ice during the entire experiment, and a calibrated thermometer immersed in the solutions invariably registered 0.2°C. The bottles were shaken once or twice only after the removal of test portions, otherwise twice each day.

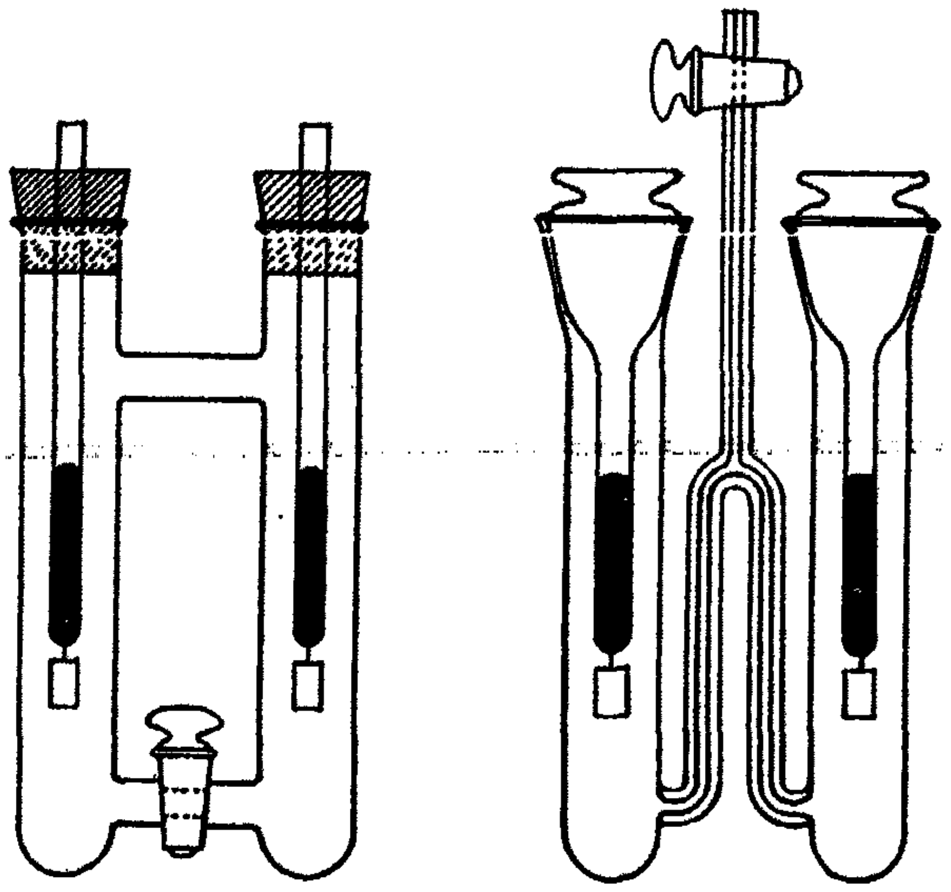

Fig. 1
Cells for E.M.F. Measurements

For each set of six analyses an 80 to 100 milliliter portion of the cold supernatant liquid was withdrawn and filtered through a sintered glass mat. Two 20.00 ml. samples were analyzed nephelometrically for silver and chloride by the standard solution method.[1] Two 10 ml. samples from the same portion were analyzed potentiometrically for silver and chloride with the two cells:

Ag/Analytical Solution/Standard Solution/Ag
Ag/AgCl/Analytical Solution/Standard Solution/AgCl/Ag.

Two forms of cell suitable for the analyses are shown in Fig. 1. An essential feature of the design is that it permits one to join the solutions just before the E. M. F. measurements are made. The silver and silver chloride electrodes were prepared in the manner described by MacInnes and Parker,[2] with the modifications suggested by Carmody.[3] However, the customary washing of the silver chloride electrodes with pure water was carefully avoided. For the measurements made at 0°C. the electrodes were placed in the cell only

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[1] J. Phys. Chem., 35, 830 (1931); 36, 1942 (1932).
[2] MacInnes and Parker: J. Am. Chem. Soc., 37, 1445 (1915).
[3] Carmody: J. Am. Chem. Soc., 51, 2901 (1929).

after it had been packed in ice for some time. In general, the electrodes were stored and rinsed in solutions of the composition in which they were to be used, and long exposure to the air was avoided.

A uniform procedure was adopted for the analyses. Each pair of electrodes was placed in a portion of the standard solution and short-circuited overnight. Following an initial E. M. F. measurement with the electrodes in the same solution, the electrodes were rinsed and allowed to stand in solutions of the composition in which they were to be used. The electrodes were then placed in position in the cell, and the analytical E. M. F. measurements were made, first at 0°C. and then at 25°C. Immediately following these observations, the contents of the cell were mixed and a final set of readings was made.

Each silver and each chloride analysis consisted of four E. M. F. readings taken over a period of thirty minutes after the cell had reached temperature equilibrium. Measurements made with Leeds and Northrup Type K and Students' potentiometers were equally satisfactory. The standard unsaturated Weston cell was compared with the laboratory standards. All of the work was done in the light of Series OA Wratten Safelights.

Discussion of Results

The initial E. M. F. readings were never greater than 0.15 millivolt and usually very much less. The final E. M. F. readings were generally about 0.2 or 0.3 millivolts. Silver analysis No. 2, System No. 2, in which the final value was 2.5 millivolts, was the only marked exception to this rule. Even in this case no correction was applied on the basis of the initial and final readings. However, there is every indication that it would be possible to make significant corrections of this nature which would improve the accuracy of the potentiometric analyses.

The results of the analyses are summarized in the following table. For the purpose of comparison, the chloride and silver concentrations in Table I are both expressed as milligrams of silver per liter. That is, the chloride concentrations have been multiplied by the factor Ag/Cl. The "silver added" in the third column gives the total silver which had been added to the system as silver nitrate, or "subtracted" as potassium chloride, at the time the analysis was made. The corresponding additions of these materials were both made on the 22d day of cooling.

The analytical E. M. F. readings were remarkably constant and reproducible. The four observations made over a period of thirty minutes rarely covered a range of more than 0.1 or 0.2 millivolts. Each value given in the appropriate section of the table is based on the average of four such readings, and is calculated from the expression: $\log C = E/0.0001984T + 0.778 - 1$. When the silver or chloride concentration, C, is expressed in milligrams per liter, as silver, E is in volts, and T is the absolute temperature. In either cell the electrode in the test solution containing excess chloride was negative, and the electrode in the test solution with excess silver was positive.

The limitations of the above expression in interpreting the E. M. F. data are recognized. The eight final chloride analyses made at 25°C. show the tendency of the silver chloride electrodes to dissolve and saturate the solutions

TABLE I

Summary of Analyses

No.	Time cooled Days	Silver added Mg/Liter:	Nephelometric Analyses		Potentiometric Analyses:			
					At 0°C.		At 25°C.	
			Chloride	Silver	Chloride	Silver	Chloride	Silver
1	16	none	0.64	0.63	0.62	0.62	0.61	0.63
	21	none	0.61	0.61	0.62	0.64	0.61	0.66
	22	none	0.63	0.62	0.62	0.61	0.61	0.59
2	18	none	0.63	0.64	0.60	0.60	0.61	0.62
	20	none	0.59	0.63	0.61	0.67	0.60	0.65
	21	none	0.62	0.62	0.63	0.62	0.61	0.63
1	26	+0.300	0.54	1.02	0.49	0.78	(0.56)	0.77
	28	+0.300	0.55	1.01	0.51	0.70	(0.58)	0.71
	29	+0.300	0.52	0.84	0.49	0.75	(0.56)	0.64
	34	+0.300	0.55	1.02	0.49	0.77	(0.56)	0.77
2	25	−0.300	0.92	0.62	0.79	0.50	(0.66)	0.51
	28	−0.300	0.94	0.57	0.77	0.49	(0.67)	0.49
	29	−0.300	0.72	0.48	0.77	0.49	(0.65)	0.47
	33	−0.300	0.80	0.49	0.78	0.49	(0.65)	0.50

in the cell. It appears that this source of error does not appreciably affect the potentiometric analyses made at 0°C. Evidence for this belief may be found in the agreement of the first six nephelometric and potentiometric chloride analyses, and also in the symmetry of the sixteen values obtained by the potentiometric analysis, at 0°C., of the solutions containing excess silver and chloride. The fact that the potentiometric chloride analyses apparently give correct values at either 0°C. or 25°C., when both the standard and test solution contain equivalent amounts of silver and chloride, may mean only that the solution of the electrodes is accompanied by no electrical effect in this unique case. Nevertheless, the observations made by the method described in this article may be used in an actual titration as evidence that the end-point has been reached. Any possibility of serious error due to the solubility of silver electrodes in the 0.3 molar nitric acid is ruled out by the agreement of the first six sets of nephelometric and potentiometric silver analyses.

Equal-opalescence "analyses" made by the method of Richards and Willard,[1] incidental to the first six sets of analyses given in the table, yielded ratios from 1.35 to 1.65, all indicating that the solutions contained excess chloride. It seems that the method leads to a pseudo-end-point in the case of the potassium chloride-silver titration. Investigators who have attempted to determine the potassium chloride-silver ratio have generally used either the above equal-opalescence method or the still more unsatisfactory procedure of Richards and Wells.[2] This observation may have some bearing on the fact that authorities have been unable to agree consistently upon an accurate value for the atomic mass of potassium. Thus, in summarizing the results of the various determinations of the potassium chloride-silver ratio made over the

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[1] Richards and Willard: J. Am. Chem. Soc., 32, 32 (1910).

[2] Richards and Wells: J. Am. Chem. Soc., 27, 459 (1905).

past quarter of a century by the classical Harvard methods, Baxter[1] concludes that "the atomic weight of potassium seems to be in some doubt."

It may be inferred from the data given in the above table that the standard solution method of analysis permits the excess or deficiency of silver in the analytical solutions to be determined to about 0.02 milligram for every ten grams of silver used, in the case of the potassium chloride-silver titration. The potentiometer may be substituted for the nephelometer in the analyses without loss of accuracy. That is, in so far as the determination of the end-point limits the experimental accuracy, it is possible to obtain analyses correct to one part in 500,000 by the use of the nephelometric or potentiometric procedures outlined in this report.

The present experiments give incidental information which is of interest in connection with the problem of making a precise adjustment to the end-point. The limitation placed on the accuracy of the eight final pairs of nephelometric analyses has been mentioned. In spite of this limitation, it seems very likely that the irregularities in the results of these analyses are in part due to the presence of colloidal silver chloride in the test systems. The additions of silver nitrate and potassium chloride must have resulted in the formation of small amounts of colloidal silver chloride under conditions in which it would be quite stable. The behavior of the colloidal material in the respective systems, on this interpretation of the analytical results, in is accord with Lottermoser's conclusion[2] that the positive silver chloride sol is more stable than the negative sol. On the other hand, it is of interest to note that the potentiometric silver analyses, at 25°C., of the same *unsaturated* solutions used in the nephelometric analyses, show no evidence of the presence of silver having its source in any such colloidal material. The potentiometric analyses at 0°C. would not be expected to reveal the presence of a colloid. Whatever interpretation is placed on the data, it is evidently advisable to minimize the removals of test portions in the titration. It is also sound practice actually to adjust the analytical solutions to the correct end-point, where the coagulation of the colloidal material is comparatively rapid. Conclusive evidence that the correct end-point has been reached may be obtained in any case by comparing the results of the nephelometric or potentiometric analyses with the predetermined solubility of the precipitated compound.

The problem of adsorption by the precipitated silver chloride has deliberately been avoided in the present work, as it is one of sufficient importance and difficulty to warrant separate treatment. While the analyses may seem to show that no measurable adsorption of silver nitrate or potassium chloride occurs, they are not necessarily conclusive, because of the preliminary treatment of the silver chloride samples. The analytical method used in these experiments would be very suitable for the study of adsorption effects by the examination of successive washings from the precipitated material, in an actual titration.

The authors take this occasion to express their thanks to Prof. N. H. Furman for his interest and co-operation in this work.

Princeton, New Jersey.

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[1] Baxter: J. Am. Chem. Soc., 50, 617 (1928).

[2] Lottermoser: Alexander's "Colloid Chemistry," I, 673 (1926).

CHEMICAL ACTION IN THE GLOW DISCHARGE. X

The Decomposition of Nitrous Oxide

BY P. D. KUECK AND A. KEITH BREWER[1]

The formulation of the principle underlying the electrochemistry of gases as presented in the previous articles of this series, has been confined almost entirely to the study of reactions involving synthesis. It becomes of interest, therefore, to see if the mechanism developed from these experiments holds for pure decomposition reactions, i.e., does the usual electrochemical equivalence law hold for both types of reaction; is the dissociation initiated by positive ions; are some ions much more efficient as reaction centers than are others; is the M/N ratio expressed by small numbers.

The decomposition of nitrous oxide is particularly suited for this investigation not only because it has been the subject of extensive investigations, but because it offers few complications to the glow discharge technique which has been developed.

Apparatus and Method

In the previous experiments it was possible to remove the products of the reaction as fast as formed by surrounding the discharge with liquid air. In the present case these products could not be removed by this means; it was necessary, therefore, to design a discharge tube which permitted a rapid diffusion of the gases so that the composition of the gas throughout the system would be comparatively uniform.

The tube used in determining the rate of decomposition is shown in Fig. 1A. The cathode was an aluminum disc one inch in diameter completely covered except on the face with a tightly fitting glass case to confine the discharge to the front surface. The anode was an aluminum rod one-quarter inch in diameter and enclosed in a glass case except at the end. The electrode separation was two millimeters; this eliminated the positive column and anode glow.

The nitrous oxide used in these experiments was obtained from the Ohio Chemical Co., and contained negligible impurities. The other gases were purified in the manner described in the previous article of this series.

The method of procedure for each series of runs was to fill the reaction system to a definite pressure, the partial pressure of nitrous oxide being varied from 100% to 10%. The progress of the reaction was determined by measuring the pressure change at fixed intervals of time, the discharge current being kept constant.

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[1] Fertilizer and Fixed Nitrogen Investigations Department of Agriculture, Washington, D. C.

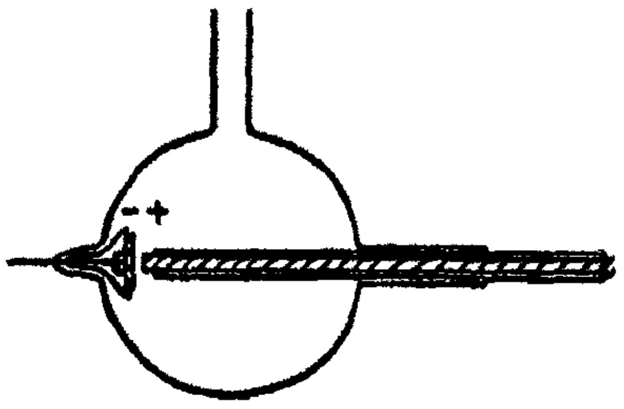

FIG. 1 A
Discharge tube for measuring the rate of decomposition.

The apparatus used to determine the concentration of the reaction products is shown in Fig. 1B. The discharge took place between the aluminum rods placed in an ignited soapstone housing in such a manner that the discharge was confined to a small pencil of glow through which the gas rapidly passed.

The condensable gases from the discharge were frozen out in a spiral immersed in liquid air; i.e., the undecomposed N_2O, the N_2O_3, and the N_2O_4. All NO formed in the discharge was converted into NO_2 and N_2O_3 in passing through the condensing trap. The concentration of NO_2 was determined by the light adsorption method at 150°C. The N_2O_3 was measured by the increase in light absorption upon the addition of oxygen to the condensed gas mixture.

The non-condensible gases (N_2 and O_2) were collected in an auxiliary discharge tube of the usual design. The amount of each gas was determined by measuring the quantity of NO_2 that could be synthesized from the mixture using the technique previously described.[1]

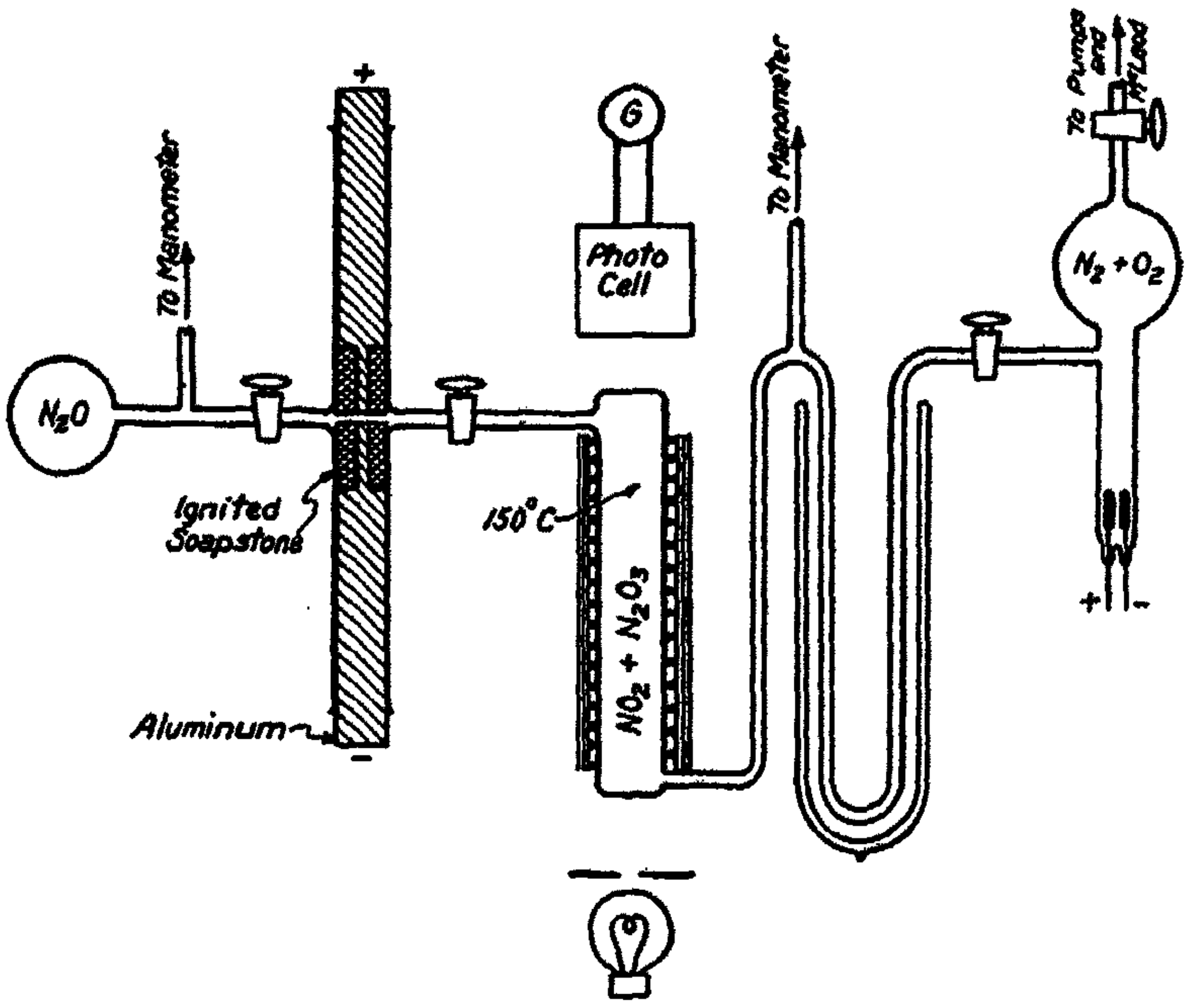

FIG. 1 B
Apparatus for measuring the relative concentrations of the immediate products of the decomposition.

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[1] Westhaver and Brewer: J. Phys. Chem., **34**, 554 (1930).

Results

The total pressure changes observed in each case showed the decomposition to go completely to the elements as a final product. The maximum rate of pressure change for each run appeared at the start of the run, the rate decreasing with time until no further change occurred at the pressure equivalent to complete dissociation.

In experiments of this type there are several methods by which the rate of reaction can be determined. (1) The tangents to the pressure-time curves can be used as a measure of the rate; (2) the time for quarter or half decomposition can be used; (3) since the experimental results were such that a straight line was obtained when the log of the partial pressure of nitrous oxide was plotted against time, the rate can be derived directly from the slope of this line. The latter of the three methods was used, since it offered by far the greater accuracy.

The partial pressure of nitrous oxide at any instant was obtained as follows: The pressure in the system at time t is expressed by

$$P_T = p_{2N_2} + p_{O_2} + p_{N_2O} = p_{N_2O} + 3/2(P_{O_2} - P_{N_2O}) \qquad (1)$$

where P_T is the total pressure, P_{O_2} the initial pressure, and p refers to the partial pressures. From this

$$p_{N_2O} = 3P_{O_2} - 2P_T \qquad (2)$$

The rate of reaction can be computed from the log p_{N_2O}-time curves since the results show

$$\frac{d \log p_{N_2O}}{dt} = S \qquad (3)$$

Since $d \log p_{N_2O} = d\, p_{N_2O}/p_{N_2O}$, this expression becomes

$$\frac{d\, p_{K_2O}}{dt} = p_{N_2O}\, S \qquad (4)$$

where $(p_{N_2O}S)$ is the rate. p_{N_2O} refers to the initial pressure in determining the initial rate for various pressures of pure nitrous oxide. Under these conditions the rate is constant, and S, therefore, is inversely proportional to p. The absence of any dependence of the rate on the initial pressure is due to the fact that the cathode fall of potential is constant over the pressure range investigated, hence the rate of positive ion formation is independent of the pressure over this range.

Factors influencing Decomposition. The initial rate of decomposition of nitrous oxide for various discharge currents is shown in Fig. 2. These measurements were made with an initial pressure of 5 mm. It will be seen that the rate of reaction is proportional to the current passing through the discharge.

The effect of the initial pressure on the rate is shown in Fig. 3. It will be observed that within the limits of experimental error the rate is independent of the pressure over a wide range.

The effect of nitrogen on the rate of decomposition is shown in Fig. 4. The current was maintained at 10 m.a., and the total initial pressure was 5 mm. in each instance. The rates observed for the various gas mixtures fell on a straight line showing the rate of dissociation to be proportional to the partial pressure of nitrous oxide.

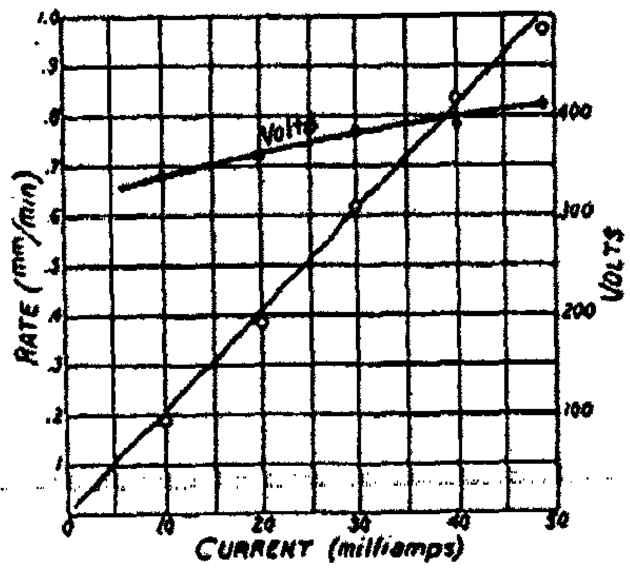

FIG. 2

The effect of the discharge current on the rate of decomposition.

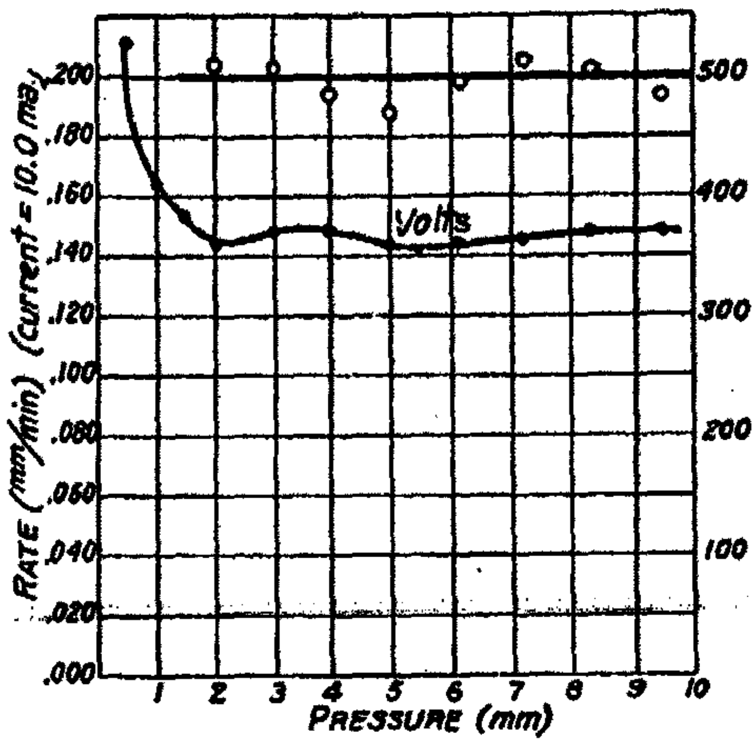

FIG. 3

The effect of pressure on the initial rate of decomposition.

The results obtained with added oxygen are very similar to those given for nitrogen, as can be seen in Fig. 5. It will be noted that the slopes of the two curves are identical, the principal difference being that both the voltage and rate curves for oxygen dropped slightly when the tube was "run in" with oxygen. It is interesting to note that an almost zero rate was observed

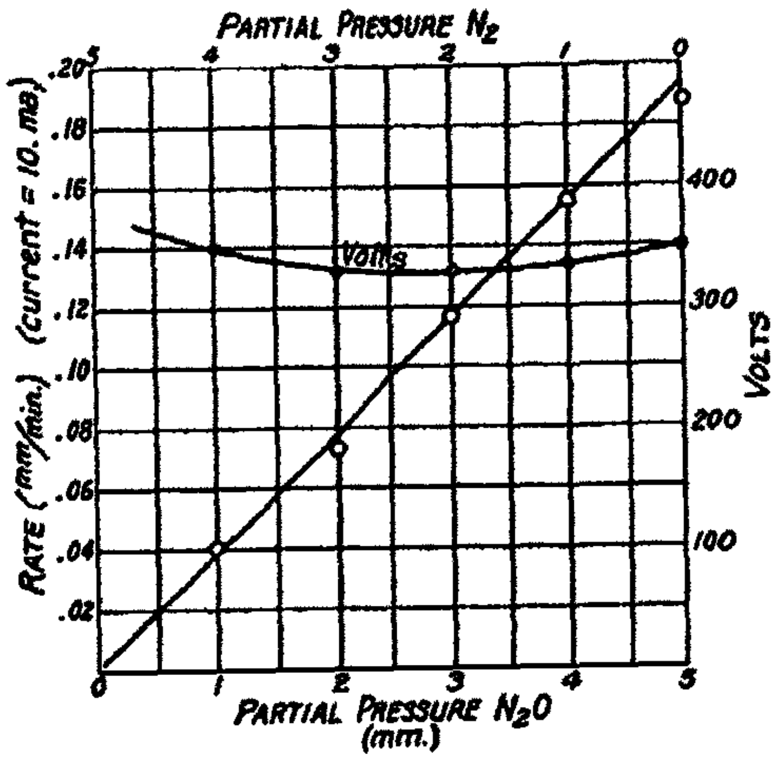

FIG. 4

The effect of nitrogen on the initial rate of decomposition.

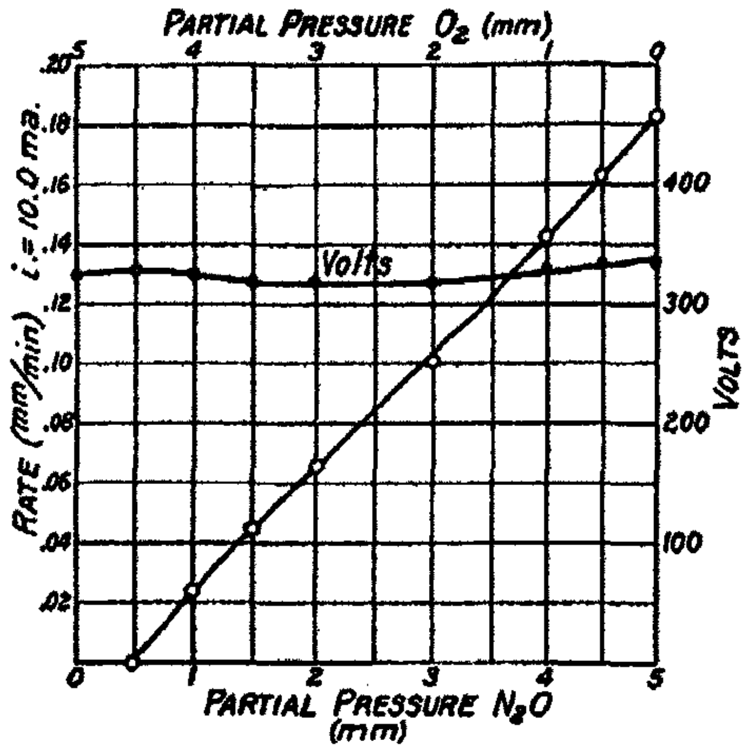

FIG. 5
The effect of oxygen on the initial rate of decomposition.

for a mixture composed of ten per cent nitrous oxide and ninety per cent oxygen. This is the only instance where no pressure change could be observed when nitrous oxide was present in the discharge.

The effect of argon on the rate of dissociation is shown in Fig. 6. The results differ from those obtained in nitrogen and oxygen in that argon materially lowers the cathode fall of potential and also that the decrease in rate due to the added argon is slightly more than a proportionality.

The results obtained in helium are illustrated in Fig. 7. It will be observed that the retarding action of helium is materially less than that given by a direct proportionality.

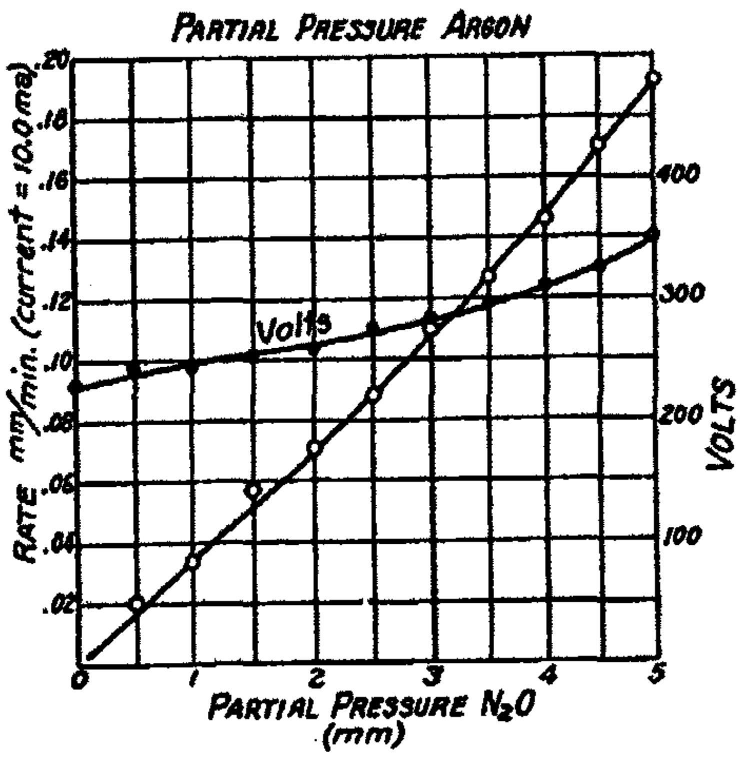

FIG. 6
The effect of argon on the initial rate of decomposition.

The Products of Decomposition. An analysis of the decomposition products showed them to be present in the same ratio irrespective of the current in the discharge, or of the pressure in so far as it could be varied. No attempt was made to determine the amount of nitrous oxide undecomposed. The results showed practically all the nitric oxide formed was oxidized to nitrogen dioxide in passing through the cooled trap; the amount of nitrogen trioxide formed was small. The final reaction was computed from the equation

$$x\,N_2O = 83N_2 + 16O_2 + y\,NO_2$$

where 83 and 16 represent the relative amounts of nitrogen and oxygen collected in the auxiliary discharge tube. A solution of this equation gives x = 100, and y = 34. The ratio of nitrogen to nitrogen dioxide is therefore 83 to 34 or 2.44 to 1.

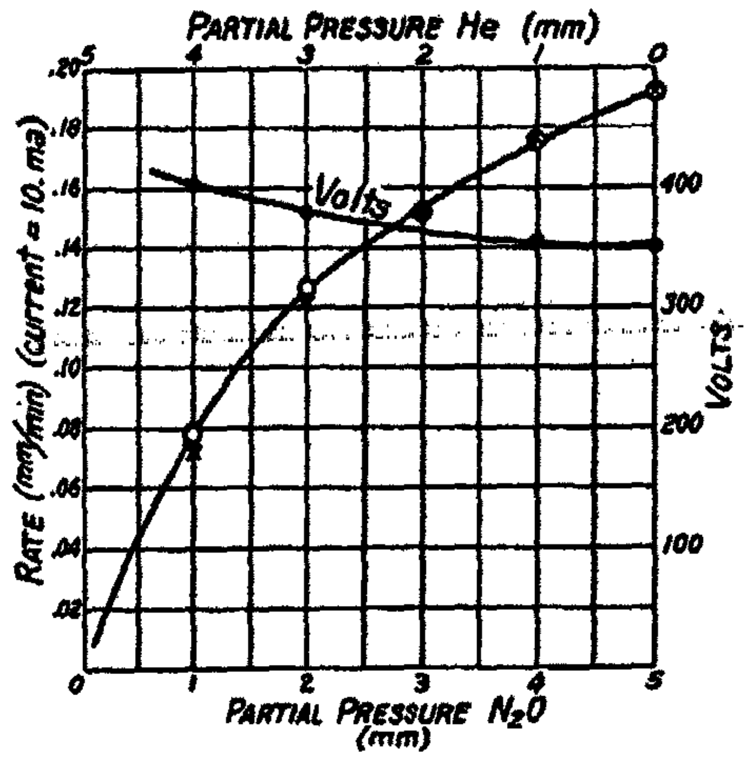

Fig. 7

The effect of helium on the initial rate of decomposition.
o = observed; x = computed

Discussion of Results

The results which have just been presented on the dissociation of nitrous oxide in the glow discharge are in general agreement with those given previously for synthetic reactions as far as the electrochemistry of the discharge is concerned. Apparently the only differences observed in any of the reactions studied are in the M/N ratios, in the minimum number of collisions that an ion must make with neutral molecules for reaction to go to completion, and in the relative ability of various foreign ions to incite chemical action.

The data given in Figs. 2 and 3 show that the initial rate of dissociation is independent of the initial pressure between wide limits and is proportional to the current. Thus the rate may be expressed by the same electrochemical equivalence law given for synthetic reactions, i.e., $dP/dt = \alpha I$. It follows from this that the chemical activity results from primary processes occurring in the discharge, the reaction being initiated by active states formed by direct electron impact; the interaction of excited states and the reactivity of states resulting from secondary processes are not appreciable. The simplest interpretation of these results is that used in the previous reaction studied, namely, that the reactivity takes place about the positive ions formed directly by the electrons ejected from the cathode.

A simple picture of the mechanism of formation of positive ions by electrons emitted from the cathode has been presented in the preceding article of this series.[1] In brief it was shown that the electrons leaving the cathode are accelerated by the cathode fall of potential through the Crookes dark space; this space is practically one ionization mean free path in length. The energy required is then expended by the electrons in the negative glow. Measurements of the rate of decay of reactivity in the negative glow show for mixtures of nitrogen and oxygen that the average path over which an electron is capable of inciting reactivity is 2.5 ionization mean free paths. The number of ions formed per electron of current is obtained directly from this value.

The relative ability of various ions to decompose nitrous oxide may be estimated from the results obtained in the presence of added gases. Thus Figs. 4 and 5 show the initial rate of decomposition in the presence of nitrogen and oxygen to be proportional to the partial pressure of nitrous oxide. It is not surprising, therefore, that the observed dissociation starting with pure nitrous oxide showed the rate at any time t to be proportional to the partial pressure of the gas remaining undissociated.

In a gas mixture containing nitrous oxide, nitrogen and oxygen, the ions are distributed among the three gases in proportion to their relative partial pressure times their efficiencies of ionization. The efficiency of ionization is defined as the average total number of positive ions formed per electron per cm. path at 1 mm. pressure and 0°C.[2] Unfortunately no accurate values are available for the probability of ionization in nitrous oxide; it is known, however, to be similar to that of nitrogen and oxygen. The observed fact that the initial rate of dissociation of nitrous oxide was always proportional to its partial pressure in mixtures containing various amounts of nitrogen and oxygen indicates that the ionization is distributed among the gases in proportion to their relative concentrations and also that the reaction is initiated primarily by N_2O^+ ions, the N_2^+ and O_2^+ ions being apparently ineffective.

These results may be expressed by the equation

$$\frac{dp_{N_2O}}{dt} = K \frac{\theta_{N_2O}\, p_{N_2O}}{\theta_{N_2O}\, p_{N_2O} + \theta_{N_2} p_{N_2} + \theta_{O_2} p_{O_2}} \tag{6}$$

in which θ is the efficiency of ionization and p is the partial pressure. The right hand term, therefore, gives the ratio of N_2O^+ ions to the total number of ions formed. Since θ is approximately the same for all three gases the rate of reaction is proportional to the rate of formation of N_2O^+ ions.

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[1] Brewer and Kueck: J. Phys. Chem., 36, 2133 (1932).

[2] Compton and Van Voorhis: Phys. Rev., 27, 724 (1926).

Attention should be called to the difference between this expression and equation (5) for the rate of reaction for various initial pressures of pure nitrous oxide. S in the former expression is inversely proportional to p but K in the present instance is independent of P. Thus, since the total number of ions formed is independent of the pressure, the reaction becomes one of an apparent zero order, when only the initial rate for various total pressures is considered. On the other hand, the fact that the rate is proportional to p_{N_2O} for every separate run shows that the course of each individual reaction follows a first order expression; this is due to the fact that the reactivity is initiated primarily by N_2O^+ ions.

The results for argon differ from those of nitrogen and oxygen only in that the rate is just slightly less than proportional to p_{N_2O}. This decrease in rate is doubtless due to the lowering of the cathode fall of potential in the presence of argon. The value of θ_A is so close to that of θ_{N_2} for electrons of energy above 50 volts that its effect is negligible.

Helium differs from the other gases tried since the rate of dissociation is greater than that to be expected from the partial pressure of nitrous oxide. The ionization efficiency of an electron in helium, however, is materially lower than in the other gases discussed. Assuming the ionization efficiency to differ by a factor of two and one-half, as is the case for nitrogen and helium, the rate of decomposition as computed from the rate of production of N_2O^+ ions alone is given by the points marked x in Fig. 7. The increase in voltage due to the presence of helium is not considered in these calculations; this correction would tend to raise the computed values slightly where P_{N_2O} is small. The agreement between the observed and computed points is such that the conclusion can again be drawn that the rate of decomposition is determined by the rate of production of N_2O^+ ions, the He^+ ions being ineffective.

The Mechanism of Decomposition

It is evident from the result just presented that the rate of reaction is determined by the rate of formation of N_2O^+ ions, and that foreign ions and the secondary processes existing in the discharge have no apparent influence on the reactivity. Any speculation involving the mechanism of reaction around N_2O^+ ions necessitates a knowledge of the ratio of molecules decomposing to the number of ions formed, $M_{N_2O}/N_{N_2O^+}$.

In the preceding article of this series two separate methods were described for computing the rate of positive ion formation in the negative glow. The number of positive ions formed under conditions similar to the present ranged from 3.4 to 3.7 per electron of current. The positive ion current is negligible above 1 mm. pressure so may be neglected in the calculations. In the synthesis of nitrogen dioxide described in the previous paper reasons were presented for believing that the positive ions striking the cathode did not contribute to the reactivity. These factors, however, are not effective for decomposition reactions so no correction for the loss of ions need be made.

The number of molecules of nitrous oxide decomposed per electron is 14.5. Hence the ratio of molecules reacting to ions becomes M/N = 14.5/3.7 = 3.92, or 4.0 within the limit of experimental error.

The M/N values obtained from α rays[1] range from 1.74 to 4. Lind suggests the theoretical ratio of 2 for clusters neutralized by electrons and 4 for clusters neutralized by negative ions. The latter concept, however, can not be applied to the glow discharge since the rate of negative ion formation is too slow in comparison with the time necessary for a positive ion to reach the walls. Loeb[2] gives 6.1×10^5 collisions between an electron and nitrous oxide molecules as the number necessary for attachment.

The mechanism of reaction around the N_2O^+ ions, therefore, must be either through a cluster of the form $(4N_2O)$, or one involving steps or limited chains. The evidence is insufficient for a determination of the final mechanism, but the fact that the M/N ratio is independent of the initial pressure favors the straight cluster concept in preference to most types of secondary processes. Further, it is difficult to devise a chain mechanism not involving nitrogen in the form of atoms, excited molecules, or ions. If any of these contributed to the reaction chains, the rate, as shown by Fig. 4, would not be inversely proportional to the amount of nitrogen present.

Again, the mechanism postulated by Gedye[3] in which it is suggested that decomposition is occasioned by excited oxygen cannot be correct in the present case, since the reaction is definitely retarded below that given by a proportionality to p_{N_2O} for high oxygen concentrations. Gedye, also, is forced to assume the thermal dissociation of two nitrous oxide molecules by collision with the activated products of reaction of each ion in order to account for an M/N = 4 ratio. The fact that the rate is independent of the total pressure as well as proportional to p_{N_2O} in the presence of various foreign gases capable of absorbing energy makes the possibility of the existence of a thermal mechanism highly problematical.

It is possible for a cluster of the $(4N_2O)^+$ type to dissociate in several ways, and hence it is not surprising that the various investigators using different methods of dissociation have observed considerable differences in the relative concentrations of the reaction products. Wourtzel[4] expressed the primary reaction as $4N_2O = 3N_2 + 2NO_2$ for α ray decomposition. Joshi[5] using the silent electric discharge suggests two modes of dissociation, the first and principal method being that given by Wourtzel and the second a straight decomposition expressed by the equation $2N_2O = 2N_2 + O_2$.

In the present experiment, where the reaction products were removed immediately from the sphere of reaction and where the pressure was much

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[1] Lind: "Chem. Effect of α Particles."

[2] Loeb: "Kinetic Theory of Gases."

[3] G. B. Gedye: J. Chem. Soc., **1931**, 3016.

[4] E. E. Wourtzel: Le Radium, **11**, 289 (1919).

[5] Joshi: Trans. Faraday Soc., **25**, 118 (1929).

lower than that used by Wourtzel and by Joshi, the reaction is expressed by the equation

$$\begin{array}{lll} & \nearrow 4N_2 + 2O_2 & \text{A} \\ (4N_2O)^+ + e & \rightarrow 4NO + 2N_2 & \text{B} \\ & \searrow 3N_2 + 2NO_2 & \text{C} \end{array}$$

in which the probability for A occurring as given by the concentration of the reaction products is approximately two times that for B, or one-half times that for C.

The energy changes involved may be an important factor in directing the mode of dissociation of the clusters, as well as in determining the M/N ratio. Reasonable values for the energy changes are

$$\begin{array}{ll} N_2O \rightarrow N_2 + \tfrac{1}{2}O_2 + 17.6 \text{ k.g.c.} & \text{A} \\ N_2O \rightarrow NO + \tfrac{1}{2}N_2 - 4.6 \quad '' & \text{B} \\ N_2O \rightarrow 3/4\ N_2 + \tfrac{1}{2}NO_2 + 10.2 \text{ k.g.c.} & \text{C} \end{array}$$

Unfortunately it cannot be told from the data whether the principal reaction is A and B, or A and C. It is true that no free NO was observed and that the N_2O_3 was never present in any appreciable amounts; however, there was always an excess of oxygen present and since the rate of oxidation of NO is high at liquid air temperatures the possibility of finding free NO or N_2O_3 is necessarily small. The fact that B is endothermic does not preclude its possibility since the N_2O^+ ions itself possesses some 320 k.g.c. of energy.

There is not sufficient evidence at present to permit the drawing of any definite conclusion regarding the dependence of the M/N ratio on the heat of reaction and on temperature. The limited data available, however, indicate a larger ratio for highly exothermal reactions. For instance, the oxidation of hydrogen and methane show twice the ion efficiency found in the case of the synthesis of nitrogen dioxide and ammonia. The intermediate value found in the present case is, therefore, in line with what might be expected from the heat of dissociation.

In discussing the decomposition of the $(4N_2O)^+$ clusters nothing has been said concerning whether the neutralization occurs at the walls or in the gas phase. In discharge tubes of the type illustrated at the right in Fig. 1B it has been shown by direct experiment that the molecules synthesized reach the walls carrying a positive charge;[1] gas phase neutralization is negligible in the negative glow. A discharge tube of the type shown in Fig. 1A however, permits a greater opportunity for gas phase neutralization of the ions. Even here, however, the chance for this type of neutralization to occur is small except in the case of excess oxygen, where the concentration of O_2^- ions becomes appreciable. It will be observed in Fig. 5 that the rate is negligible in mixtures of 90% oxygen and 10% nitrous oxide, and also that the rate curve bends downward with an increasing partial pressure of oxygen. These lowered yields evidently result directly from the presence of gas phase

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[1] Brewer and Kueck: J. Phys. Chem., 35, 1281 (1931).

neutralization wherein the M/N ratio is smaller than that observed for wall neutralization. This change in ratio occasioned by the mode of neutralization may account for the fact that the values given for α rays vary from 1.7 to 4.0, depending on the conditions of the experiment.

Summary

The rate of decomposition of nitrous oxide in the glow discharge is independent of the initial gas pressure and is proportional to the current. It may be expressed, therefore, by the general equation for the electrochemistry of gases, namely $dP/dt = \alpha I$. These results are interpreted to indicate that the reactivity is initiated by positive ions formed in the discharge.

The effect of added nitrogen, oxygen, argon, and helium on the rate of reaction was always such that the proportionality between the observed rate and the rate in pure nitrous oxide was equal to the relative concentration of N_2O^+ ions formed in the mixture and in the pure gas. Thus the reaction appears to be initiated by N_2O^+ ions, and to be little affected by N_2^+, O_2^+, A^+, or He^+ ions.

The ratio of $M_{N_2O}/N_{N_2O} = 4$ was obtained, the error involved in the calculation appears relatively small.

An analysis of the initial decomposition products showed that the cluster decomposes in part directly into N_2 and O_2 and in part either into NO_2 and N_2 or into NO and N_2, the data not being sufficient to decide between the two processes.

I. MOLECULAR WEIGHT IN DIFFERENT STATES OF AGGREGATION

BY G. ANTONOFF

I. INTRODUCTION.

The notion of molecular weight has been established as a result of work with gaseous matter, and owing to the Avogadro hypothesis it has become possible to express the same in definite units. Thus, when the matter is in a gaseous state, there is a rational method permitting to determine experimentally the molecular weight of a substance.

But as soon as the matter is presented in another state than the gaseous, nothing definite is known about its molecular state, and the difficulty is in the want of methods for its determination. This problem, however, important it appears to be, is very little advanced yet, in spite of the fact that there is quite a lot spoken about it in the literature. The substances in the liquid state are believed to be, according to the prevailing view, either "normal," if their molecular weight is said to be the same as in the gaseous state, or "associated" when the molecular weight is supposed to be a certain multiple of that in a gaseous state.

These views, however, are based on a number of empirical rules, whose theoretical foundation is very poor. Besides, their agreement with facts is also highly illusory.

Under such circumstances, it is nowadays realised by some authors that one cannot continue like that, that accumulation of empirical rules does not lead us anywhere, and that some general principle is necessary, a principle analogous to that of the Avogadro hypothesis,[1] which would give a rational solution of the problem for other than the gaseous states.

The object of this work is to propose such a principle on a basis of an evidence, which appears to some people *too simple to be true,* as the immense amount of work previously done has created the belief of an extreme complexity of the problem; I therefore come across difficulty in convincing other people, especially as the results obtained are in contradiction with such theories as that of van der Waals, whose views are accepted by many people as a Gospel. And yet his theory, in spite of the enormous amount of facts accumulated has not given the solution of the problem of the molecular weight of liquids at all.

I treat the subject quite differently on the whole, but I accept together with van der Waals the existence of molecular forces, which account for the surface tension in matter of all states of aggregation. I arrive at quite different results.

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[1] W. E. S. Turner: "Molecular Association," 4 (1915).

To follow the views expressed in the following pages, it is, therefore, necessary to place one-self in an entirely different point of view, and no compromise appears to be possible between the two.

However, I must add, that the views I was led to are by no means novel. They can be shown to have some features of the theory of De Heen, which was completely abandoned and superseded by that of van der Waals. The reason of it is chiefly due to the fact that at the time there was not enough experimental or other evidence to serve as a foundation to his theory. His theory may be called a chemical theory.

When I started this work, I had an entirely open mind and for quite a long time I worked without any theory of my own. On a basis of experimental evidence, I was led to such deductions, which enabled me to establish a general principle, which is incompatible with the van der Waals theory. At the same time, it unquestionably leads to a kind of a chemical theory, and permits making deductions which are in perfect agreement with the experimental evidence. Moreover, it gives an explanation for some important facts which remained unnoticed merely for the reason that the accepted theories did not allow any room for them.

On the other side, the empirical rules, such as the relation of Eötvös—Ramsay and the like show a very poor agreement with experimental evidence, so poor that it is necessary to shut one's eyes not to see that this relation is not a representation of a true law. It is often possible to force the experimental figures into an empirical formula, but the closer examination of errors will immediately disclose the falsehood of it.

On the contrary anybody who wishes to verify some of my results and repeat some of my calculations, will see at once that *they are strictly exact* and conform with the experimental data within the limits of experimental errors in the proper sense of this word.

I have been recently criticised on the ground that I am alone who has arrived at such results, as exposed in the following chapters.[1] To this I must add that apart from De Heen a number of present day authors arrived at similar views, such as Drucker,[2] Harver,[3] Duclaux[4] and some others. One can also add that the recent investigation by means of X-rays by Katz[5] is also in favour of such views and is against the theory of van der Waals. According to Katz it gives "une image de la structure des liquides bien differente de celle qui nous avait donné jadis M. van der Waals."

Thus, the novelty of my work lies not so much in the views I arrived at, as in the general principle which leads to them. Owing to it, in the subject which appeared hopelessly complicated, everything becomes extremely simple, and so far I have not come across a single case amongst the material I investigated, which would be in disagreement with my theory.

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[1] G. G. and I. N. Longinescu: Soc. Roumaine des sciences, **33** (1931).

[2] Z. physik. Chem., **68**, 616 (1909).

[3] J. Phys. Chem., **16**, 451 (1912); **17**, 386 (1913).

[4] J. Phys., [6] **5**, 33 (1924); **8**, 336 (1927).

[5] Réunion Internationale de Chim. Phys., Activation et structure des molécules, Paris, 408 (Oct. 1928).

This theory can be expounded in different ways, but for the time being I prefer to follow the different stages in the order which corresponds to the natural development of this theory. It originated in such a way that I began to work out a certain theory of surface tension with the view of explaining some experimental results of mine. This theory is on the whole conformable with the classical theories; in other words, I operate with the same notions, putting them in a somewhat different shape, and it will be reproduced in the following chapter, starting from the first principles. This theory, quite unexpectedly, has led me to the conclusions which resulted in the theory of states of aggregation, as exposed in the following chapters.

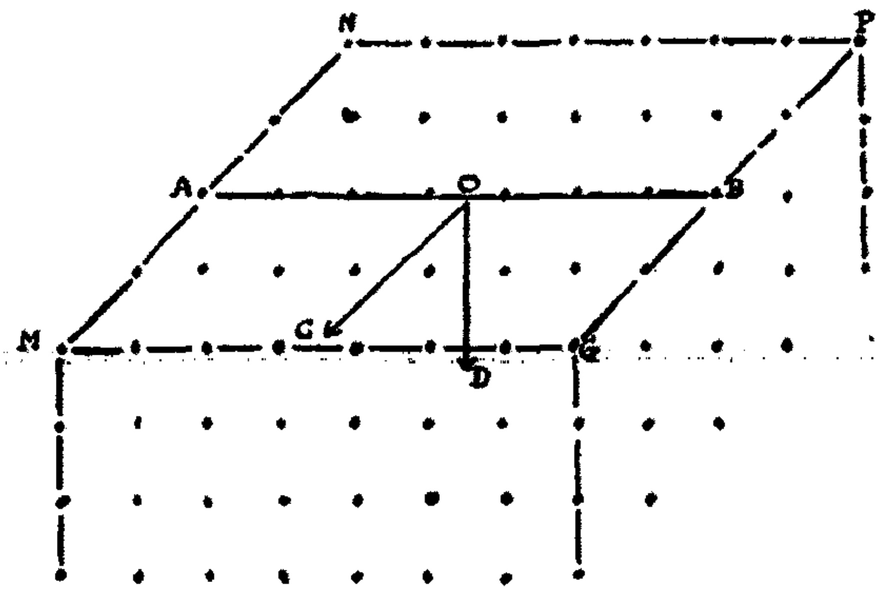

FIG. 1

II. SURFACE TENSION AND MOLECULAR STRUCTURE.

Imagine a crystal of rectangular form, which consists of molecules at an equal distance from one another. This is represented by dots in Fig. 1. I take a case of a non-polar substance where each dot represents a molecule, and not an ion, as in the case of sodium chloride, the case which was treated in detail by Max Born.[1] Each molecule is supposed to exercise a uniform field of force, no matter what is its nature, which may be different in various cases.[2]

This hypothesis is not the only one possible. But the result obtained remains substantially the same, and independent of the actual form of law of attraction. For this reason I limit this investigation to one form only.

Imagine a line AB in the surface, connecting one row of molecules. The adjacent rows of molecules will exercise a pull on the line AB. Consider at first only the forces acting in the surface MNPG tangentially to it. The effect of molecules situated on one side of the line AB, summed up together, is resulted in a force OC, *which is generally called the surface tension.*

It can be shown in a similar way that owing to the presence of molecules situated below the surface MNPG, there will be also a pull exercised on line AB in the direction perpendicular to OC and acting, inwards, represented in the drawing by the line OD. It will be of the same order of magnitude as OC

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[1] Sitzungsber. preuss. Akad. Wiss., **48,** 901 (1919).

[2] J. E. Lennard-Jones: Proc. Phys. Soc., **43,** 461 (1931).

and will be somewhat bigger, as molecules on either side of the line AB will act jointly in this case. The field of force, according to the prevailing theories is of such nature that the force varies inversely as a high power of the distance. Consequently in the summing up of the forces due to individual molecules, the adjacent row of molecules will contribute the most important term in the sum. The total force acting on the whole surface MNPG inwards will be obtained by summation of forces acting on all rows in the surface. *This inward force per unit area of the surface is generally called molecular, or normal pressure.*

It thus appears that if the number of molecules and their distance from one another is known, one can easily derive the normal pressure from the breaking stress of the crystal, and thereby also, calculate the surface tension.

However, in practice, it is not possible to proceed in this way, as one gets ridiculously low figures from the breaking experiments,[1] incompatible with other evidence. This is generally attributed to the fact that the crystal is never perfect and always has small invisible cracks, which diminish the resistance to traction to a considerable extent.

For these reasons, Born[2] in trying to estimate the surface tension of rock salt proceeded in an inverse way: he determined the compression of a crystal under external pressure. He has arrived at the conclusion that there exist also repulsive forces making themselves felt at compression, owing to which the substance resists to further compression.

I do not intend to use this method experimentally, and I therefore assume for the sake of argument that I am dealing with an ideal crystal. I denote by F a balance-force existing between two adjacent molecules at a distance d, where d is the intramolecular distance. This resultant force is equal to the difference between the attractive and repulsive forces and at a distance d it is positive, i.e. is an attraction.

If the distance between two adjacent molecules is d, in a length md there will be m molecules. Per unit length there will be $1/d$ molecules. Let the number of molecules per unit volume be n

Then, $1/d = n^{1/3}$.

The expression for surface tension can be found as follows.

Imagine two rows of molecules, as in Fig. 2.

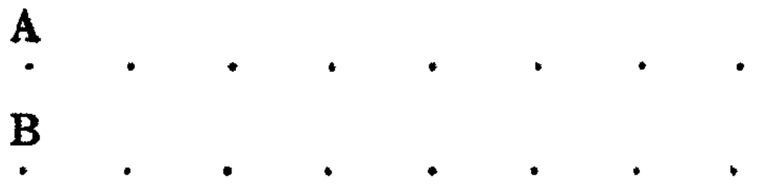

FIG. 2

Force between A and B = F

Between A and the adjacent row commencing with B, the force will be:

$$F + AF + BF + \ldots = F(1 + A + B \ldots), \text{ where}$$

A, B, etc. . . . are rapidly diminishing terms, if the force diminishes rapidly with the distance.

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[1] Antonoff: Phil. Mag., 44, 63 (1922); Z. physik. Chem., 102, 388 (1922).

[2] Loc. cit.

The whole attraction of one row by the other will be then:

$$\begin{array}{l}
F + AF + BF + CF + \ldots \\
F + 2\,AF + BF + CF + \ldots \\
F + 2\,AF + 2\,BF + CF + \ldots \\
F + 2\,AF + 2\,BF + 2\,CF + \ldots \\
\cdot \qquad \cdot \qquad \cdot \qquad \cdot \\
\cdot \qquad \cdot \qquad \cdot \qquad \cdot \\
\cdot \qquad \cdot \qquad \cdot \qquad \cdot \\
F + 2\,AF + 2\,BF + CF + \ldots \\
F + 2\,AF + BF + CF + \ldots \\
F + AF + BF + CF + \ldots
\end{array}$$

The summation gives:

$$Fn^{1/3} + 2\,A\,Fn^{1/3} - 2\,AF + 2\,BFn^{1/3} - 4\,BF + 2\,CFn^{1/3} - 6\,CF + \ldots$$

Only terms containing $n^{1/3}$ need be kept, n being of the order of 10^{21}, which gives:

$$Fn^{1/3}(1 + 2\,A + 2\,B + 2\,C + \ldots) = Fn^{1/3}\,K$$

This is the expression for attraction of two adjacent rows.

This is not yet the expression for surface tensions as on either side there are other rows of molecules which ought to be taken into consideration. Also the rows of molecules below the surface. All these summations will be of similar character and will ultimately lead to an expression of the same type, having the constant somewhat different from that in the expression just deduced. Thus, with sufficient accuracy one may assume that the surface tension (α) is equal to:

$$\alpha = K\,F\,n^{1/3} \qquad (1)$$

Thus, the surface tension appears to be a simple function of n— the number of molecules per unit volume, the quantity which is as important for the liquid and solid states, as the Avogadro constant for the gaseous state.

Now, proceeding in a similar way, one can also deduce the expression for the normal pressure.

Assuming that the field of force is uniform, it can be seen that the inward force on a row of molecules per unit length OD will be practically the same as the force acting in the surface tangentically to it, OC in Fig. 1, and will only have a slightly different constant. Its effect per unit area of the surface, as the normal pressure is generally expressed, will be then obtained by summation of forces due to all rows of molecules per unit area.

Thus, if we denote the normal pressure by P,

$$P = K\,Fn^{1/3} \times n^{1/3},$$

where K is not the same as in expression (1), or

$$P = K\,Fn^{2/3} \qquad (2)$$

From expressions (1) and (2) it follows:

$$P = K\alpha\,n^{1/3} \qquad (3)$$

where K is not the same as before. This equation establishes the relation between the normal pressure and the surface tension for a crystal.

The same theory can be applied to the liquids with the difference that in this case, the above magnitudes will acquire *statistical values.*

Owing to kinetic effects there can be no question of any definite position of molecules at a determined distance. The conditions on the surface will be also complicated by the fact that the molecules with the speeds above the average will leave the liquid and spread in the surrounding space in form of a vapour. The formation of vapour is probably the reason why the normal pressure of liquid cannot be measured in a direct way as a breaking stress of a column of liquid. A slight presence of gases causes a formation of vapour, which disturbs the experiment. Thus, the normal pressure of a liquid cannot be measured in a direct way. But, the surface tension of a liquid can be deduced from the breaking stress of its film, which constitutes a beautiful method whereby it is measured in the form which follows directly from its definition.[1]

Thus, the equations just deduced (1), (2) and (3) appear from the first sight to be of not much use, considering that the surface tension (α) alone can be measured experimentally.

Thus, although these formulae indicate a simple relation between the surface tension and n—the number of molecules per unit volume—we are not yet in position to determine the same. It was shown by myself in some other[2] publications, that the surface tension of a solid can be determined by measuring the field of force more or less directly. This method does not involve the quantity n, and the surface tension can be deduced without the knowledge of the same.

If one compares the value obtained by this method for rock salt, and that calculated by Born, under the assumption that it has the structure as indicated by the X-ray method, there appears to be a certain contradiction which is probably due to the fact that the molecular weight of the solid is not what it is assumed to be. Some experiments of W. H. Bragg seem to corroborate this view.[3]

It will be shown later on, that in special circumstances these equations can be solved all the same and thus important information can be derived as to the molecular weight of matter in different states of aggregation.

It will be seen that this can be attained by applying the above equations to systems consisting of different phases in equilibrium with one another. For purely methodical reasons, the easiest way of proceeding is to use systems capable of separating into two liquid layers. Their properties will be described in the following chapter and it will be indicated in what manner their properties can serve for the solution of the above problem.

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[1] This is the justification of my method of procedure, as I am interested mainly in liquid systems. If I wanted to deal with solids, I would have to proceed in the same way as Born.

[2] Phil. Mag., **2**, 1258 (1926); **3**, 792 (1927).

[3] Nature, **111**, 428.

III. EQUILIBRIUM BETWEEN TWO LIQUID LAYERS.

The formation of two liquid layers takes place very much in the same manner as when a solid powder is suspended in a vehicle, i.e. in a liquid of some sort. The solid matter after having settled down will form a bottom layer, if it is specifically heavier than the liquid, or a top layer if it is lighter. But in both cases the particles of the solid are suspended in a vehicle.

Something similar takes place when the matter forming another layer is a liquid. Particles of it are distributed among the particles of the other, this latter liquid assuming the rôle of the vehicle, or a solvent as it should be called in a case of true solutions. This is illustrated in the adjoining drawing, representing schematically a vessel containing two liquid layers. The space left blank represents the vehicle. The particles of the liquid represented by big dots form a bottom layer in Fig. 3 and the top layer in Fig. 4. The small dots represent the particles of vapour.

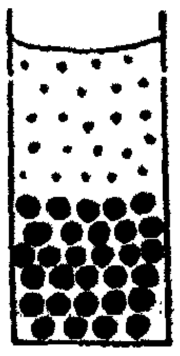

FIG. 3

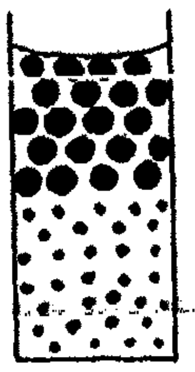

FIG. 4

The liquid thus suspended sends its vapour into the remaining part of the vehicle, as well as into the outside space. It is convenient for sake of argument to have the two layers enclosed into a ring-shaped vessel. Then both layers will have a free surface in contact with the vapour. This vapour must obviously be the same for both layers, otherwise there would be a perpetual distillation. Thus from consideration of equilibrium the both layers must have the same vapour pressure,

$$p_1 = p_2,$$

where p_1 is the vapour pressure of one layer and p_2 that of the other.

Both vapours must be obviously also of the same composition. This is known under the name of the law of Gibbs-Konovalov.

It should be pointed out that two liquid phase systems such as ether and water are generally spoken of as a solution of ether in water (lower layer) and a solution of water in ether (upper-layer). Investigation of properties of such systems shows that this is not the case at all. The only way to explain their properties is to assume the view as above, i.e., *that both layers are solutions in the same solvent.* In mixing two liquids with limited solubility, it is not possible to say which of them will play the rôle of a vehicle, or a solvent in the case of true solutions, by simply looking at them. This can be concluded by observing the freezing point curve of the system, Fig. 5. This curve is very typical for the systems forming two liquid layers. It indicates that both liquid layers give off the same ice. It can be also seen that the curve always contains an eutectic point. The two concentrations A and B corresponding to two saturated solutions, constituting the upper and the lower layer, are situated on one side of the eutectic point. This, together with the fact that they separate the same ice, indicates that both layers are solutions in the same solvent.

If two solutions in the same solvent have the same freezing point, the same vapour pressure,[1] Fig. 6, they must contain the same number of molecules dissolved per unit volume, according to the elementary theory of solutions. The theory of solutions, however, is in most cases valid only for dilute solutions, although there are known cases when the ideal laws hold true also in concentrated solutions. The causes of these deviations not being exactly known, one must be careful in drawing conclusions. Although the elementary theory indicates that the two solutions contain an equal number of molecules, I do not want to accept it, unless this same can be corroborated by independent evidence. This can be derived from conditions of equilibrium expressed in terms of surface tension.

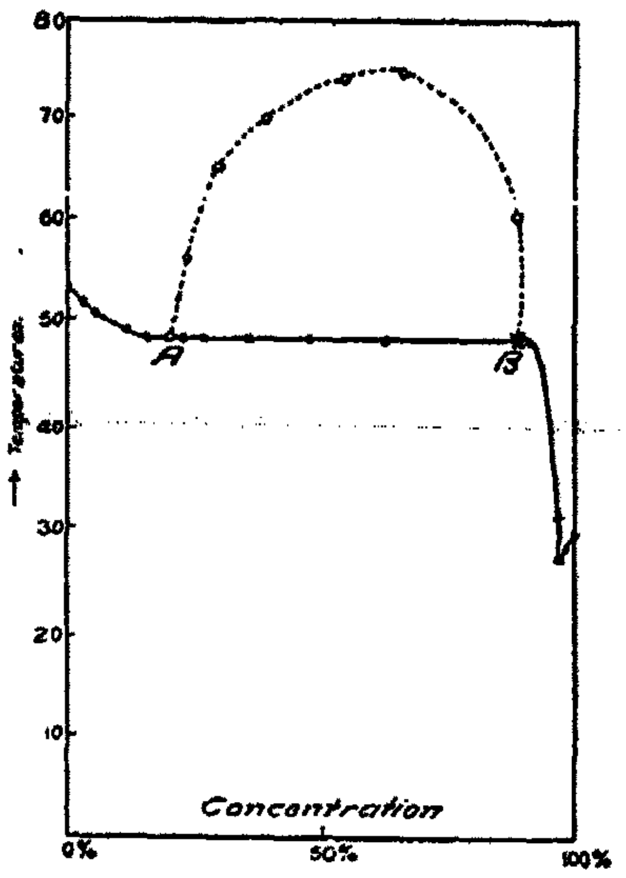

FIG. 5

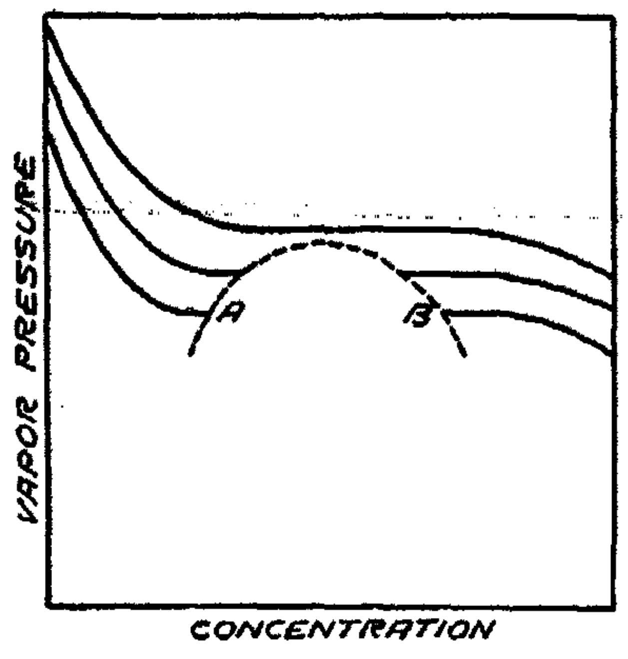

FIG. 6

I found experimentally in 1907[2] that in a state of equilibrium, the following law can be found to be true:[3]

$$\alpha_{12} = \alpha_1 - \alpha_2, \quad (4)$$

where α_{12} is the interfacial tension, α_1 and α_2 the surface tensions of two satu-

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[1] In Figs. 5 and 6 the dotted curve is the so-called solubility curve, within which the system consists of two layers. Outside it the system is homogeneous. Points A and B correspond to saturated solutions constituting the two superposed layers.

[2] Antonoff: J. Chim. phys., 5, 372 (1907).

[3] It may be mentioned here that in the course of time, a number of authors tried to repeat my work, and some of them without success. This problem presents great difficulties experimentally. It is not always easy to choose an appropriate method. It is often very difficult to obtain and maintain equilibrium in the course of work. Besides that, some of them did not fully realise the meaning of equilibrium between two phases. As this matter is important, I treat it in a separate paper, Kolloid-Z., 59, 7 (1932).

rated layers against their common vapour. I generally call it the "law of difference."

Now making use of the formulae (1) (2) and (3) of the foregoing chapter, one can deduce this law and demonstrate its theorical significance.[1]

One can take it for granted that when two liquid layers are in equilibrium, the relation

$$p_{12} = p_1 - p_2 \tag{5}$$

will hold true, where p_1 and p_2 are the normal pressures of the two liquid phases, and p_{12} is the resultant force. It was shown on p. 2410 that the relation between the normal pressure and the surface tension is of the form

$$p = K\alpha n^{1/3}, \tag{3}$$

where α is the surface tension and n is the number of molecules per unit volume, and K is a constant. On a basis of the equation (3), one can express (5) as follows:

$$P_1 = K\alpha_1 n_1^{1/3},$$
$$P_2 = K\alpha_2 n_2^{1/3},$$
$$P_{12} = K\alpha_{12} n_{12}^{1/3},$$

or

$$\alpha_{12}\, n_{12}^{1/3} = \alpha_1\, n_1^{1/3} - \alpha_2\, n_2^{1/3}.$$

The expression becomes identical with

$$\alpha_{12} = \alpha_1 - \alpha_2, \tag{4}$$

assuming that the value of K[2] is the same in all cases, if

$$n_{12} = n_1 = n_2.$$

It may be pointed out that:

$$\alpha_{12} = \alpha_{21} \quad \text{i.e.}$$

one gets the same result if one measures α_1 against α_2 or inversely, α_2 against α_1.

Consequently

$$n_{12} = n_{21}, \quad \text{i.e.}$$

on both sides of the surface of contact the molecular concentration is the same, and it is equal to that at the free surface of both layers. It is obvious that n_1 and n_2 comprise the number of particles of the solvent, which is obviously the same in both layers. This investigation shows that n molecules of one kind

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[1] It should be mentioned that these equations were deduced for pure substances. Now we will deal with heterogeneous systems. I take it for granted that the magnitudes involved are a rectilinear function of molecular concentration. So that in the following investigation all K, α and P with indices and without will represent values obtained by the rule of mixtures. This assumption appears justified in cases where there is no chemical action between molecules, that is to say, when we have exact information as to the number of molecules in the system.

[2] One can see from the theory of surface tension as on p. 2410 that K depends on the distance between the particles. As we have to deal with equimolecular systems, K must be the same in the above cases, provided the molecules occupy the same volume in both layers, or else their volume is negligible compared with the intramolecular distance. I assume that this must be actually the case, as in all systems I investigated, I never came across cases where these phenomena might make themselves felt.

(1) and n molecules of another kind (2) are each distributed between m mols of solvent. Let γ be the surface tension of the solvent.

γ_1 be the surface tension of the system composed of mols (1)
γ_2 be the surface tension of the system composed of mols (2)

Then the surface tension of one solution α_1

$$\alpha_1 = \frac{\gamma m + \gamma_1 n}{m + n}.$$

The surface tension of the other solutions α_2

$$\alpha_2 = \frac{\gamma m + \gamma_2 n}{m + n}, \text{ and}$$

$$\alpha_1 - \alpha_2 = \frac{\gamma m}{m + n} - \frac{\gamma m}{m + n} + \frac{\gamma_1 n}{m + n} - \frac{\gamma_2 n}{m + n}.$$

Thus, the factor contributed by the solvent, being the same in both systems, disappears in the difference $\alpha_1 - \alpha_2$.

Let us assume now that the solvent vanishes from the system, everything else remaining the same, i.e., m = 0.

Then $$\alpha_1 - \alpha_2 = \gamma_1 - \gamma_2.$$

The meaning of this speculation will be seen on p. 2419, whereby the rectilinear form of relationship appears quite justified.

The surface concentration according to existing theories, may sometimes differ from that at the interior of the solution.

Consider first the simplest case, when the concentration of the surface layer is the same as at the interior. In such case, the two liquid layers must be equimolecular, i.e. *they contain equal number of molecules per unit volume*, and this is the condition under which the law (4) of difference must necessarily be true.

If the surface concentration differs from that at the interior, the same must apparently be the case, for the following reason: we saw that both layers in equilibrium must have the same vapour pressure and the same composition of vapour. The change of molecular surface concentration therefore must be the same for both layers. And the two layers also in this case must be equimolecular.

Thus the conditions:

$$p_1 = p_2 \quad \text{and}$$
$$\alpha_{12} = \alpha_1 - \alpha_2$$

must be recognised as conditions of equilibrium.

The first condition must obviously be always observed as otherwise there would take place a perpetual distillation. The second is a natural consequence of it, and the fact that the experimental evidence indicates a full agreement between the two, appears to be the proof that the ideal gas laws hold true in such cases. If we make use of the evidence as to the molecular state just derived from other data, everything appears in strict agreement with the ideal laws. *I therefore conclude that in most cases the other factors, which might disturb, these laws, do not come into play at all.*

If such was the case, one might expect the law:

$$\alpha_{12} = \alpha_1 - \alpha_2$$

not to be true.

As regards the causes of deviations from the ideal gas laws, many authors have already expressed the opinion that they may be due to the want of exact knowledge of the number of molecules in a given volume. If the actual number of them was known to us, these laws would show themselves valid. The above evidence seems to corroborate this view. In other words these deviations are not due to molecular forces at all. The systems discussed in this paper are far from being ideal, and yet they are in strict agreement with the simple gas laws. The confirmation of this view I can see also in the following facts. The two liquid layers in equilibrium always have the same freezing point. Amongst systems I investigated there were some in which the surface tension of both layers differed enormously. In some other cases the both layers had very nearly equal surface tensions. In both cases, however, the freezing point of the two superposed solutions was the same. If the molecular forces affected the freezing point, this might be different.

Experience has convinced me that the apparent departures from the law of difference can be attributed to some special factors which may disturb the state of equilibrium. In this paper I leave such cases quite out of my consideration, and discuss them elsewhere.[1]

The main object of this chapter is to show that the two solutions forming the two superposed layers in equilibrium are equimolecular, i.e. they contain the same numbers of molecules per unit volume.

This means that on addition of one of the components, the molecules added combine with some molecules in solution without increasing their number.

This also means that if in one layer the average molecular weight of the dissolved substance is A, a number of these molecules will combine with one another to form the molecules of the other layers. This can be expressed by the equation:

$$nA = A_n,$$

where "n" is the factor of association. The actual value of A may not be known,[2] and it may be difficult to determine the same for the want of a suitable method. This, however, is of no importance to us.

We went into all these details because these systems bear an intimate analogy with systems liquid-vapour, where the same phenomena take place *according to precisely the same laws, only without the solvent, which is replaced, so to say, by the vacuum.* In these systems, A represents nothing else but the molecular weight of the vapour, which can be determined by the known method.

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[1] Loc. cit.

[2] Owing to phenomenon of solvation A may comprise some particles of the solvent. Apart from this the solvent retains properties of pure solvent.

IV. SYSTEMS LIQUID-VAPOUR.

Investigation of critical phenomena shows that there is a marked analogy between systems separating into two liquid layers and cases when a pure substance separates into a liquid and vapour at its critical point.

It was pointed out by van't Hoff that in solutions the dissolved matter very often behaves in such a manner, as if it were in a gaseous state; in other words, in this condition it obeys ordinary gas laws.

Thus, it can be shown that in some cases a substance can undergo a process of condensation within a solvent in the same manner, as an individual substance condenses in a space not otherwise filled at its critical point.

The study of systems separating into two liquid layers presents the advantage that the experimental work is easier and one can apply a number of methods for their investigation, which are not applicable for systems liquid-vapour.

Two liquid layers in equilibrium are iso-osmotic solutions as van't Hoff would call them. I use this expression to convey the idea that these solutions being in equilibrium, exercise the same pressure on one another.

It was shown on p. 2412 that in case of partially miscible liquids one of them distributes itself in the other and forms lower or upper layer according as to it is specifically lighter or heavier than the other. Thus, we have such a picture before us, as if liquid and its vapour were incorporated into a solvent, conserving their characteristic properties. It thus appears that, in a sense, the solvent plays the rôle of "vacuum."

The van't Hoff's law says:

The iso-osmotic solutions contain at a given temperature, in the same volume, the same number of dissolved molecules, and this number is the same as if the dissolved matter was gaseous.

From the above analogy it follows **that liquid and vapour in equilibrium contain an equal number of molecules per unit volume.** This must be always true for systems in equilibrium and they need not be ideal at all, just as it was stated on p. 2415 for systems liquid-liquid.

Vapour and liquid are also iso-osmotic, in the sense that they exercise the same pressure on one another. It is not possible in this case to make use of the freezing point method, as it was done for the systems liquid-liquid. By investigation of the latter systems one can see that the systems liquid-vapour are really the same thing, only without the solvent, which only plays the rôle of a medium in which the system is distributed.

The same can be also made clear from surface tension consideration, although here again we are restricted in the use of methods for systems liquid-vapour. But the investigation of two liquid layers in the vicinity of the critical point explains everything.[1] At the critical point these systems separate into two liquid layers of equal volume, the surface of separation being flat. About 2°-3° below the critical point, it still remains flat, and there is no capillary rise in this region. The two liquid layers formed can be easily separated from

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[1] Antonoff: J. Chim. phys., 5, 364 (1907).

one another and it can be shown by capillary method that they have the same surface tension in the critical region, i.e. in the notation as before,

$$\alpha_1 = \alpha_2.$$

This is quite natural as in the critical region, i.e. all round the critical point, the surface tension does not vary with concentration.

The fact that there is no capillary rise at the interface between the two liquid layers in the vicinity of the critical point shows that in this region the interfacial tension $\alpha_{12} = 0$.

In other words: $\alpha_{12} = \alpha_1 - \alpha_2 = 0.$

which is nothing else but a particular case of (4) the law of difference.

In the systems liquid vapour, we can observe the same characteristics in the critical region,[1] viz. the meniscus is flat, and there is no capillary rise. The flat meniscus means $\alpha_1 = \alpha_2$ where α_1 is the surface tension of the vapour and α_2 that of the liquid.

The want of capillary rise means $\alpha_{12} = 0$, where α_{12} is the interfacial tension at the interface liquid-vapour, which is usually measured by capillary method, and commonly called the surface-tension. α_1 and α_2 cannot be measured for the want of method, but owing to their equality, one can conclude that equation (4) can be also established in this case, in the form:

$$\alpha_{12} = \alpha_1 - \alpha_2 = 0.$$

which is valid for the critical region.

One can thus conclude that this equation being particular form of (4), p. 2413, that at least in the critical region *gas and liquid are equimolecular*, as the relation (4) was established subject to that condition. The fact that the above law verifies itself for systems liquid-vapour as well, indicates that the surface tension of the solvent contributes as much to the surface tension of one layer as the other. This follows also from considerations of p. 2410 and justifies the assumption made there. To this case is applicable the same investigation only K, α and p with indices or without will represent corresponding values for pure substances and not solutions. The experimental methods do not allow us to go any further. For systems liquid-liquid, these properties can be studied not only in the critical region, but at temperatures well beyond it, and the remarkable analogy between these phenomena constitutes here again the proof that all above conclusions can be also applied to systems liquid-vapour. It was shown by myself that the law of difference (4) can be extended to systems liquid-vapour already sometime ago[2] and nowadays this is being realised also by some other authors.[3]

It will be seen later on that there exist other evidence indicating that systems liquid-vapour are governed by the same laws as the systems liquid-

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[1] Wolf: Ann. Chim. Phys. (3) **49**, 270 (1857); Drion: (3) **56**, 221 (1859); Clark: Phil. Mag. (5) **10**, 145 (1880).

[2] Antonoff: Phil. Mag., **1**, 1121 (1926).

[3] J. L. Shereshefsky: J. Phys. Chem., **35**, 1712 (1931); N. Barbulescu: Physik. Z., **31**, 48 (1930).

liquid. See below. Now, I want to point out the importance of the conclusion we arrived at, viz. **that vapour and liquid are equimolecular. This gives us a rational method of establishing the molecular weight of the liquid.**

The molecular weight of the vapour can be found from its density. If the liquid contains the same number of molecules per unit volume, its molecular weight M_l can be deduced from that of the vapour M_v in the following way:

$$M_l = \frac{M_v \delta_l}{\delta_v},$$

where δ_l is the density of liquid and δ_v that of vapour.

The ratio of these two is nothing else but the factor of association, showing how many simple gaseous molecules form one molecule of a liquid.

The above relation indicates that the molecular weight of a liquid must be variable with temperature. Investigation of these effects requires careful consideration and before proceeding with the question of molecular weight, I shall consider in detail the effect of temperature on properties of liquids.

V. EFFECT OF TEMPERATURE ON PROPERTIES OF LIQUIDS AND VAPOURS AND THE LAW OF RECTILINEAR DIAMETER.

When investigating the properties of liquids and their vapours as a function of temperature, one often gets difficulties due to phenomena of supersaturation: the liquid may not evaporate, or a vapour may not condense at temperatures at which these phenomena are due. From this point of view the systems liquid-liquid present the great advantage because these phenomena never take place, and condensation or the inverse takes place sharply at a determined temperature. This is not difficult to understand. Vapours require a presence of a liquid to do away with supersaturation. When the condensation takes place within another liquid, the latter being a liquid, the condensation or the inverse process always takes place without a lag.

This is important to note in considering the properties as a function of temperature, which are subject to the same laws in systems liquid-liquid and liquid-vapour. For this reason, I prefer to consider the properties of systems liquid-liquid in the first place. A very convenient object for this kind of work is, for example, the system aniline-amylene (trimethyl-ethylene), which has its critical temperature of solution at about 14°C. I determined its so-called solubility curve in such a way that solutions of different concentration were subjected to different temperatures at which they separate into two liquid phases, if they were homogeneous before, or vice-versa. This "clouding temperature" can be observed very sharply especially in the vicinity of the critical point, where two phases are of nearly equal volume, and the separation appears in form of a very thick milk. Thus, in the vicinity of the critical point, every observation can be reproduced several times with a marked accuracy, and with always concordant result. By plotting the concentrations against the temperatures (clouding temperature) one gets a curve having appearance of an assymmetric parabola.

When I did this experiment for the first time, I found that in some places *the observations fell off the* smooth curve quite appreciably. Thus, for example in some observations in the critical region, where the separation into two layers is very sharp and the temperature can be read off up to 0.01°C. easily, some of the points fell off the smooth curve as much as about 0.5°C. I did not have any idea whatever as to what these phenomena could be due to, and there was a general tendency to attribute these deviations from the smooth curve to experimental errors or to a bad work rather than to intrinsic causes.

At the same time, quite incidentally I had an opportunity of plotting the figures for latent heats of vaporisation of pure liquids, against temperatures, figures which I found in the literature, and which showed at more or less regular intervals quite distinct signs of discontinuity, i.e. there could be observed at some parts of the curve some kinks, Fig. 7, just as I observed them in the solubility curve as mentioned above.

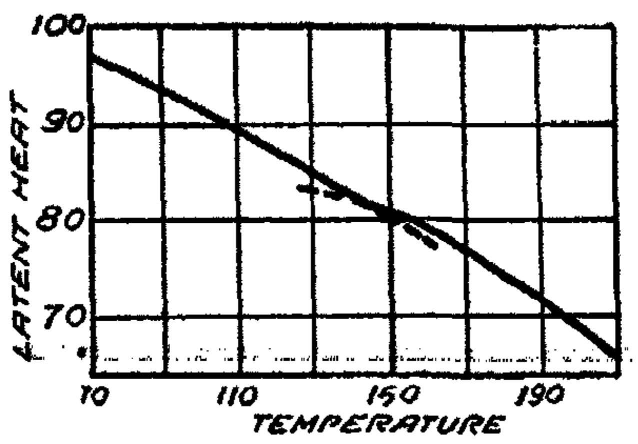

Fig. 7

Having begun to realise that these effects are well above the limits of experimental errors, I repeated twice more the experiments with aniline-amylene. It is true that the absolute figures found with each sample of amylene were different. Amylene is not a very well defined substance, consisting in varying proportions of several isomers according to the mode of preparation and purification. But in all cases, I found the kinks in the curve, and one of them particularly well pronounced was situated in the vicinity of the critical point.

But if one plots densities of solutions against temperature, one also gets curve having the shape of an asymmetric parabola, but it appears practically smooth. A much greater accuracy is necessary to see whether there are also kinks in this curve or not. It may be that in this latter case these phenomena are masked by a kind of compensation. This becomes clear if one plots the densities against concentrations, this curve having a very peculiar shape.[1] Knowing the limits of experimental error and the accuracy of my observations, I can see **that these discontinuities are an intrinsic property of matter.**

In the system phenol-water, the same phenomena of discontinuity can be observed very clearly. Phenol is a substance chemically well defined, capable of being obtained in a state of extreme purity.

If we examine figures for other systems found by other authors, *it can be seen that practically all of them may be shown to exhibit one or several kinks.* The examples of such data are quite numerous, and can be found, for example, in the Landolt-Börnstein Tables.

I noticed long ago that in the data for latent heat of vaporisation for pure liquids, the same phenomena are observed. This I observed at first in figures which were already in existence some 30 years ago or even more. Investigating

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[1] Antonoff: Phil. Mag., 1, 1127 (1926).

other data, which have become known in the course of time, one can notice exactly the same, and this applies to figures of different authors.

These data are not due to direct observations of latent heats of vaporisation, but are calculated on a basis of a certain theory, from densities. It is known that densities can be measured with considerable accuracy, and it is therefore interesting to see whether the density-temperature curves reveal anything of the same kind.

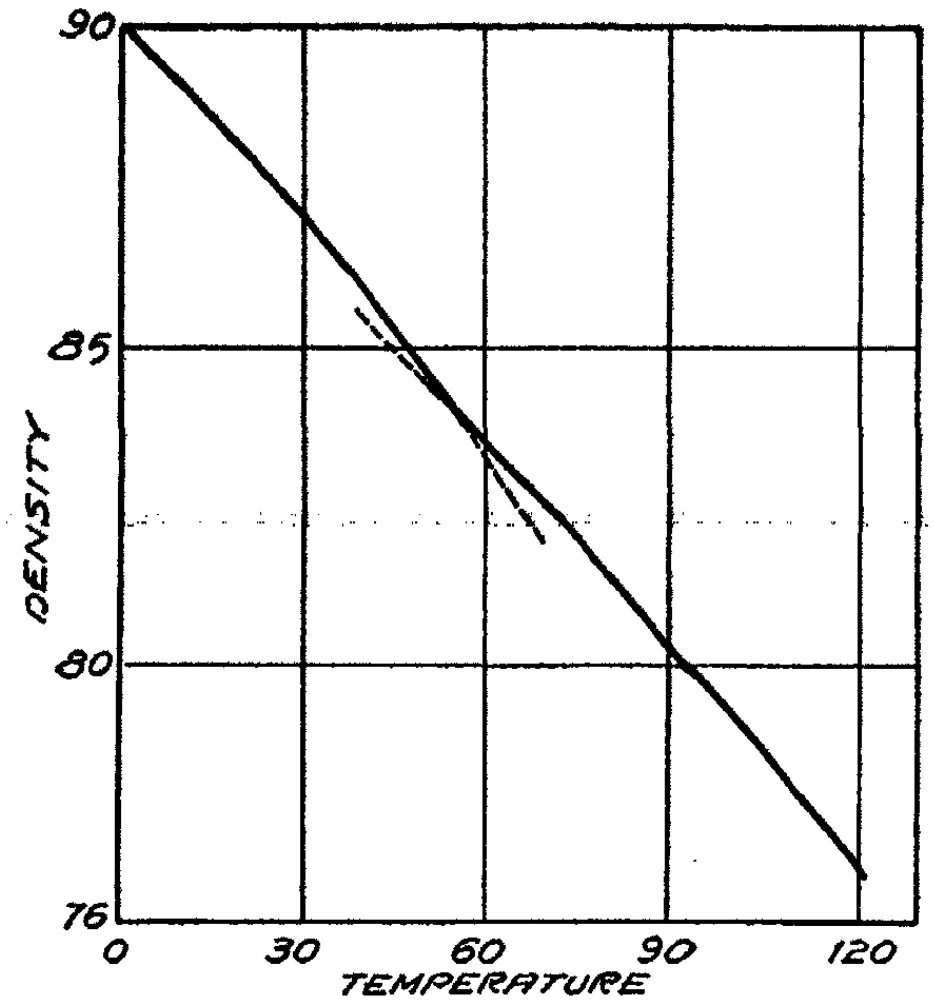

FIG. 8

These discontinuities as a matter of fact can be seen if the densities are given with three decimal places. The existing figures are generally given with four decimals, the last being doubtful.

The density-temperature curves have the kinks not quite so well pronounced as in latent heat of vaporisation curves. This is due to the nature of the relation,[1] whereby these affects are accentuated, but these kinks correspond to the same temperatures in both curves.

The density curves plotted on a millimeter paper on such a scale that one-tenth of a mm. corresponds to a unit in a fourth decimal place, show in some cases the kinks sufficiently clearly that they can be well noticed, as can be seen from one of the adjoining curves, Fig. 8.

It is, however, much better to demonstrate these phenomena mathematically, the method showing itself much more sensitive.

To represent graphically, it is better to take either the sum of densities of the liquid (δ_l) and that of the vapour (δ_v), or their difference. The nature of

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[1] The latent heats L were calculated by the formula of J. E. Mills:

$$L = K(\sqrt[3]{\delta_l} - \sqrt[3]{\delta_v}).$$

these relations is such that in the first case we get a rectilinear curve as the two curvatures compensate each other in this case. Whereas, if we take the difference $\delta_l - \delta_v$, and plot it against temperatures, the curvature becomes much more pronounced. Just if we plot the difference $\delta_l - \delta_v$ which I shall denote hereinafter with the letter δ without an index, the whole curve for δ beginning from the critical point can be expressed as a series of exponential equations, such as:

$$\begin{aligned} Ae^{\lambda\delta} &= T + A, \\ A_1e^{\lambda_1\delta} &= T + B_1, \\ A_2e^{\lambda_2\delta} &= T + B_2, \\ &\text{etc.} \ldots \end{aligned}$$

And this is the most convenient form for treating the subject mathematically. In these notations T is the temperature counted from the critical point as o, downwards, A, A_1, A_2, etc., λ, λ_1, λ_2, etc., B_1, B_2, etc., are constants characteristic for the equation between two kinks. Thus, the nature of the relationship remains the same for all ranges of temperature, the constants varying only, and changing bruskly when a new portion of the curve begins after a kink.

The first equation naturally differs in such a manner that it contains two identical constants A and A, as δ must become = o at the critical point.

To calculate individual values of δ_l and δ_v one can take advantage of the fact that $(\delta_l+\delta_v)/2$ *is a straight line in the intervals of the curve between two kinks.* This expression is known under the name of rectilinear diameter of Cailletet-Mathias. This, however, is a straight line, only between two kinks, and *it has a character of a zig-zag line* on the whole. Thus one can put:

$$\frac{\delta_l + \delta_v}{2} = \frac{T + a}{b}, \tag{1}$$

where a and b are constants.

On the other side, the exponential equations as above can be represented as:

$$\delta = \delta_l - \delta_v = \frac{\log.\left(\frac{T + B}{A}\right)}{0.4343\lambda}. \tag{2}$$

From these two equations values of δ_l and δ_v for a given interval between two kinks can be calculated, viz.:

$$\delta_l = \frac{T + b}{a} + \frac{1}{2}\,\frac{\log.\left(\frac{T + B}{A}\right)}{0.4343\lambda}, \tag{3}$$

$$\delta_v = \frac{T + b}{a} - \frac{1}{2}\,\frac{\log.\left(\frac{T + B}{A}\right)}{0.4343\lambda}. \tag{4}$$

The two expressions differ only in so far as the logarithmic term comes in with the opposite sign. Thus, in the expression for $\delta_l + \delta_v$, the logarithmic terms disappear, and the remaining expression is that of a straight line. On the contrary, in the expression $\delta_l - \delta_v$, the two halves of the logarithmic term add up, and the discontinuity is of a much more pronounced character and is much better visible on a drawing than when δ_l and δ_v are plotted themselves.

Thus, for example, for hexamethylene between 280°C. (its critical point) and 0°, the equations giving acccurate values of δ are as follows:

$$\begin{array}{lll|r}
(1) & 0{,}027\, e^{20.97\delta} & = T + 0{,}027 & 274\text{—}280^\circ \\
(2) & 2{,}328\, e^{6.961\delta} & = T + 5{,}20 & 260\text{—}274^\circ \\
(3) & 7{,}591\, e^{4.743\delta} & = T + 18{,}71 & 190\text{—}250^\circ \\
(4) & 18{,}20\, e^{3.665\delta} & = T + 52{,}93 & 120\text{—}180^\circ \\
(5) & 25{,}03\, e^{3.351\delta} & = T + 77{,}31 & 60\text{—}110^\circ \\
(6) & 66{,}30\, e^{3.258\delta} & = T + 1000.1 & 0\text{—}500^\circ
\end{array}$$

In the column on the right hand side are given the approximate intervals of temperature between which the given equations are valid. See also Table I on p. 2427.

The kinks can be seen fairly well on a drawing, Fig. 12. The deviations from the smooth curve due to experimental errors are not visible to the eye as a rule, the accuracy of the measurements being well above. Thus each portion of the curve between two kinks appears quite smooth. This together with the fact that *the constants of the equations are so distinct for each portion* is the best proof that these kinks are real and not due to experimental errors.

Similar equations can be deduced for any other substance, whether "normal" or "associated" in the sense in which these words are nowadays used. Thus, the same result is obtained whether the substance contains the group OH or not. The form of relationship remains the same at all intervals of temperature, and so far I know one case only when it does not hold true, is the case of water at about 4°C.

All these facts can be interpreted only in one way, viz. all liquids must be associated and their degree of association must vary with temperature. Effectively, if it were not the case, or if the degree of association did not vary with temperature, one would expect a different type of relationship. One would expect perhaps a linear form of relationship, but the very fact that it is a case of an exponential equation, suggests that there must be here involved some molecular changes.

At the critical point $\delta_l = \delta_v$, the liquid and vapour, both, contain an equal number of molecules per unit volume, i.e.:

$$\delta = \delta_l - \delta_v = 0.$$

It is δ, i.e. the excess density of the liquid compared with that of vapour, which follows the exponential law as a function of temperature. It is interesting to deduce this relation theorically.

The quantity δ and its variation with temperature must be intimately connected with the formation of complex molecules. Let us call m the number of complex molecules per unit volume, and let us assume that $d\delta/dT$ is proportional to the rate of formation of complex molecules, i.e.

$$\frac{d\delta}{dT} = K\frac{dm}{dT}.$$

The law connecting m with temperature must be of the form

$$\frac{dm}{dT} = \frac{K}{T+B},$$

$$d\delta = \frac{KdT}{T+B} = K d\ln(T+B),$$

$$\delta + e = K\ln(T+B).$$

By putting $K = 1/\lambda$ this expression can be presented in the form:

$$Ae^{\lambda\delta} = T + B. \tag{5}$$

The expression thus deduced is identical with the expression found empirically on a basis of experimental data.

It is not difficult now to imagine the whole mechanism of these transformations. Consider a unit volume of the saturated vapour (A) and a unit volume of the liquid (B). Both will contain an equal number of molecules per unit volume, as it follows from this theory. Let us now cool the system down.

The density of A will diminish owing to the loss of a certain number of molecules, say n, which will depart owing to condensation. At the same time the molecules will concentrate themselves owing to thermal effect, assuming that contraction is a linear function of temperature.

On the other side, in the volume B the liquid will become denser because its number of molecules had to diminish by n, in this case, not through departure, but owing to association. At the same time, the system contracted according to a linear law.

Thus, in accordance with this theory both liquid and vapour remain equimolecular in spite of the changed temperature. This picture is in good agreement with equations (3) and (4) deduced empirically (p. 2422). Thus, it becomes clear why the average density $\delta_l+\delta_v/2$ is a linear function of temperature, i.e.

$$\frac{\delta_l + \delta_v}{2} = \frac{T + a}{b}. \tag{6}$$

On the other hand, we have deduced (5) which together with (6) will give equation (3) and (4). This is what one may call the theory of rectilinear diameter. Up to now there did not exist any theory of it at all.

Between two kinks, the above equations give an accurate expression of existing facts. The part of the straight line between two kinks intersect each other sometimes at a quite appreciable angle, which may serve as a method of locating the kinks, see Fig. 9.

The discontinuous character can be also seen in other properties of liquids, but it can be attributed in most cases to density measurements, as the same comes as a factor in calculating these properties. Thus the same character can be observed also in latent heats of vaporisation, viscosities and surface tensions.

The latent heat of vaporisation (L) follows the law of the same form as above, i.e.:

$$C\,e^{\mu L} = T + D,$$

whereas viscosities and surface tensions can be expressed by a formula containing the temperature in the exponential, i.e. $\alpha + B = A\,e^{\lambda T}$, where α is the surface tension, which formula is an accurate expression with given constants for an interval of temperature between two kinks. For example, for ethyl acetate this formula acquires the form $\alpha + 33.62 = 33.19e^{.0024T}$ for the interval of temperature 150-110 T approximately, and

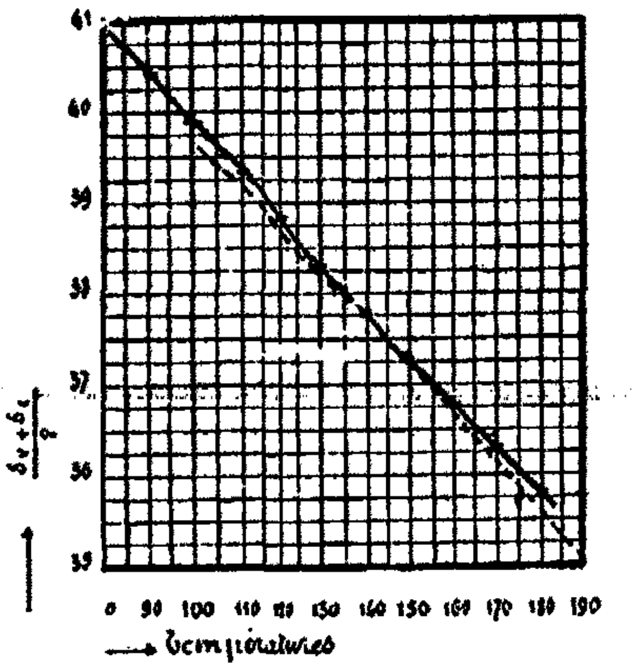

FIG. 9

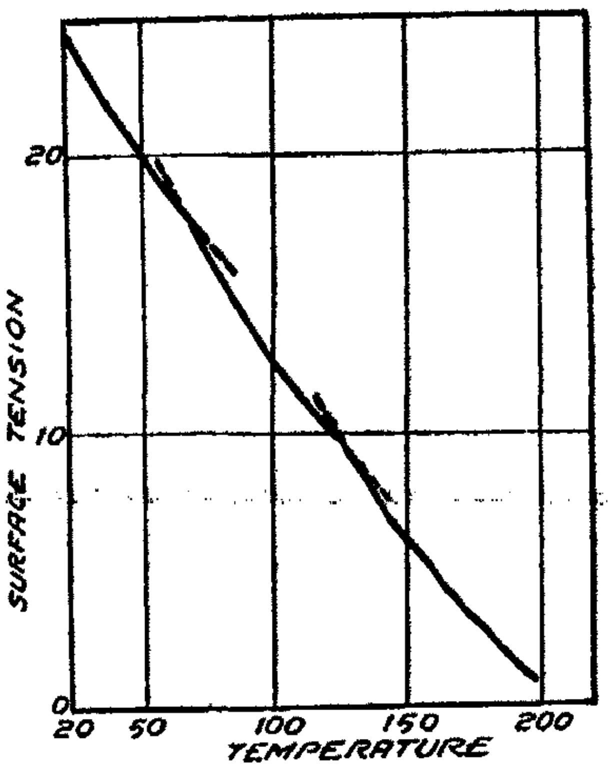

FIG. 10

$$\alpha + 21.32 = 20.93e^{.0035T}$$

for the interval 100-70 T.

Similarly for viscosities (η) the expression $\eta + c = De^{\mu}$ can be shown to be true.

Curve (Fig. 10) is an example of a surface-tension curve as function of temperature. This is generally believed to be a straight line. Considering the drawing and examples of calculated values, I ask myself, ***how can such curves be mistaken for a straight line?***

It is an obvious mistake to draw a continuous curve on a basis of experimental data such as they are. In such case, the deviations from the smooth curve are of a systematic character. The experimental points appear periodically below and above the smooth curve and these deviations are far too large to be regarded as due to experimental errors.

If one calculates by the formulae given by myself, one can see at once that the true law has been guessed, and such deviations that may take place between the calculated values and experimental are obviously due to experimental errors, but they are very small and practically not visible on the curves of the size indicated here.

Apart from all evidence presented hereinbefore, the most striking proof and demonstration of these phenomena lies in the constants of the equations given on p. 2423. They are so distinctly different for every subsequent change that the discontinuous character of the properties in question appears beyond all doubt.[1]

VI. MOLECULAR WEIGHT IN THE LIQUID STATE AND ITS VARIATION WITH THE TEMPERATURE

It was shown on p. 2419 that the molecular weight (M_l) of a liquid can be deduced from that of the vapour (M_v) if the latter is known, by the following relation: $M_l/M_v = \delta_l/\delta_v$, where d_l and d_v are the densities of liquid and vapour. This ratio is nothing else but a factor of association, showing how many gaseous particles form one particle of the liquid. Let us call it X.

Thus, $X = M_l/M_v = \delta_l/\delta_v$.

From what we saw in the last chapter, X must vary with temperature.

By plotting X against the temperature one can find its value corresponding to the kinks. It is convenient to find the kinks from the δ curve because the form of the curve is exponential, which makes the calculations easy, and also in the δ curve the kinks are much more visible, than either in δ_l or δ_v curves, as it was already explained before. It is also possible to use the latent heats of vaporisation, which amounts to the same as they are calculated from densities.

This work is laborious and has to be done on a sufficiently large scale to make the kinks visible.

This is illustrated in Table I (giving some numerical data for hexamethylene). In column 1, T represents the temperatures counted from the critical point as zero; in column 2, $\sqrt{t}$— the temperature in the centigrade scale. In columns 2 and 3, δ_v and δ_l are the densities of vapour and liquid borrowed from the paper of Sydney Young.[2] In column 6, δ exp. are values obtained as a difference between δ_l and δ_v. In column 7 δ calc. are the values calculated by the equations mentioned on p. 2423 whose numbers are given in column 9. Column 8 shows the difference between δ exp. and δ calc.

The horizontal lines in the table separate figures between which a kink is situated and give thus the rough indication of its position. In some places figures are found between two horizontal lines. This is done in cases where, apparently owing to interpolation, the figures do not fit the curves on either side.[3] It is obvious that near the kinks interpolation is not safe. It is seen from columns 6 and 7 that the agreement between experimental values of δ and calculated, is in most cases very good.

Although the kinks in some cases may not be well visible to the eye on the drawing, they are well perceptible to the calculus. I can always base the

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[1] Further details can be found in my paper Phil. Mag., 1, 265 (1925).

[2] loc. cit.

[3] These facts were taken into consideration in drawing the curve Fig. 12, where the position of kinks is roughly indicated in accordance with Table I.

TABLE I

1 T	2 t	3 δ_l	4 δ_v	5 δ_l/δ_v	6 $\delta_{exp.}$	7 $\delta_{calc.}$	8 diff.	9 Formula
280	0	0.79675	0.00014		0.7966	0.7967	+0.0001	
270	10	.7874	.0002		.7872	.7872		
260	20	.7779	.0003		.7776	.7777	+0.0001	(6)
250	30	.7685	.0005		.7680	.7680		
240	40	.7591	.0007	1084	.7584	.7583	−0.0001	
230	50	.7496	.0011	681	.7485	.7485		
225				**576**				
220	60	.7400	.0016	462	.7384	.7384		
210	70	.7306	.0022	332	.7284	.7283	−0.0001	
200	80	.7206	.0029		.7177	.7177		
190	90	.7106	.0038		.7068	.7067	−0.0001	(5)
180	100	.7003	.0049	143	.6954	.6954		
170	110	.6898	.0063	109	.6835	.6835		
165				**96.0**				
160	120	.6791	.0082	82.8	.6711	.6711		
150	130	.6680	.0099	67.5	.6581	.6581		
140	140	.6565	.0123		.6442	.6442		(4)
130	150	.6448	.0151		.6297	.6297		
120	160	.6325	.0182	34.7	.6143	.6143		
110	170	.6200	.0219	28.3	.5981	.5981		
102				**24.0**				
100	180							
90	190	.5926	.0314	18.9	.5612	.5612		
80	200	.5780	.0374	15.5	.5406	.5407	+0.0001	
70	210	.5626	.0444		.5183	.5183		(3)
60	220	.5456	.0525		.4931	.4931		
50	230	.5271	.0625	8.43	.4646	.4645	−0.0001	
40	240	.5063	.0750	6.67	.4313	.4313		
30	250							
20	260	.4533	.1111	4.15	.3422	.3422		
18				**4.00**				
15	265	.4354	.1248	3.48	.3106	.3105	−0.0001	
10	270	.4125	.1433	3.01	.2692	.2695	+0.0003	(2)
6	274	.3891	.1634	2.40	.2257	.2257		

equation of a curve on three points situated between two kinks in such a way that the agreement with experimental figures will be perfect. But if one chooses points situated on either side of the kink, no smooth curve will ever agree with experimental figures, and the deviations will have systematic character, which makes quite obvious the existence of the kink.

The figures given in Table I do not indicate the exact position of the kinks. To find the more accurate position of the kink, one can draw two portions of δ curve and find the exact temperature of the kink by interpolation. One can also prolong the range of calculated values of δ beyond the temperature of the kink. From this moment the calculated values begin to depart bruskly from the experimental ones.

This is illustrated by Fig. 11, where (the bottom part) differences are plotted against temperatures, in such a manner that for the temperatures above 100 T the values of δ calc. are equal to δ exp. and their difference = 0. Below 100 T these differences begin to grow systematically. The line drawn on these points crosses the abscissae at about 102 T, which is the temperature of the kink. The top part of the drawing shows the values of X plotted against the same temperatures. At 102° the value of X read off the drawing is about 24.

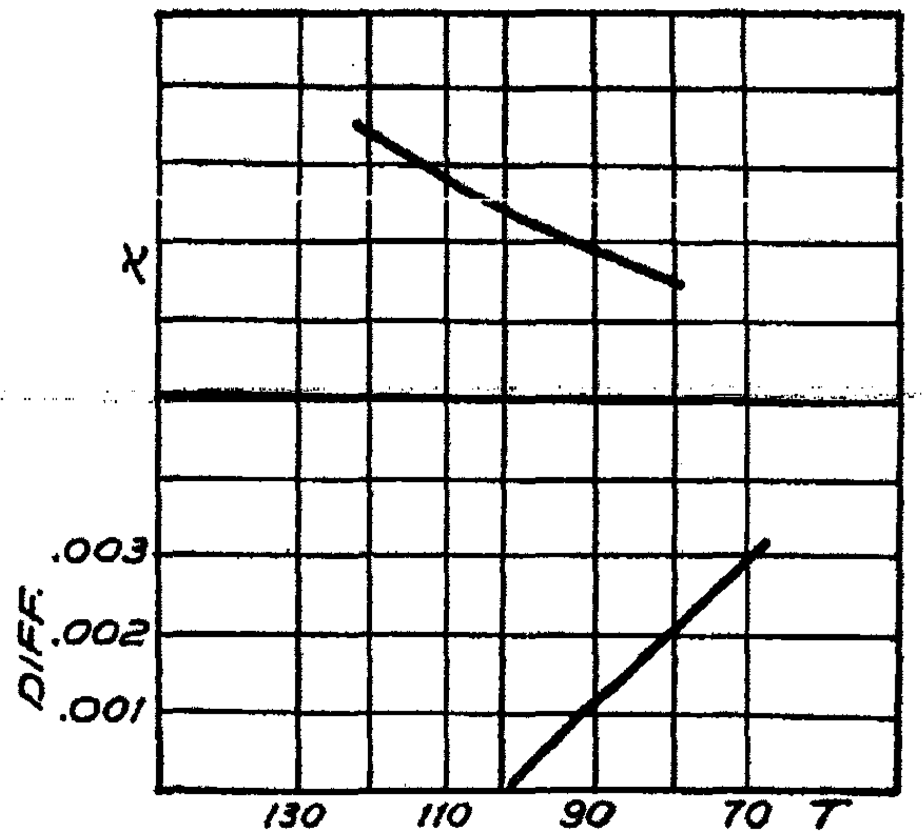

Fig. 11

I choose this point because here the data are more reliable. Near the critical point they are not good enough to enable us to say anything definite. It may be that the value of X = 4 at 18 T is corresponding to a kink. But it may be that the kink is situated between 40 and 30 T, with the value of X = 6.

Although the figures at temperatures further distant from the critical point than 102 T, are most accurate, the determination of X corresponding to a kink becomes more difficult, because dX/dT becomes too large, and a small error in the determination of the temperature of the kink affects X enormously.

Thus I choose as a base the value of X = 24 at 102° T. Then, one can observe a value of X = 96 at 165 T, which is probably the accurate value, corresponding to the kink, as 24 × 4 = 96. Accordingly the table indicates another kink at 225 T with X = 576 = 96 × 6, as the most probable value.

Thus, the process of association of hexamethylene according to this evidence, must consist of the following stages. In the first place, there must be a change (1), not indicated in the table. It commences from the critical point and ends about 3-4 degrees below it, when X passes through the value 2.

$$A + A = A_2. \qquad (1)$$

About changes of this sort it will be spoken more in detail on p. 2432. Now A_2 either combines as:

$$2\ A_2 = A_4$$

$$\text{or:}\quad 3\ A_2 = A_6. \qquad (1)$$

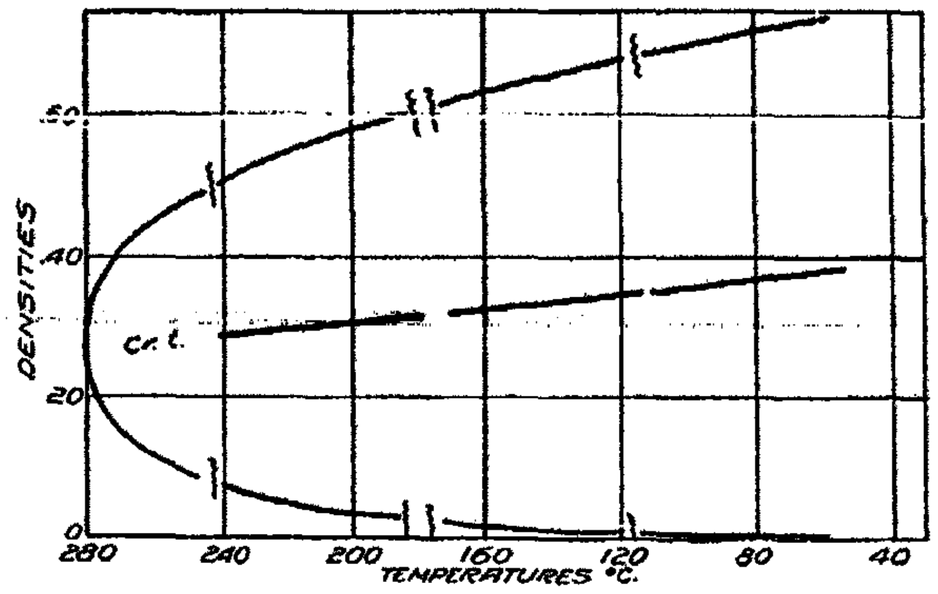

FIG. 12

The following stages will be accordingly

$$6\ A_4 = A_{24} \quad \text{or}$$

$$4\ A_6 = A_{24}. \qquad (3)$$

The existing data cannot settle this point with certainty. But this has no effect on further results.

According to the table two more changes can be observed:

$$4\ A_{24} = A_{96} \qquad (4)$$

$$6\ A_{96} = A_{576}. \qquad (5)$$

In Fig. 12 is given the curve of densities of hexamethylene, the lower branch of the parabola being the densities of vapour, the upper branch is that of the liquid; both meet at the critical point (cr. t. on the drawing). I have indicated the approximate position of kinks, as I have found them mathematically. Near the critical point nothing definite can be seen, the data not being sufficiently accurate, owing to great experimental difficulties. The horizontal line in the middle is the so-called *rectilinear diameter.* For this substance the discontinuities are just above the limit of visibility. One can see from the drawing that the rectilinear diameter is not rectilinear, but is a zig-zag line.

The character of these curves is always the same, and examination of various substances shows that the same phenomena have in some particular cases much more pronounced features. Several examples, where the kinks are well visible are given in Figs. 7, 8 and 9. Fig. 7 shows a kink in the curve of latent heats of vaporisation. Fig. 8 shows a kink in a density curve for benzine. Fig. 9 gives an example of rectilinear diameter for the same substance, where the angle of intersection of two straight lines is clearly visible. Fig. 10 gives an example of a surface-tension curve of methylformate; its discontinuous character is well pronounced.

Sometimes, when the curve is not very well pronounced, I detect the kinks by means of a flexible steel rule. A natural curve can fit well the curved line between two kinks but not otherwise.

It is interesting to mention that in most papers published by the Leiden physical laboratory on this subject, there is a mention of the deviations from the rectilinear diameter and these deviations are stated to be well above the limits of experimental errors, viz. they vary between 0.5 and 2%. It is seen from the above that these deviations are one of the manifestations of the same fact, viz. of the discontinuous character of density curves.[1] I can also give some more examples. Thus for ethyl acetate I found following results. The values of X corresponding to the kinks are as follows:

$$X = 2, 6, 18, 36, 144, 684, \text{etc.} \ldots$$

This shows that the process of association consists of a series of consecutive reactions taking place in accordance with the law of multiple proportions.

The individual stages of which can be represented by the following equations: (See also p. 2416).

		Approximate range of temperature
(2)	$3\,A_2 = A_6$	230°-246°
(3)	$3\,A_6 = A_{18}$	190°-210°
(4)	$2\,A_{18} = A_{36}$	150°-180°
(5)	$4\,A_{36} = A_{144}$	100°-140°
(6)	$A_{144} = A_{684}$	50°- 90°
	etc. . . .	

Thus, at temperatures corresponding to the kinks, the liquid consists of only one kind of molecules (Molekülgattungen).

For this liquid, the equations for δ were calculated as follows:

$$(1) \quad .120\, e^{14.96\delta} = T + .120$$

$$(2) \quad 2.463\, e^{6.649\delta} = T + 5.60$$

$$(3) \quad 5.406\, e^{4.360\delta} = T + 12.80$$

$$(4) \quad 13.39\, e^{3.328\delta} = T + 37.64$$

$$(5) \quad 20.05\, e^{2.986\delta} = T + 62.72$$

$$(6) \quad 94.43\, e^{1.754\delta} = T + 228.31$$

$$(7) \quad 237.1\, e^{1.186\delta} = T + 459.65$$

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[1] Communications from the Phys. Lab., Univ. of Leiden, Nos. 131, 145, 162, 172, etc.; the details can be also found in my paper, J. Chim. phys., 25, 497 (1928).

In deducing the molecular equations, I omitted the change immediately following the critical point (1) and one corresponding to the low temperature (7). The (1) I omitted because in the vicinity of the critical point special conditions prevail, of which the mention will be made later on. The (7) is left out because the vapour density becomes at room temperatures too low and the results become inaccurate.

By these equations, the δ curve can be constructed for the intervals of temperature roughly indicated on the right hand side. The intersection of two curves on either side of a kink gives value of δ corresponding to a kink at a certain temperature, which can be calculated or read off the drawing. To determine X one can extrapolate the values of δ_l and δ_v corresponding to the temperature at which the δ curve indicates a kink, and their ratio gives the value of X.

As an example of a liquid called associated, containing OH, I can quote the propyl alcohol for which I found the following changes:

	Intervals of temperature
(2) $6\,A_2 = A_{12}$	250°-210°
(3) $3\,A_{12} = A_{36}$	200°-170°
(4) $4\,A_{36} = A_{144}$	150°-130°
(5) $18\,A_{144} = A_{2590}$	120°- 50°

The corresponding equations for d being:

$$(2) \quad 5.160\, e^{4.838\delta} = T + 12.33$$
$$(3) \quad 11.90\, e^{3.787\delta} = T + 34.30$$
$$(4) \quad .1947\, e^{8.788\delta} = T - 47.40$$
$$(5) \quad 2.744\, e^{5.588\delta} = T - 1.30$$

Here again I omit changes (1) and (6) for the same reasons.

It can be seen that the law in this case is just the same as in cases of so-called normal liquids. The only difference which one can notice is perhaps this:

The constants in consecutive changes do not vary in the same regular way, and also the coefficient 18 appears very high. It may be that this irregular character has something to do with the group OH, but at the same time it may be due to some sort of error in experimental results owing to which an intermediate change is overlooked. Such is always possible in some individual cases, as the precision of measurements is not everywhere the same, but even then such omission has no effect on subsequent results. But speaking generally, *I regard these results as beyond all doubts.* Most of these data are borrowed from the work of Sydney Young,[1] whose figures for densities are most probably accurate within less than 0.5%, which accuracy is quite sufficient to warrant the above deductions.

As an illustration of similar behaviour of systems liquid-liquid, I shall give the example of phenol and water, the numerical data being borrowed from the Tables of Landoldt-Börnstein.

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[1] Proc. Roy. Dublin Soc., 12, 374 (1910).

In this case, instead of densities, I deal with concentrations and to make the kinks more conspicuous,[1] I plot the excess concentration C ($C = C_2 - C_1$), where C_2 and C_1 are concentrations of two liquid layers in equilibrium, against temperatures calculated from the critical point (i.e. about 80°C.) taken as zero, in degrees centigrade.

Proceeding in the same way as above I determine the temperatures corresponding to the kinks in the C curve, and then interpolate the values of C_1 and C_2 for this temperature.

Thus, assuming that the factor of association

$$X = C_2/C_1$$

I found

$$X = 2, 4, 8 \ldots\ldots$$

corresponding to the kinks in the curve.

Thus, there is an evidence of two changes

$$(2) \quad 2\,A_2 = A_4$$

$$(3) \quad 2\,A_4 = A_8.$$

The question now arises when and how the change (1) has arisen, i.e.

$$A + A = A_2.$$

In this case as well as before, I treat this change separately, because in the critical region special conditions prevail, which I shall now discuss more in detail.

It was already mentioned that the change immediately following the critical point is probably of the form $A\,e^{\lambda\delta} = T + A$, i.e. the constant on both sides is the same. This is necessary to bring δ to zero, when the critical point is reached. I must, however, add that the experimental work in the critical region is very difficult and it has not been sufficiently well investigated.

However, certain evidence indicates that also the nature of the change is somewhat peculiar.

I consider that the above equation is valid within about 3° from the critical point.

If one has three points on this part of the curve, the whole equation can be established and serve for the accurate location of the critical point.

Both phases in the vicinity of the critical point have the same vapour pressure and the same surface tension. This means that separation into two phases in the critical region takes place without an appreciable expenditure of energy.

Independence of these properties[2] from concentration above the critical point makes me believe that already then the particles of the system combine with one another. Following assumption will be in agreement with the experimental evidence.

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[1] See also Phil. Mag., 1, 1129 (1926).

[2] The curve Fig. 6 is horizontal in the neighborhood of A and B, the points corresponding to two superposed layers in equilibrium. The experiment shows that the curve remains horizontal even above the critical point, where the whole system is homogeneous.

Suppose that 1/3 of molecules above the critical point combines with another 1/3. Thus, the number of complex molecules must be equal to the remaining number of simple ones. Above the critical point these molecules are distributed at random. Owing to diminution of kinetic energy, at the critical point and below, the complex molecules begin to settle down, this process of separation taking place without expenditure of energy. The system separates into two phases of equal volume, containing an equal number of molecules per unit volume, according to this theory. Just 2-3 degrees below the critical point, one can generally observe a kink, the ratio of concentrations, resp. densities being two to one.

Thus, the system has given place to a phase consisting of double molecules, by the time the first kink is reached. From this point, a new reaction starts consisting in polymerisation of double molecules, represented by equation

$2\ A_2 = A_4$, as in case of phenol-water, or

$3\ A_2 = A_6$, as in another example cited above.

And this gives the beginning to what I have called the ordinary changes.

All above is equally applicable to systems liquid-vapour and systems liquid-liquid, so that it is quite unnecessary to treat the two things apart.

The phenomena viewed from the above point are typical phenomena of dissociation (resp. association), the latent heat of vaporisation being nothing else but the heat of dissociation.

VII. SOLID STATE.

If the question of the molecular state of liquids was little advanced hitherto, still less is known about conditions prevailing in the solid state.

If one takes into consideration the evidence provided by the X-ray analysis, the question may even arise, whether one can speak of the molecular weight of a solid at all. If one atom is simply linked with the other, the molecule of it will be as big as the piece of solid we choose to take. In such case the very notion "molecular weight" loses its meaning.

There is, however, sufficient evidence indicating that the atoms in a solid must be also associated into groupings, each group forming, so to say, a unit, representing the smallest mass of a solid, capable of individual existence. One can mention in the first place that W. H. Bragg,[1] as a result of his investigations with X-rays, arrived at the conclusion that the phenomenon of association must also take place in a solid. It is also known that the tensile strength of materials existing is not what it should be in accordance with elementary theories, if it were merely due to cohesives forces acting between individual atoms. Existence of certain groupings might explain this discrepancy.

The chief argument in favour of such view, in my opinion, consists in the behaviour of solids when they are in equilibrium with other phases, namely at the melting point. At this point the solid is in equilibrium with

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[1] Loc. cit.

the liquid. The liquid and solid, both are in equilibrium with their common vapour. Thus, if a liquid is associated and its molecular weight is a certain multiple of that of the vapour, the same must be also true for the solid. We saw before that conditions of equilibrium between two phases are:

$$p_1 = p_2 \qquad (1)$$

and

$$\alpha_{12} = \alpha_1 - \alpha_2. \qquad (2)$$

As far as the first condition is concerned, it is applicable to the solid state as well, at its melting point.

About the second condition, it is difficult to speak with certitude, because it cannot be proved experimentally for the want of methods. I can only say that the tension at the interface solid-liquid at the melting point is generally appreciable, because the meniscus is well curved, indication that the solid has a higher surface tension. As the first (1) condition is necessarily satisfied and the second (2) is only a natural consequence of it, personally I have no doubt whatever, that the law of equilibrium is general for all states, and I therefore believe that the degree of association of the solid at the melting point must be represented by the ratio:

$$X = \delta_s/\delta_v,$$

where X is the factor of association, δ_s density of the solid and δ_v that of vapour.

Judging from the thermal expansion of solids, I conclude that the degree of association of solids does not change, as a rule, with temperature, as it is the case with liquids.

In some individual cases the change in the molecular structure may take place also in a solid, as in the case of tin, which is known to change its structure on cooling. The unit of solid matter thus indicated by this theory may possibly be the actual limit of what the solid matter may attain in a high degree of dispersion.

VIII. GENERAL PRINCIPLE.[1]

We have seen that in various instances of systems in equilibrium, such as liquid-liquid, liquid-vapour and liquid-solid, there is one general condition, viz. **the phases in equilibrium exercise the same pressure upon one another, and they are equimolecular, i.e. they contain an equal number of molecules per unit volume.**

I assume that matter in all three states of aggregation is subject to the laws of kinetic theory, only that the mean free path differs widely, and is very small in the solid state compared with the gaseous. The particles having speeds above the average detach themselves from one phase to penetrate into another, where they must, according to my view, regroup themselves. Thus particles of liquid entering into vapour must dissociate and vice-versa.

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[1] Antonoff: Réunion internationale de Chim. Phys., Activation et structure des molécules, Paris, 272 (Oct. 1928).

Let us imagine now that the interface between two phases is covered with an impermeable ideal membrane, such that no particles of either kind can go through it. On one side there will be n molecules per unit volumes of one mass, and n molecules of a different mass on the other side. And these both bombarding the membrane from both sides will produce the same pressure.

Imagine now another case. Take two ideal gases occupying equal volume at the same temperature and pressure (case Avogadro). If the two gases are separated by an ideal impermeable membrane, they will be in equilibrium with one another. Without the membrane they will mix together and the analogy with previous cases will disappear. Here again we have n particles of one kind on one side, and n on the other and they produce the same pressure on the membrane. *It is obvious that all systems mentioned are subject to the same law of kinetics.*

Speaking generally, **the systems exercising outwardly the same pressure at the same temperature are equimolecular,** i.e. contain an equal number of molecules per unit volume. This is equally applicable to gaseous matter, liquid or solid. This pressure is equal to the pressure of the gaseous phase, which can be measured in the ordinary way.

Thus, the case Avogadro, in a sense, may be regarded as a particular case of the general principle herein formulated, but it is believed to be accurate in ideal systems, i.e. such where the molecular forces do not come into play.

In this paper it was shown that the phases in equilibrium obey the above law as a result of all internal and external forces. The molecular forces not only have not been neglected, but form the basis of the whole investigation.[1]

IX. SUMMARY.

It was established that all systems exercising outwardly the same pressure at the same temperature are equimolecular, irrespective of their state of aggregation.

In particular, two or more phases in thermal equilibrium contain the same number of molecules per unit volume.

Thus, in the case of pure substances the molecular weight of its vapour being known, the degree of association of this substance in another phase can be calculated as a ratio of density of this phase to that of the vapour. In the case of liquids, this ratio X, called the association factor, is:

$$X = \delta_l/\delta_v,$$

where δ_l is the density of liquid and δ_v that of vapour. As the density of vapour diminishes with decrease of temperature, and the density of liquid

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[1] This is the point of divergence between this theory and that of J. Duclaux (Loc. cit.); he believes in association, but he does away with molecular forces altogether. Such extreme view has the inconvenience that there is no way of explaining the phenomenon of surface tension, which plays such an umportant rôle in these matters and which cannot be accounted for without the attractions due to molecular forces. I do not follow either G. G. or N. J. Longinescu (Loc. cit.) who attribute my results to neglect of molecular forces.

increases accordingly, the molecular weight of a liquid attains high values at low temperatures.

These densities vary with temperature in a discontinuous manner, showing kinks at certain intervals.

Between two kinks the curves run according to a definite law, for which there is given an accurate formula. The form of the equation is always the same, only the constants differ for each portion of the curve between two kinks.

At temperatures corresponding to kinks the degree of association, as measured by the above ratio, passes through whole and simple numbers.

The association thus takes place according to the law of multiple proportions, and consists of a number of successive reactions, one reaction beginning when the other is at an end. At the kinks the liquid consists of only one kind of molecules.

At the melting point of a substance, the solid being in equilibrium with its liquid and vapour, the molecular weight of the solid at this temperature can be calculated. There is no evidence of any changes in the solid state comparable with those of the liquid, and the degree of association of a solid appears to remain the same at all temperatures.

STUDIES ON OVERVOLTAGE. V*

A Moving-Coil Oscillograph Commutator System for the Study of Overvoltages and Transfer Resistance[1]

BY A. L. FERGUSON AND GRAHAM M. CHEN[2]

In previous articles[3] it was shown that difficulties inherent in the commutator rendered the commutator-potentiometer system undesirable for the measurement of overvoltage and transfer resistance. The present article is a description of a commutator oscillograph system which is much superior for such determinations.

The moving coil oscillograph has been used by Reichinstein,[4] LeBlanc,[5] Lattery[6] and Miller[7] in studies of transient phenomena at electrode surfaces in electrolytes. In all these cases a source of intermittent direct current was used and the electrodes were connected directly to the oscillograph. The method was finally rejected because the oscillograph drew considerable current for its operation and thus changed the potentials of the electrodes under investigation while those potentials were being measured. This difficulty was partially overcome by Holler[8] through the use of a vacuum tube amplifier. He used the new arrangement to study polarization and the nature of "transfer resistance" or as he called it "boundary resistance." His oscillograph required 150 milliamperes for full-scale deflection which made it necessary to use a three-tube amplifier. Even then it required 15 millivolts change in grid potential to produce a change of 1 milliampere through the oscillograph circuit; which means the arrangement is not suitable for accurate work.

The cathode ray oscillograph has been adopted by Newbery[9] for the study of polarisation and overvoltage. It is ideal in respect to its capacity to accurately follow extremely rapid changes of potential. Vibrations having a frequency of 10^6 per second may be recorded. It is also especially desirable in that it draws practically no current from the source. A marked disadvantage, however, is that it gives a deflection of only one millimeter per volt. By the use of an amplifier it is possible to secure deflection of one millimeter per 100 millivolts. Another very serious difficulty is that the

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* Contribution from the Chemical Laboratory of the University of Michigan.

[1] The oscillograph used was purchased from the Faculty Research Fund of the University of Michigan which thus made this work possible.

[2] The junior author wishes to acknowledge his indebtedness to the China Foundation for the Promotion of Education and Culture for the granting to him of a fellowship which made it possible for him to continue his research work at the University of Michigan.

[3] Ferguson and Chen: J. Phys. Chem., **36**, 1156, 1166 (1932).

[4] Reichinstein: Trans. Faraday Soc., **9**, 228 (1914); Z. Electrochemie, **16**, 916 (1910).

[5] LeBlanc: Z. physik. Chem., **5**, 469 (1890); Trans. Faraday Soc., **9**, 251 (1914).

[6] Lattery: Trans. Faraday Soc., **19**, 827 (1924).

[7] Miller: J. Franklin Inst., **19**, 771 (1925).

[8] Bur. Standards Sci. Paper, **20**, 153 (1925).

[9] Proc. Roy. Soc., **107A**, 487 (1925).

energy of a single discharge of the cathode ray tube is so slight that many discharges are necessary to affect the photographic plate. In fact Newbery found that the plates had to be exposed for 30 sec. while the circuit through his electrode system which was being measured was made and broken about 14 times a second. It is, therefore, a serious question as to how much confidence can be placed in values obtained with such an arrangement. This topic will be discussed more fully later.

The Einthoven string galvanometer has been used by some to record electrode polarisation phenomena. Bowden and Rideal[10] have used it extensively for this purpose. Concerning their work, however, Newbery states that "the maximum frequency of the string galvanometer, which is about 300 per second is far too low, and unreliable results have been obtained by using it for this purpose, as it is quite incapable of following the extremely rapid changes of potential which occur."

In order to determine with a high degree of accuracy whether there is any kind of a surface resistance over which a portion of the applied potential is lost before it reaches the electrode it is necessary to have an instrument: (1) that will give a complete discharge curve from the time of opening the switch; (2) that will show the path of the curve during the first 0.001 second of the discharge interval; (3) that has a sensitivity of about one millimeter per millivolt; (4) that responds instantly to the variation of current through it; and (5) that draws no current from the electrodes under investigation. No apparatus or method thus far described in the literature fulfills these requirements. The present paper is a description of such an apparatus and method.

Apparatus and Material

The oscillograph used was a modification of the two-element Osiso made by Westinghouse Electric Co. The supersensitive element gives one centimeter deflection per milliampere. Energy to operate the element was supplied by a two-tube resistance coupled amplifier. A diagram of the amplifier is given in Fig. 1a. As the first tube, T_1, a CX322 was used, and the second, T_2, was a power tube CX371. R_1 and R_2 represent two noninductive resistances of 850,000 and 50,000 ohms respectively, R_2 being variable. The space charge grid g_1 was maintained positive 4.5 volts with respect to the filament, while the screen grid g_2 was connected to the negative side of the potential under investigation and acted as a control grid. The grid g_3 in the power tube was made 22.5 volts positive to the filament. Two milliammeters, A_1 and A_2, were employed to measure the filament currents which were held constant by the variable resistances, r_1 and r_2. The output current from the power tube could be measured by either the ammeter, Am_1, or the oscillograph, osiso; see Fig. $9b_2$.

The amplifier was calibrated by applying known potentials to the grid circuit, and measuring the corresponding plate currents with a milliammeter. The amplification curve, plate current against grid potential is given in Fig. 2.

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[10] Proc. Roy. Soc., 120A, 61 (1928).

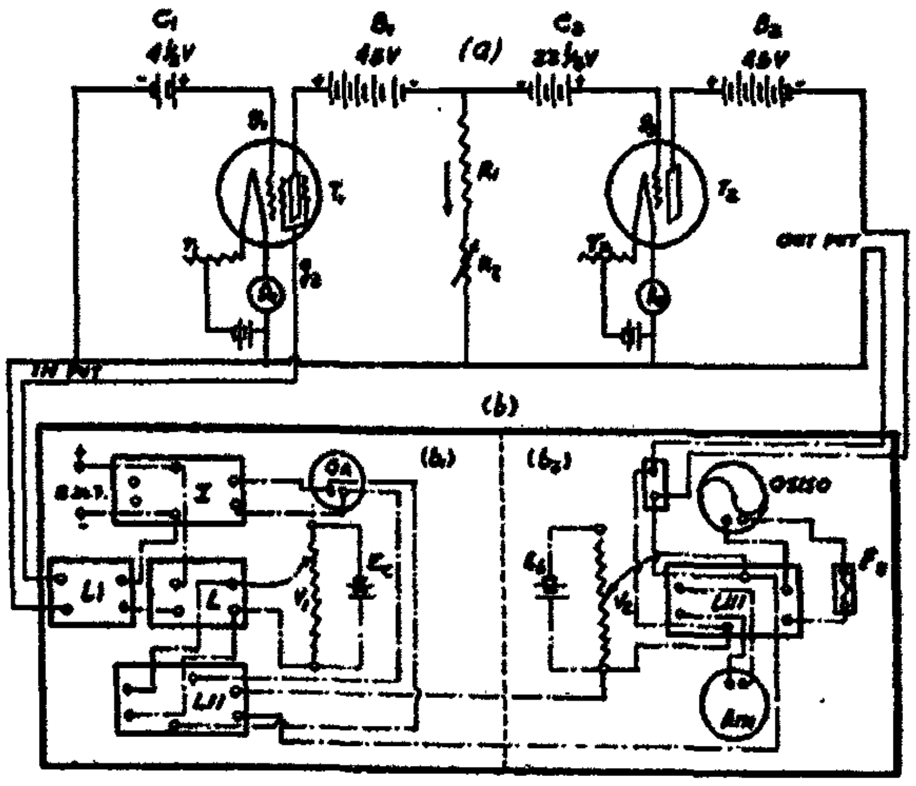

Fig. 1

The amplifier circuits are shown in 1a. The arrangement for connecting the unknown E.M.F. in series with a known potential V_1, and the resulting potential to the potentiometer or amplifier is shown in $1b_1$. The arrangement for connecting the output of the amplifier to either the milliammeter or the oscillograph is shown in $1b_2$.

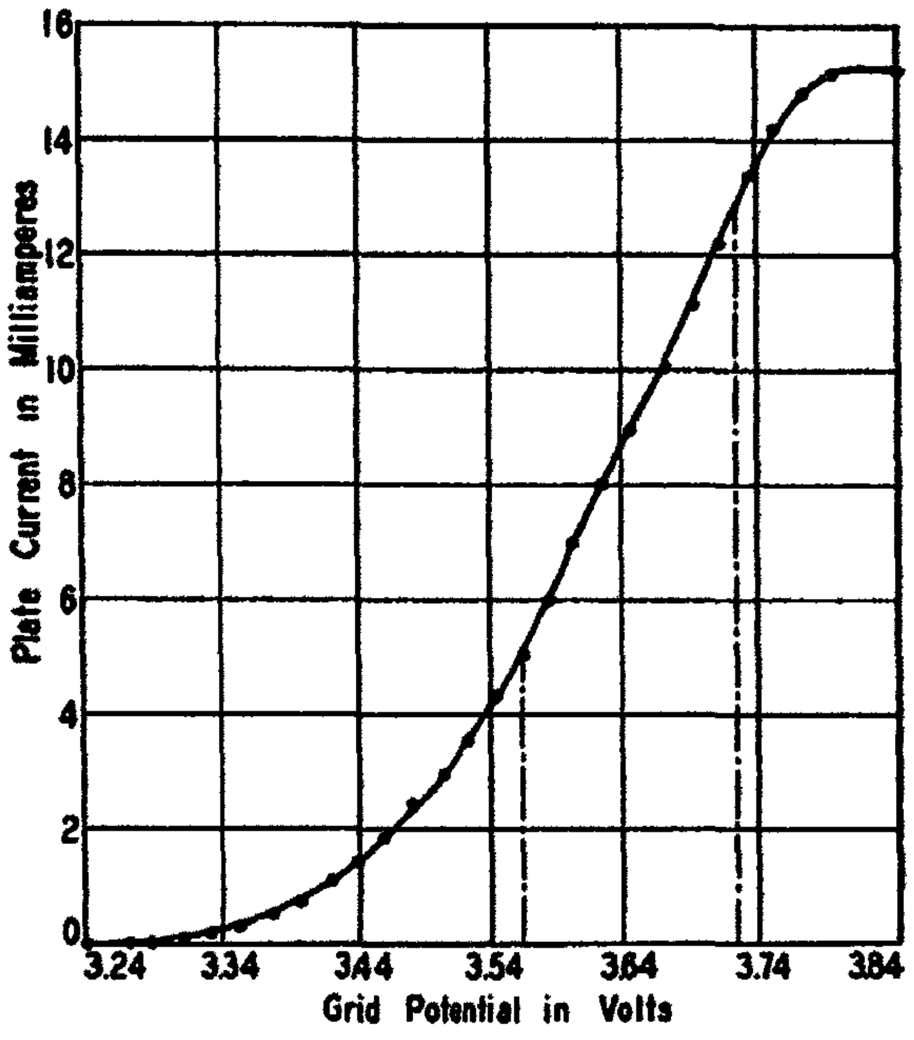

Fig. 2

Calibration curve of amplifier.

For all experiments in the present investigation, the linear portion of the curves used is between the grid potentials, −3.564 and −3.724 volts, as indicated by the distance between the two vertical lines. This difference of potential, 160 m. v., gives rise to a plate current of 7.8 ma.

The polarising current was interrupted intermittently with the direct connected motor driven commutator described in an earlier paper.[11]

The cell system and the switch board are the same as that described in an earlier article.[12]

The whole set up is a combination of the apparatus employed in the earlier commutator-potentiometer method with the addition of an amplifier and oscillograph. In Fig. $1b_1$, the symbol, G.A., for simplicity, represents the entire potentiometer assembly described in the earlier articles. By means of switches I, L, and LI in Fig. $1b_1$, the unknown potential, E.M.F., may be measured either by the potentiometer as in the previous work or by the oscillograph. When the potentiometer is used, switch I is closed to the right and the other two are open; when the oscillograph is used, switch I is open and L and LI are closed. By means of the switch LIII a milliameter may be substituted for the oscillograph indicated in Fig. $1b_2$ as osiso. The potential divider E_c is used to insert a known voltage V_1 in series with that under investigation in order to control the total potential applied to the grid of the amplifier. Another potential divider E_b is used to insert a known potential V_2 in the plate circuit in order to control the current passing through the oscillograph.

With this apparatus it was possible to measure potential changes of one millivolt and a time interval of 0.0001 second. With slight modification the sensitivity could be increased even more if desired.

Experimental

The manipulation of switches for the various measurements when the oscillograph is used is the same as given in Table I of an earlier article.[12]

By setting the r.p.m. of the commutator at a definite ratio to that of the drum of the oscillograph, any desired number of complete cycles of the charging and discharging curve may be obtained on one film.

The following symbols are used in connection with the various oscillograms.

1. For measurements made by the commutator method.

A = potential of anode against anode standard.
A_i = potential of anode against cathode standard.
K = potential of cathode against cathode standard.
K_i = potential of cathode against anode standard.
S = potential of anode against cathode.
I = potential of anode standard against cathode standard.
Z and Z_1 = zero lines for the two vibrating elements.
c = the beginning of charge.
d = the beginning of discharge.

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[11] Ferguson and Chen: J. Phys. Chem., **36**, 1156 (1932).

[12] Ferguson and Chen: J. Phys. Chem., **36**, 1166 (1932).

FIG. 3

Calibrated film. The potential used for each line is given at the left end of the line. The zero of the vibrator is indicated by Z′.

2. For measurements made by the direct method.

   The same symbols are used as in the commutator method except a prime is added to each.

To calibrate the films, known potentials from a potential divider were measured by the potentiometer system then applied to the amplifier and the resulting plate currents were first measured with a milliammeter then applied to the oscillograph and the steady deflections of the vibrating element recorded as straight lines on the film. Such a calibrated film is shown in Fig. 3. It was necessary, of course, in all of the work to maintain the filament currents for T_1 and T_2 very constant. Frequent recalibrations were made.

Oscillograms were taken by both the commutator and direct methods on the same film and practically simultaneously, using the same voltage V_1 in the grid circuit and the same balancing potential V_2 in the plate circuit.

Data obtained with the commutator and reported earlier[11] indicated that one source of discrepancy between the direct and commutator methods is contact resistance of the brushes on the disk, especially at high speeds. This same phenomenon was studied by means of the oscillograph. The results are shown in Fig. 4. The only factor changed to produce the different lines

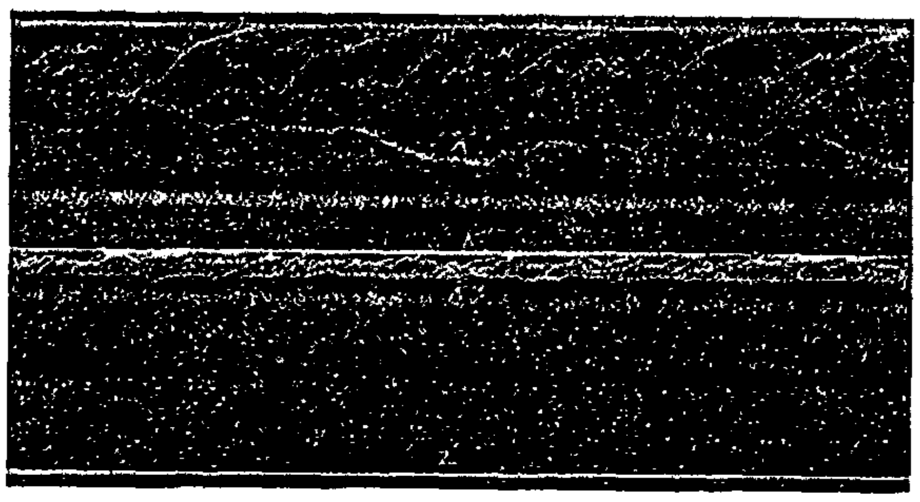

FIG. 4

Single electrode potentials of the anode A′ to A″, and of the cathode K′ to K″ obtained by the commutated-direct method at r.p.m.s. from zero to 800.

was the r.p.m. of the commutator. The smooth lines A′ and K′ represent the anode and cathode potentials respectively with the commutator stationary, which corresponds to the direct method. Lines A″ and K″ represent the potentials at the r.p.m. 800. The lines between A′ and K′, and A″ and K″ correspond to intermediate r.p.m.s. These oscillograms confirm the earlier conclusions that the electrode potentials decrease with increase in r.p.m. of the commutator due to increase in brush contact resistance. The zigzag nature of the curves is due to variation in contact resistance. The corresponding currents through the polarisation cell were measured, also, at the same time, and the data show a decrease in current with an increase in r.p.m. for a constant total applied potential; as the r.p.m. increases from 0 to 900 the current decreases from 220 ma. to 120 ma. This decrease is due to an increase in brush contact resistance.

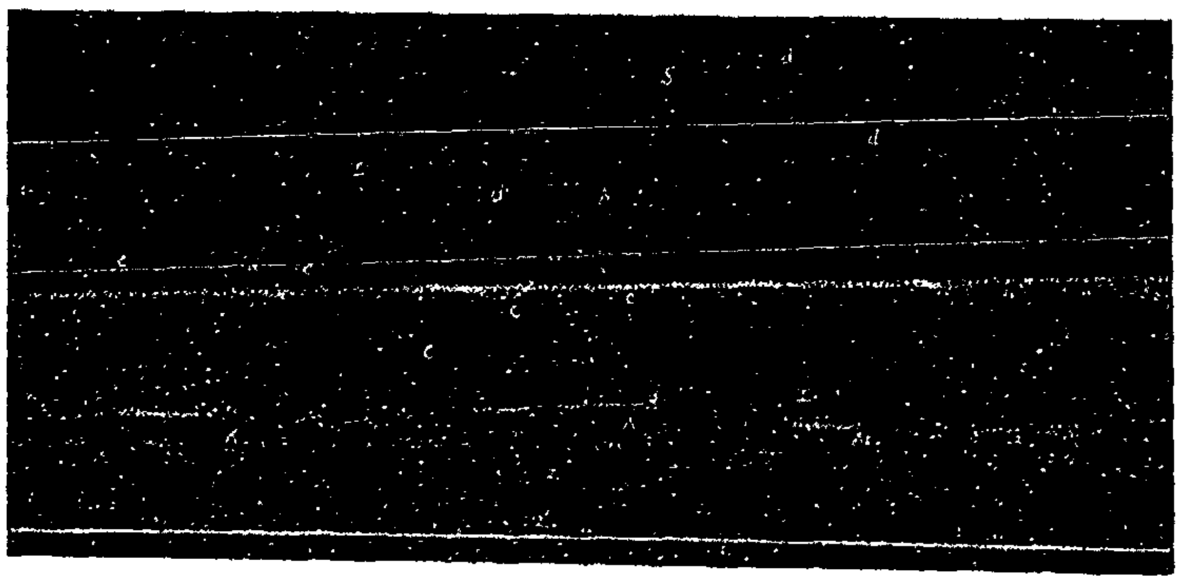

Fig. 5

The curves represent the potentials of the following systems (the numerical values are for the direct method obtained with the potentiometer).

S = potential of anode vs cathode standard. Bottom, 1.847V; top, 2.047V.
A = potential of anode vs anode standard. Bottom, 1.142V; top, 1.275V.
K = potential of cathode vs cathode standard. Bottom, 0.703V; top, 0.735V.
I = potential of anode standard vs cathode standard. Bottom, 0.002, top, 0.039.
c = beginning of charge.
d = beginning of discharge.

In all measurements made with the oscillograph the I.R. drop through the connecting wires, discussed in an earlier paper, was reduced to a minimum by using heavy leads only six inches long.

Some of the oscillograms obtained with platinized platinum electrodes in 2 N H_2SO_4 are shown in Figs. 5 and 6. A large number of such oscillograms were taken under a variety of conditions particularly for as wide a range of current density as possible and for various speeds of the commutator and the film drum. The two shown here are typical. In these figures curve A shows the change in potential of the anode during charge and discharge; curve K, the change in cathode potential; curve S, the change in total potential across the cell; and I the I.R. drop through the solution between the electrodes.

Curves A and S are strikingly similar to those shown in Figs. 4, 5 and 6 of an earlier article,[12] obtained so laboriously by means of the commutator and potentiometer. These curves furnish strong confirmation of a conclusion drawn on the basis of the earlier work to the effect that potentials measured over the whole or any part of the charge or discharge intervals, as has been done so frequently in the past by other investigators in this field, must be averages and practically meaningless. There are three sets of curves in Figs. 5 and 6; the set at the bottom of Fig. 5 was obtained with a current density of 0.0005 amp.; the set at the top with a current density of 0.0089 amp.; the set in Fig. 6 with 0.0221 amp. The lower part of S in Fig. 6 is missing because the total change in potential across the cell is greater than it is possible to record on the film.

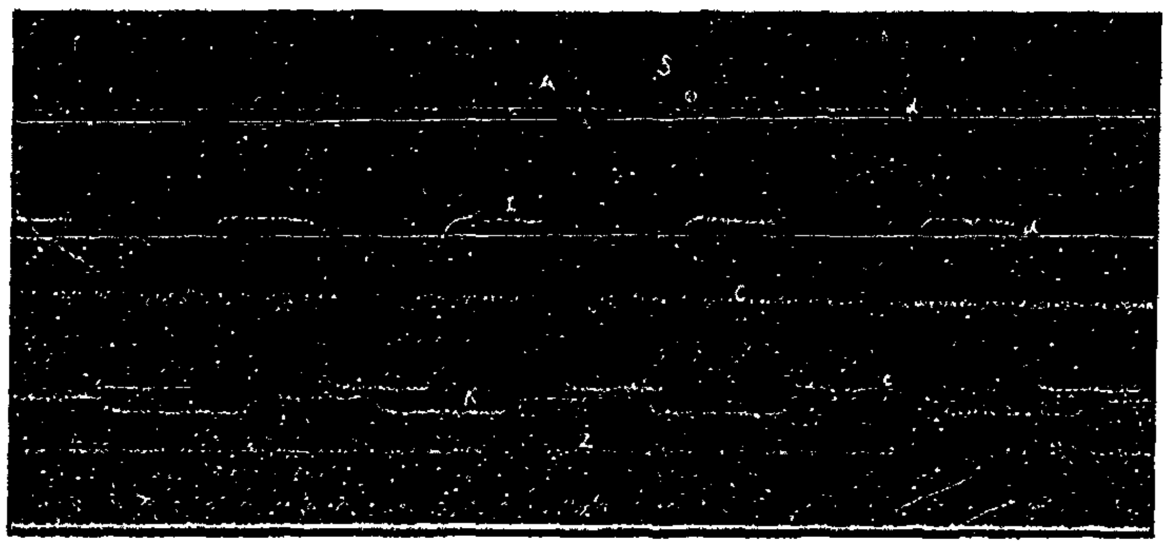

Fig. 6

The curves in this figure are for the same systems as in Fig. 5 except for higher applied potentials. The values by the direct method are: S = 2.172, A = 1.335, K = 0.740, I = 0.097, and the polarising current = 0.0221 amp.

At the bottom of these and all other oscillograms to be given later is represented the curve for a 120 cycle circuit.

It was pointed out in the earlier work (Fig. 5, Ref. 12) that there was an indication that the charging current reached a maximum early in the charge interval then decreased very slowly. There is a slight indication of this same phenomenon in these I curves. This is shown much more conclusively in Fig. 7.

The oscillograph proved to be an excellent means for making a direct comparison of the direct and commutator methods for measuring polarisation. Oscillograms were taken by both methods on the same film and practically at the same time and thus under identical conditions. Typical photographs are given in Figs. 7 and 8. The records of potentials obtained by the direct method appear as straight lines marked A′, K′, I′ and S′. The numerical values for these potentials as measured by the potentiometer are given under each figure. The curves obtained by the commutator method are designated in these figures with the respective symbols without the primes.

These curves demonstrate several points. Firstly, the curves for anode potential, A, by the commutator method show maximum values identical

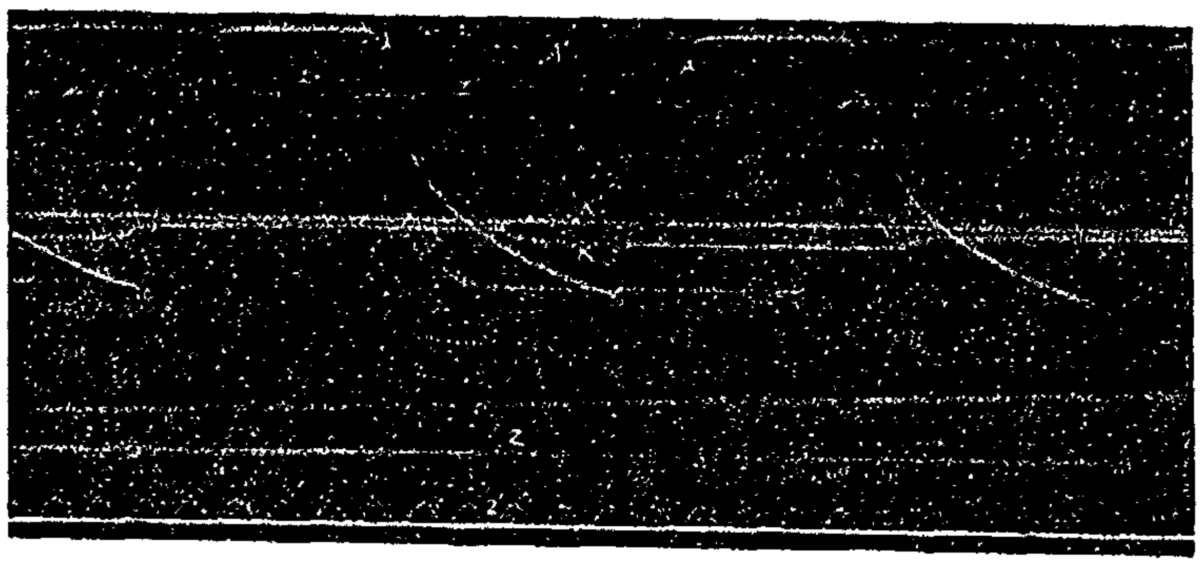

Fig. 7

The curves show the potentials of various systems by both the direct and commutator methods. A′ = 1.335, K′ = 0.740, I′ = 0.097, current = 0.0221 amp.

with the corresponding values, A′, by the direct method. This confirms the statement made by Ferguson and Van Zye[13] that "the commutator and the direct methods would give the same values if measurements by the commutator method could be made at the instant the polarising current is interrupted." This point of view was greatly strengthened by the work of the present authors[12] with their improved commutator potentiometer; and oscillograms shown here eliminate any question that might have remained. Secondly, the maximum potential of the cathode by the commutator method is always slightly less, for low current densities, than the value given by the direct method. Such a phenomenon was not anticipated, but there is no doubt of its reality. In magnitude the difference amounts to two to five millivolts. This difference can not be due to a transfer resistance since such a resistance would cause a vertical drop at the beginning of discharge and would result in a difference in electrode potential on charge and discharge but could not cause a difference between the maximum value by the commu-

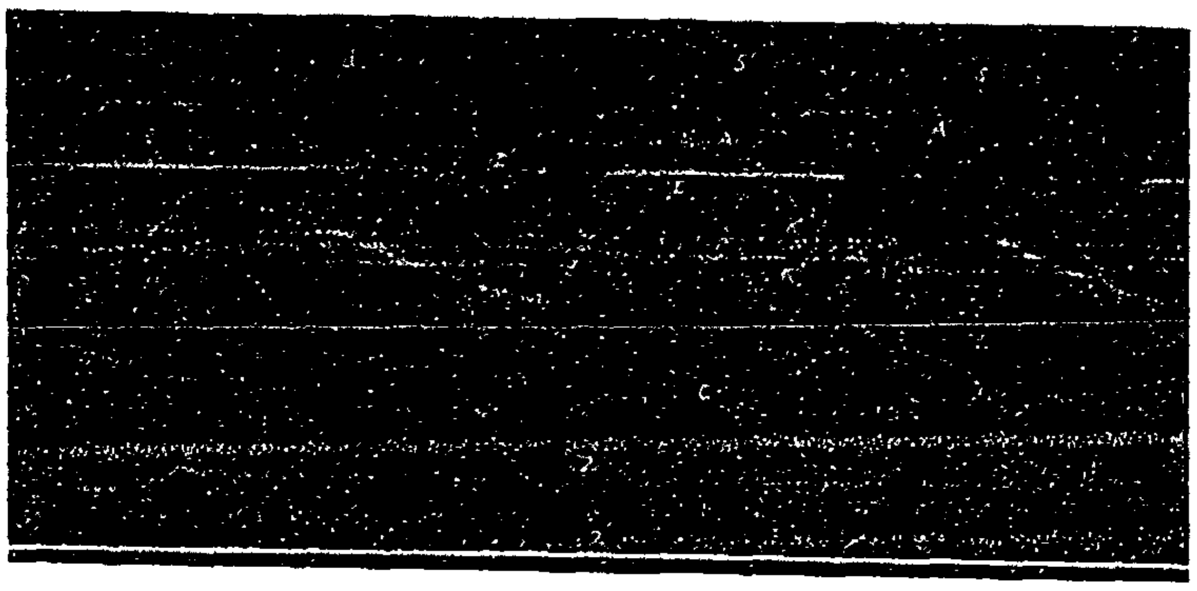

Fig. 8

The curves show the potentials of various systems by both the direct and commutator methods. S′ = 1.289, K′ = 0.735, I′ = 0.042, current = 0.010 amp.

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[13] Ferguson and Van Zye: Trans. Am. Electrochem. Soc., 47, 227 (1925).

tator method and the value by the direct method as observed here. It should be noted that the total potential, S, across the cell measured by the commutator is less than the value given by the direct method by approximately the same amount as the cathode difference. The S curve is still rising and the probability is that K is also rising and, if sufficient time were allowed, the values by the two methods would become identical. This point of view is supported by other data not given here which show that at higher current densities the curves rise to a maximum much more rapidly and the values by the two methods are identical. There is a slight indication of that in Figs. 7 and 8. At the higher current density used in Fig. 7 the difference between the K and K′ curves is less than the difference in Fig. 8 where a smaller current density was used. The S curve could not be shown in Fig. 7 because the change in potential was too great to fit on the film.

Thirdly, these curves show that the current I by the two methods is practically identical. As already pointed out there is a slight tendency for the current by the commutator method to be a little higher than by the direct method during the early part of the charge interval; but it drops off slowly as the charge interval continues. This is clearly evident in Fig. 7. The decrease in I is probably due to the corresponding increase in K.

Fourthly, it is shown that time is required for the electrodes to reach an approximate maximum value. For the current densities of the order used in these experiments, this time is about 0.008 second for the cathode and 0.04 second for the anode. This means that at least that amount of time must be allowed charge and discharge intervals by any method used to compare the commutator and direct methods. Oscillograms not shown here were taken that prove this point.

Fifthly and finally, these curves give no evidence of a vertical drop at the beginning of the discharge intervals such as was found by Holler and Newbery, other than that due to the I. R. drop through the solution. These curves confirm, therefore, all previous work done in this laboratory to the effect that there is no such thing as transfer resistance or any other kind of boundary resistance at the surface of platinized electrodes during the electrolysis of a 2 N solution of sulfuric acid.

Summary

1. An oscillograph-commutator system is described that is very well adapted to the study of transient electrode phenomena.

2. Oscillograms are given showing changes in various potentials during charge and discharge intervals.

3. Oscillograms are given showing a direct comparison of the polarisation potentials as determined by the commutator and direct methods.

4. The work with the oscillograph described in this paper confirms in every respect the work with the commutator-potentiometer system described in earlier papers.

A PHOTOGRAPHIC STUDY OF THE GROWTH OF ELECTROLYTIC STRIATIONS

BY ROBERT TAFT AND OREN R. BINGHAM[1]

In a previous paper[2] we have reported upon the electro-deposition of copper in the presence of gum arabic. In that study the effects of the gum arabic upon the form and mass of the cathode deposit are ascribed to the mutual adsorption of gum arabic and copper oxides upon the surfaces of the newly formed copper crystals. Deposits obtained in those cases where the concentration of gum arabic was high or the hydrolysis of copper sulfate was relatively extensive were very markedly striated.

Such striated deposits have been known for many years, although a satisfactory explanation of their growth has never been made. It has been recognized that the convection currents set up in a "still" electroplating bath, as well as the presence of a foreign substance, were essential for their formation i.e. some material (usually organic in nature) other than the metallic salt and water forming the plating bath. The most serious attempt to explain the formations of such deposits has been that of Rosa, Vinal and McDaniel[3] in connection with the striations encountered in the silver coulometer. Their explanation is as follows: the presence of certain types of impurities leads to the reduction of traces of Ag^+, forming colloidal silver. This colloidal silver finds its way to the cathode and is deposited upon silver crystals growing upon its surface. This deposition of colloidal silver distorts the crystal structure of the growing silver deposit; the deposit now "grows by preference upward in the direction favored by the upward movement of the liquid." These deposits tend to form elongated structures, which in time grow into one another, developing well defined ridges, or striae. In time the striae will disappear by growing into each other laterally.

The data of Marie and Buffat[4] and of Taft and Messmore[5] offer a somewhat different explanation of the cause of striations obtained by depositing copper in the presence of gelatin. These authors found that gelatin (or its degradation products) was actually present in the copper deposit, the weight of the deposit being materially enhanced by its presence. Further, it seems fairly well established that the gelatin finds its way into the deposit as a result of adsorption upon the depositing copper crystals. The growth of striations in such solutions has been explained by this assumption, i.e. adsorption of gelatin by copper.[6]

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[1] Presented before the Kansas Academy of Science, McPherson, Kansas. April 16, 1932.

[2] J. Phys. Chem., 36, 2338 (1932).

[3] Bur. Standards Bull., 9, 263 (1912).

[4] J. Chim. phys., 24, 470 (1927).

[5] J. Phys. Chem., 35, 2585 (1931).

[6] Cf. Taft and Messmore: Loc. cit.

In the case of the deposition of copper in the presence of gum arabic under the conditions mentioned in the opening paragraph of this paper, the striations offered such contrast to the base metal as to make it appear feasible to study the growth of such striations photographically. Such a study should furnish information bearing on the cause of the formation of striated deposits as well as furnishing a record of many of the statements already found in the literature concerning their growth, but for which there is no record save description.

Our method for recording the growth of such deposits was to construct a wooden cell, some 4 × 4½ × 6½ cm. in dimensions. One end was fitted with a window made from optical glass and cemented in with de Khotinsky cement.[1] An anode was made of heavy copper sheet coiled to allow a clear vision of the far end of the cell through the window. The cathode of platinum (2.5 cm. on a side) was placed at the end opposite the window and was then illuminated from above by a 400 watt focusing spot light. The arrangement is shown diagrammatically in Fig. 1. Powerful illumination was necessary because of the very considerable absorption of light by the electrolyte, copper sulfate. A view camera fitted with a Bausch and Lomb Tessar lens was set up in front of the window and focused upon the cathode. A series of photographs of the cathode was then made as electrolysis continued, without disturbing either the electrolytic cell or the camera. In order to reduce the time necessary for illumination (which would induce local heating) super-speed panchromatic cut film was used as the recording medium, the exposure necessary being 10 seconds at f 16, with a lens of 7½″ focal length and at bellows extension of 22″. Electrolyses were carried out at room temperature, which for the Series 1 photographs was 32°C, and for the Series 2 set was approximately 40°C. The Series 1 photographs were obtained in a solution containing 0.5 M copper sulfate and 1.5 grams of gum

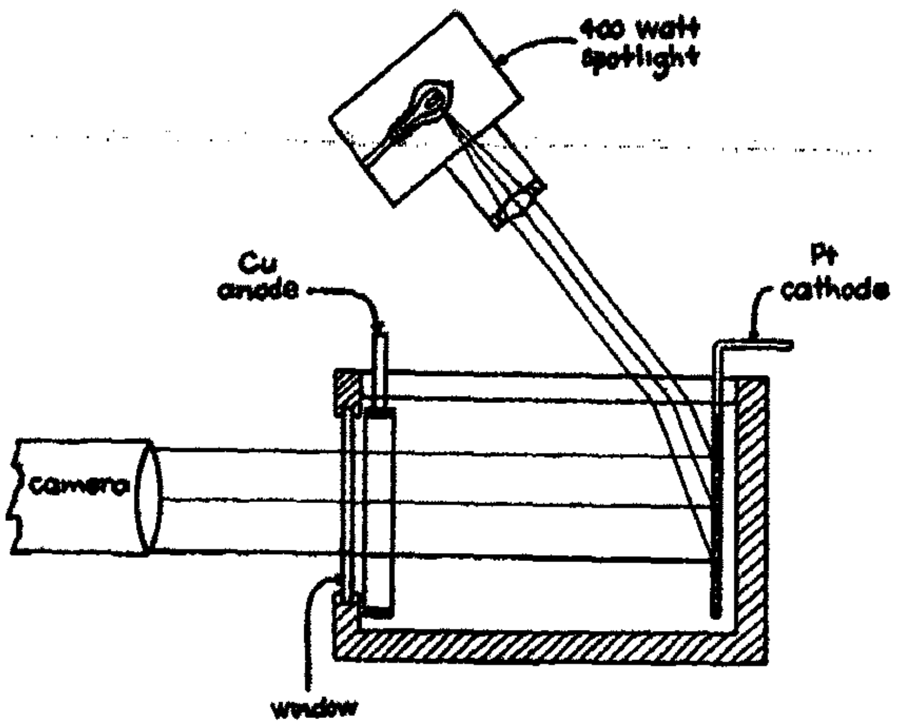

Fig. 1

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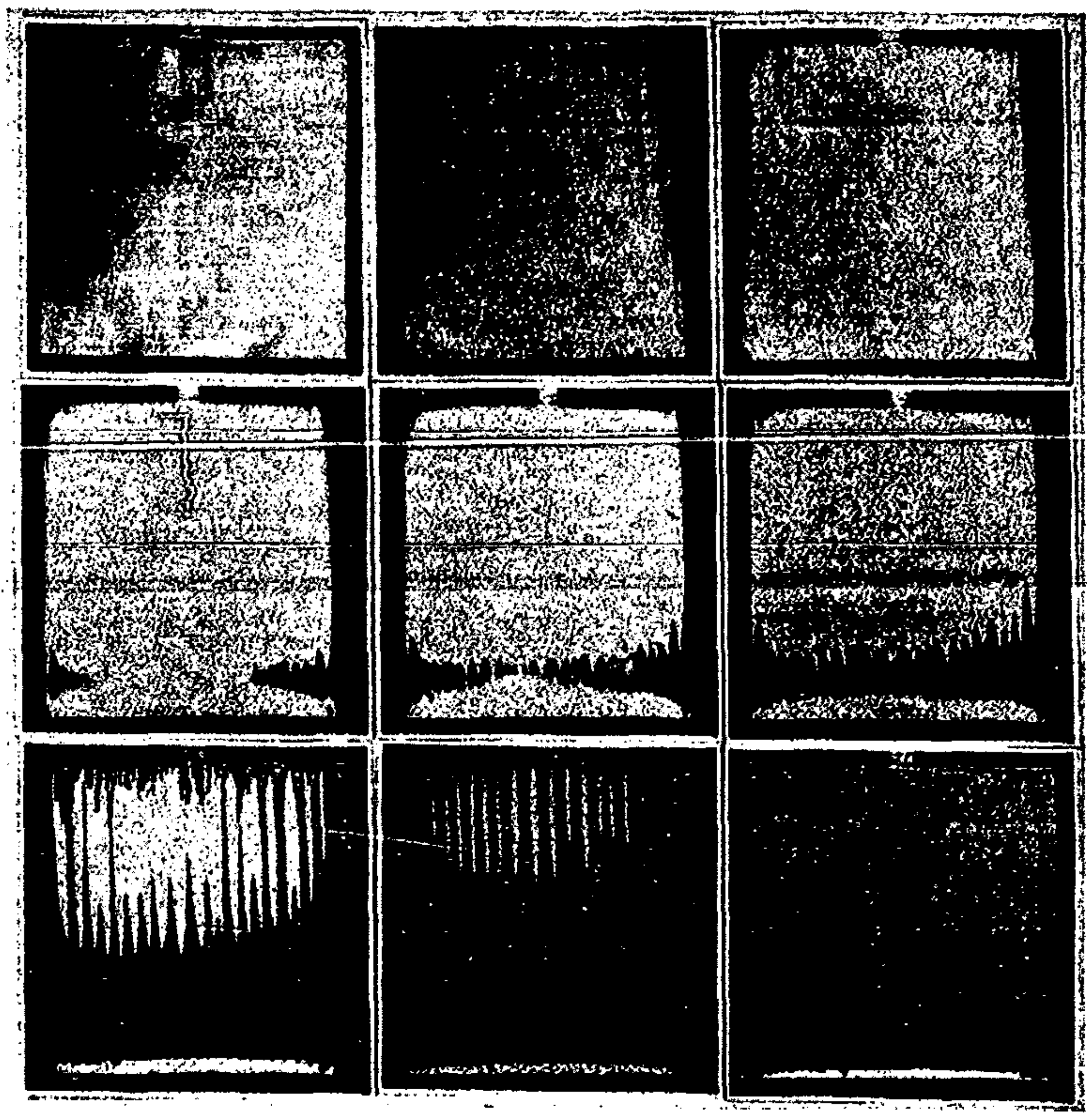
[1] The entire interior of the cell was coated with this cement to render it solution-proof.

arabic per 100 cc. of solution at a current density of 2 amperes per square decimeter. The form of the deposit obtained from zero time up to 2 ½ hours is shown in Series 1, a to i inclusive.



SERIES 1

The growth of the Cathode Deposit in 0.5 M $CuSO_4$.

Current Density, 2 amperes per square decimeter; 32°C; 1.5 grams of gum arabic per 100 cc of solution. The deposit was photographed at the following time intervals: a, 0.0 minutes; b, 5 minutes; c, 25 minutes; d, 40 minutes; e, 50 minutes; f, 60 minutes; g, 1.75 hours; h, 2.25 hours; i, 2.5 hours.

Our explanation of these deposits is as follows: Due to the form of the anode and also to the well-known tendency of current lines to converge on edges, the initial current density will be considerably greater around the edges of the cathode than upon the main face of the cathode. This results in an initial greater deposition of copper around the edges of the cathode, resulting as we have already pointed out[1] in an increasing hydrolysis. As a result of this hydrolysis, cupric hydroxide is formed, which, together with the gum arabic, is adsorbed upon these areas forming a dark-colored deposit. The extent of this process is not great, as the second photograph (Series 1,

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[1] Taft and Bingham: Loc. cit.

No. b) still shows the scratch marks around the edges of the base metal (compare Series 1, No. a). There *is* a deposit of dark color around the edges (with the exception of the bottom edge) which apparently prevents, temporarily, the further deposition of copper. It will be shown later in this paper that the addition of gum arabic produces an increase in the cathode polarization which could account for prevention of copper deposition in this area. The increased polarization around the edges diverts the current lines to the face of the cathode where apparently the correct density is quite uniform and copper (the light-colored area) is laid down. (As we have already pointed out, this copper may contain some copper oxides or gum arabic as a result of adsorption). As electrolysis proceeds, however, the solution around the cathode becomes more dilute for two reasons. First, due to the difference in transport number of sulfate and copper ion, there will be a more or less uniform dilution of the electrolyte in this region; second, due to the deposition of copper upon the cathode and the solution of copper at the anode, a well established convection current will be set up, the solution becoming progressively more dilute as it rises up the face of the cathode. As a result of these dilution effects, there will be produced more and more cupric hydroxide. When the concentration of this substance reaches a certain value, it is adsorbed simultaneously with the gum arabic,[1] producing the dark colored area. The formation of this dark-colored area first becomes appreciable in the photograph of Series 1, No. d, although careful examination will show it in Series 1, No. c. Series 1, No. d is produced after some forty minutes of electrolysis. The time at which this phenomenon first became apparent could be reproduced to the minute in duplicate trials. Once it has started, the dark area bridges rapidly across the electrode, at the same time growing upward. The rising electrolyte (after it leaves a given dark area) becomes richer in copper oxide as dilution continues up to a certain value[2] and poorer in gum arabic, due to its increased adsorption when in the presence of cupric hydroxide. In addition to the dilution of the gum arabic caused by its adsorption there is also a diluting tendency due to the migration of arabate ions[3] toward the anode. These two effects are sufficient to prevent further deposition of the dark-colored material until the solution behind the advancing front supplies the necessary gum arabic, which, we must assume, is not extensively adsorbed upon the dark-colored area already laid down.[4] In this way the dark-colored deposit continues to grow upward, the small initial

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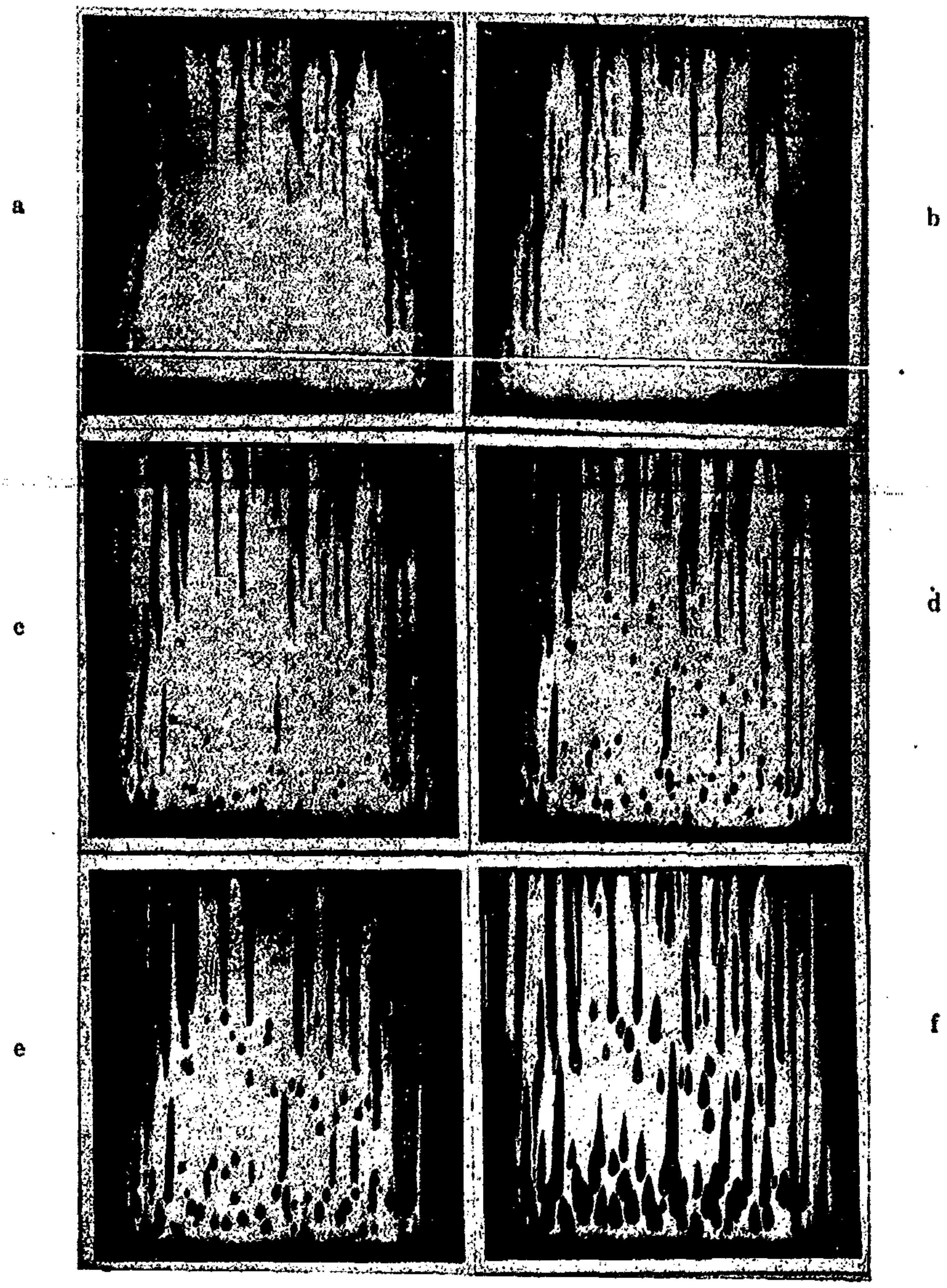
[1] As we have pointed out in our first paper, there is apparently a factor similar to a solubility product involved, i.e. when $C_{\text{gum}} \times C_{\text{copper oxide}}$ (C's representing concentrations) exceeds a certain value, the dark-colored area is produced. In fact, the formation of this dark-colored area appears very similar to a supersaturation phenomenon. The original dark areas appear very suddenly and grow quite rapidly during the first interval of their formation, the rate of growth diminishing after the first few areas have been formed.

[2] It must be remembered that the concentration of cupric oxide (or hydroxide) is the result of two factors, the extent of hydrolysis of the salt and also of its concentration.

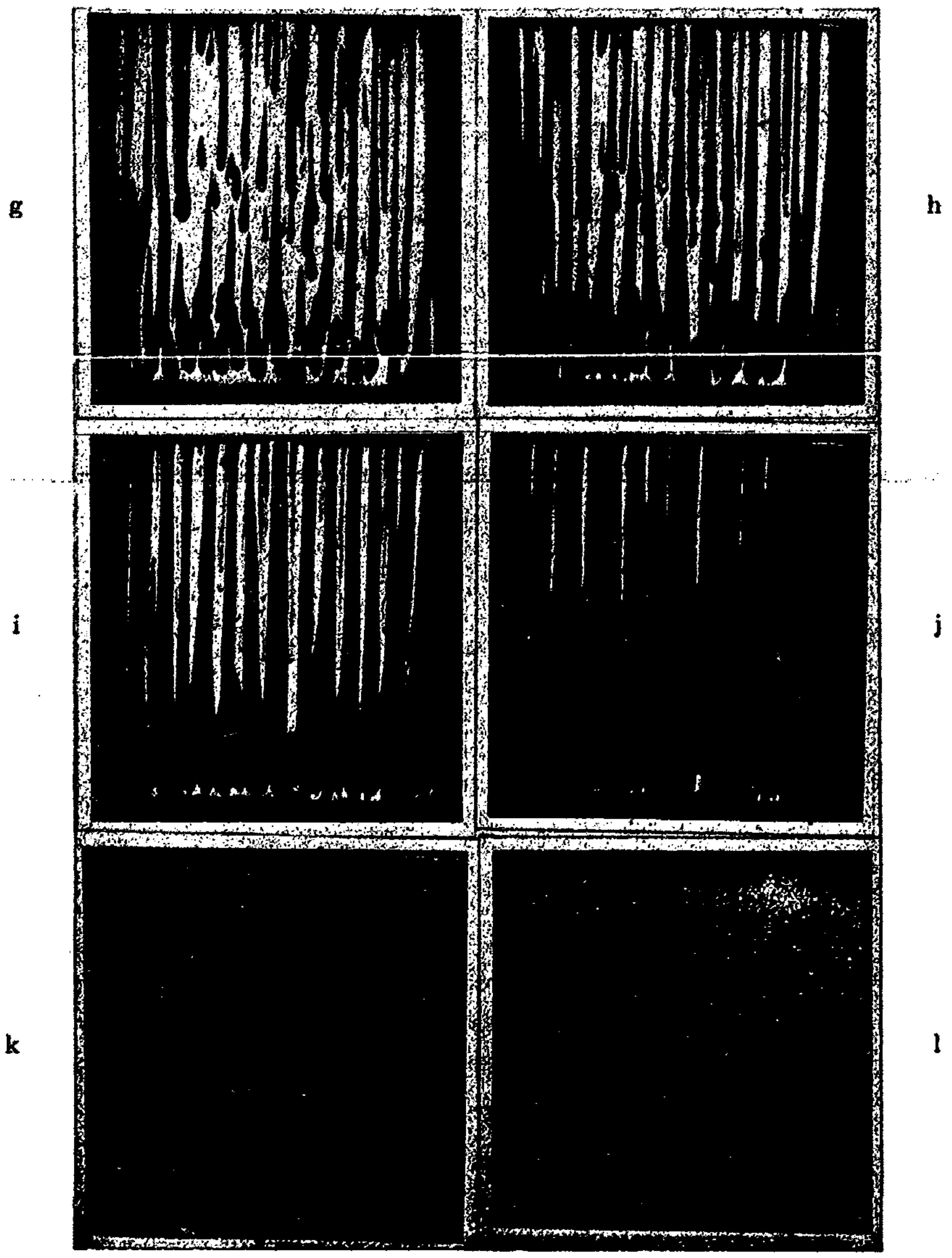
[3] Cf. Taft and Malm: J. Phys. Chem., 35, 874 (1931).

[4] As we have already pointed out, the formation of the dark-colored deposit also likely prevents the deposition of copper in this region, as long as there are any copper areas present. The prevention of copper deposition in this region increases the effective current density in the remaining region.



SERIES 2

The growth of the Cathode Deposit in 1 M $CuSO_4$. Current Density, amperes per square decimeter; 40°C; 1.5 grams of gum arabic per 100 cc. solution. The photographs were taken at the following time intervals: a, 30 seconds; b, 3.5 minutes; c, 15 minutes; d, 20 minutes; e, 25 minutes; f, 45 minutes; g, 60 minutes; h, 1.5 hours; i, 2 hours; j, 3 hours; k, 4 hours; l, 5 hours.



SERIES 2

The growth of the Cathode Deposit in 1 M $CuSO_4$. Current Density, 2 amperes per square decimeter; 40°C; 1.5 grams of gum arabic per 100 cc. solution. The photographs were taken at the following time intervals: a, 30 seconds; b, 3.5 minutes; c, 15 minutes; d, 20 minutes; e, 25 minutes; f, 45 minutes; g, 60 minutes; h, 1.5 hours; i, 2 hours; j, 3 hours; k, 4 hours; l, 5 hours.

differences in the height of the dark-colored area (due to slight differences in concentrations of copper oxide and gum arabic) becoming greatly magnified as time proceeds, Series 1, Nos. e, f, g. In order to accept this explanation of the form of the deposits, it is, however, necessary to make the additional assumption that the dark-colored deposit is more readily adsorbed by itself than by the copper crystals,[1] this adsorption taking place upon the upper edge of the dark-colored deposit already laid down. The rising current of electrolyte then accounts for the striae as suggested above.

The striae developed when a higher concentration of copper sulfate (1 M) is employed are more striking than those shown in Series 1. It should also be recalled that these, i.e. the Series 2 photographs, were made at a higher temperature than the Series 1 set.

Ross, Vinal and McDaniel[2] have called attention to the fact that increasing the concentration of the electrolyte makes electrolytic striae coarser and more distinct. A comparison of our Series 1 and 2 photographs shows this very clearly. In the case of our Series 2 photographs it is evident, as would be expected, that with the increased concentration of electrolyte, the areas at which cupric oxide and gum arabic are present in sufficient concentration to produce the dark-colored material are more widely separated. Further examination of the photographs shows that the striae result from these initial areas. Thus, in the fifteen minute deposit of Series 2, small circular areas[3] first become visible. The striae grow vertically from these initial areas, finally giving rise to the very distinct striae of Series 2, No. h. Eventually the striae grow together to give a deposit more or less homogeneous in appearance. Further electrolysis (Series 2, No. l) does not change the form of the deposit. Evidently when the surface has reached this condition, deposition (at a higher negative potential) of both copper and adsorption of copper oxide and gum arabic occurs uniformly over the entire surface.

As we have already pointed out, the addition of gum arabic produces an increase in the cathode polarization. The method pursued for determining

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[1] This assumption, we feel, is justified from the form of the striae in the Series 2 deposits, for example No. g of this series. The rounded bottom of these striae is always thicker than the upper part, indicating the small amount of dark-colored product formed below the striae is adsorbed upon coming in contact with the material already laid down. As the adsorbable material formed is slight, the upper part of the striae can only grow by the formation of new material. This can only take place until deposition of copper *above* the dark area begins again.

[2] Loc. cit.

[3] The circular form of this initially deposited dark-colored material and the drop-like form which the bottom of these areas assumes as the areas grow, indicate very clearly that interfacial forces are at work. Free adsorption (i.e. spontaneous adsorption) of the dark-colored substance would lead to a reduction of the interfacial tension at the boundary, copper-solution. As we feel that free adsorption has been proved (Taft and Bingham: Loc. cit.), these rounding forms can scarcely arise as a result of an increase in the interfacial tension. Rather, they must be due to an increase in the plasticity of the material in the deposit. As we have already shown (Taft and Bingham: Loc. cit., Fig. 5), even small amounts of gum arabic in a copper plating bath produce slipping and displacement of the various crystal surfaces over each other. The large amount of gum arabic and copper oxide present in the solutions from which the Series 2 deposits were obtained would undoubtedly produce a still more plastic substance.

this polarization was that of Haring.[1] The polarization measurements were carried out at a constant temperature of 30°C. Some of our results are tabulated below in Table I and shown graphically in Fig. 2.

TABLE I

Cathode Polarization at 30° of 0.5 M $CuSO_4$, volts

Current Density Amperes per sq. dm.	Con. of gum arabic, grams per 100 cc.	
	0	0.15
0.16	0.022	0.038
0.32	0.029	0.054
0.48	0.036	0.061
0.64	0.041	0.069
0.80	0.047	0.072
0.96	0.058	0.083
1.12	0.071	0.096
1.28	0.085	0.11
1.44	0.096	0.13
1.60	0.11	0.15
2.00	0.15	0.19
2.40	0.18	0.22

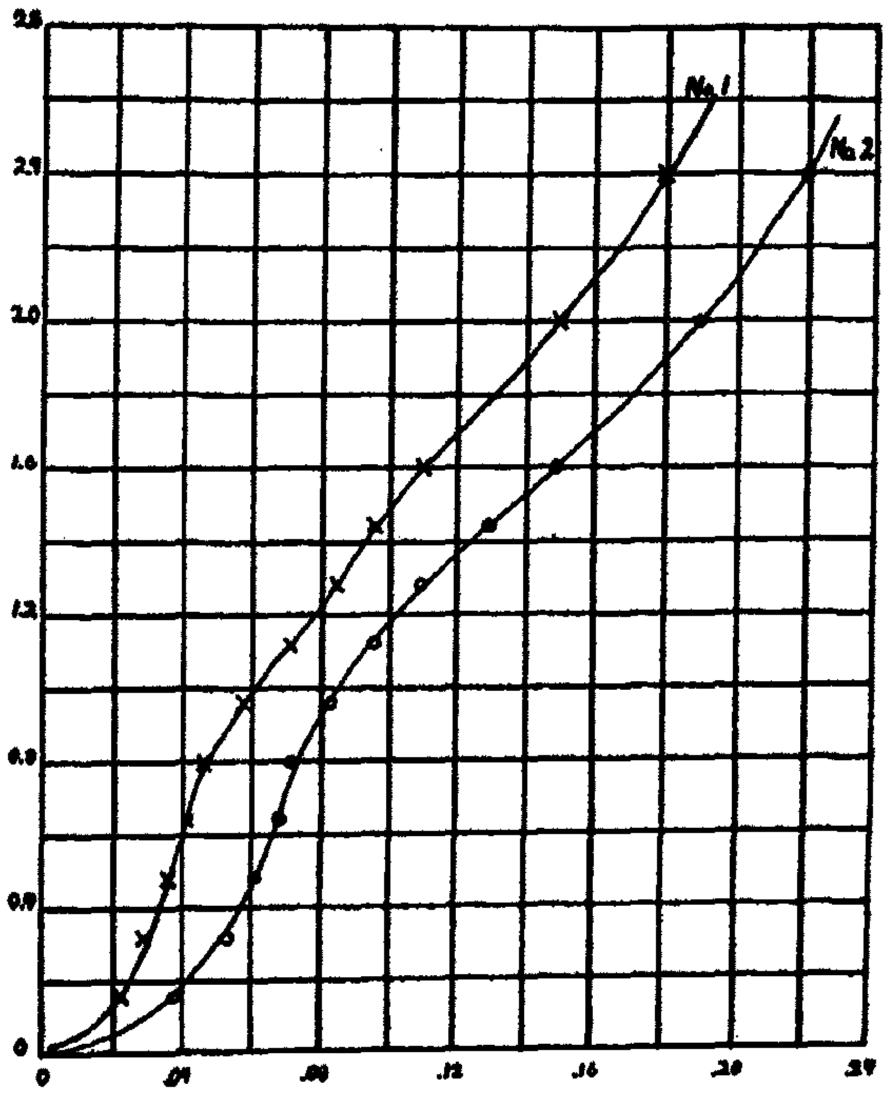

FIG. 2

Abscissae, Cathode Polarization, volts; Ordinates, Current Density, amperes per square decimeter. Curve No. 1 is for 0.5 M $CuSO_4$; No. 2 for 0.5 M $CuSO_4$ + 0.15 grams of gum arabic per 100 cc. of solution.

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[1] Trans. Am. Electrochem. Soc., 49, 417 (1926).

Similar measurements carried out at lower concentrations of gum arabic gave polarization values intermediate between those given, indicating that polarization becomes greater, at a given current density, the greater the concentration of gum arabic. Incidentally, if the polarization values of Table I are compared with those obtained during the deposition of copper in the presence of gelatin by Taft and Messmore a marked difference is observable. The polarization curves of Fig. 2 duplicate each other in form quite closely. On the other hand, in the presence of gelatin a very marked increase in polarization occurs at a current density of 0.8 amperes. They interpreted this increase to be due to the formation of complex cations between gelatin and copper. Its absence in the present case could be presented as an argument against the existence of any such complex cations of gum arabic and copper.

Summary

1. A photographic record of the growth of electrolytic striations of copper produced in the presence of gum arabic is presented. The formation and growth of these striae can be explained by assuming adsorption of a gum arabic-copper hydroxide complex upon the surfaces of the electrodeposited crystals of copper.

2. The cathode polarization of copper is increased by the presence of gum arabic.

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SOME SOLVENT PROPERTIES OF SOAP SOLUTIONS

Part III. The System Sodium Oleate, Sodium Chloride, Water, Ethyl Acetate

BY E. LESTER SMITH

In the first paper of this series, it was shown that soap solutions have a powerful solvent action for organic liquids of all types. A few observations were also made on the phase equilibria involved on salting out soap solutions in the presence of organic liquids.

It was obviously desirable to investigate in the fullest possible detail one particular quaternary system comprising a pure soap, a salt of the same base, water, and an organic liquid; some of the generalisations made in the earlier paper were in fact based on a knowledge of the behaviour of the system selected. After some preliminary work, it was decided to study the system sodium oleate, sodium chloride, water, and ethyl acetate at 25°. Sodium oleate was chosen because it is more soluble than most sodium soaps and also because it was believed that at 25° it would yield only the two phases, isotropic solution or gel, and curd, and that the anisotropic phases, middle soap and neat soap, would appear only at higher temperatures. This assumption was in fact fallacious and the equilibria proved to be much more complicated than was originally expected. Sodium chloride was chosen as the most generally used salting out agent in previous studies of soap systems. Ethyl acetate had two advantages over most available solvents; when the work was started it was one of the very few organic liquids known which was not permanently emulsified by soap solutions; also being an ester, it could readily be estimated in solutions by saponification with excess of standard alkali and back-titration with acid.

The ready hydrolysability of ethyl acetate, while facilitating its estimation, also introduced an element of risk, namely that the hydrolysis alkalinity of the soap solutions might be sufficient to cause decomposition of the ester during the time necessary for the attainment of equilibrium in the systems. McBain and others[1] have shown that the hydrolysis alkalinity of soap solutions is commonly of the order of N/1000, while the concentration of ethyl acetate in sodium oleate solutions may reach 3N. Calculations from the known velocity constant[2] indicated that very considerable decomposition of ester and consequently of soap should occur in less than an hour. Fortunately however, ethyl acetate throws back the hydrolysis of soap in the same way as alcohol does. The addition of neutral ester to an aqueous sodium oleate solution, deeply coloured with phenolphthalein, discharges the colour in-

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[1] McBain and Martin: J. Chem Soc., **105**, 957 (1914); McBain and Bolam: **113**, 825 (1918); Beedle and Bolam: J. Chem. Ind., **40**, 27T (1921); McBain and Hoy: J. Chem. Soc., **1929**, 589.

[2] Smith: J. Chem. Soc., **1927**, 170.

stantly. The pH of the solution cannot then be much above pH 8, corresponding to an alkali concentration of little more than N/1,000,000. This should not be enough to cause appreciable decomposition of ethyl acetate within a day. In practice, slight decomposition can only be detected by the appearance of an abnormal amount of free fatty acid in the ester layer in equilibrium with the soap solution. Such irregularities were not encountered except in the case of solutions which had stood overnight, and normally analyses were completed within a few hours of preparing the mixtures.

The four possible ternary systems will first be considered in some detail. These are best represented graphically in the manner usual for such systems, namely in equilateral triangles, which can later be fitted together to build the tetrahedron which is necessary to express the composition of phases containing all four components. Thus the four corners of the tetrahedron represent the pure components, the six edges the binary systems, the four faces the ternary systems, and the three-dimensional space within the figure, the quaternary system.

In conformity with McBain's usual practice three of the corners represent respectively: 1 *mol* (304 gm) of sodium oleate, 1 *mol* (58.46 gm) of sodium chloride, and 1 *kilo* of water; the remaining corner was made to represent 1 *kilo* of ethyl acetate, which brings this component into line with the other solvent present (the water) and gives a better-spaced diagram than would the use of the sol instead of the kilo. Again following McBain's practice, concentrations of sodium oleate and sodium chloride are expressed throughout in *weight* normalities, i.e. the mols of substance associated with 1 kilo of water, instead of in 1 litre of solution.

The Ternary System Sodium Oleate, Sodium Chloride, Water

A number of soap, salt, water, systems have been studied in detail by McBain and his colleagues,[1] who have shown that all such systems are variants of a single type. The system under study is no exception to this general rule, but is noteworthy in that it shows to an unprecedented degree certain phenomena of metastable equilibria; these phenomena were noted incidentally by McBain and Langdon[2] but were of unimportant magnitude in the case of the system sodium palmitate, sodium chloride, water, which they were studying.

From preliminary measurements of the solubility of sodium oleate, it was anticipated that although it was more soluble than sodium palmitate, it would behave at 25° like that soap does below 70°, yielding only the two phases isotropic solution and curd. Indeed if the system is studied exactly according to McBain's technique, this appears to be the case. Almost the whole of the diagram is then occupied by a field representing heterogeneous mixtures of curd and isotropic solution or lye, the field of isotropic solutions

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[1] McBain and Burnett: J. Chem. Soc., **121**, 1320 (1922); McBain and Langdon: **127**, 852 (1925); McBain and Elford: **1926**, 421; McBain and Pitter: **1926**, 893; McBain and Field: J. Phys. Chem., **30**, 1545 (1926); McBain, Lazarus and Pitter: Z. physik. Chem., **147**, 87 (1930).

[2] Loc. cit.

being limited to a small area in the neighbourhood of the water apex. The technique in question consists in preparing a large number of sealed glass tubes containing sodium oleate solutions, with and without salt, allowing them to curd out, and then observing the temperatures (Tc) at which the curd just redissolves. By suitable interpolation, it is possible to calculate the composition of solution in equilibrium with the curd at 25°. It happens that all such solutions, except those very poor in soap, are gels; since Laing and McBain[1] have shown that these clear isotropic gels do not constitute a phase distinct from the fluid isotropic solutions, this is of no consequence, except that the contents of the tubes cannot be mixed adequately by agitation and a long time has to be allowed for the attainment of equilibrium.

If however, one endeavours to check the values of Tc so obtained, by observing the temperatures at which curd separates on slowly cooling the tubes, the findings are entirely different. Although ample time may be allowed (up to several weeks), curd does not appear until the temperature is reduced many degrees below that at which the curd redissolved. Frequently however, at an intermediate temperature the solution becomes cloudy from separation of globules of a second liquid phase, which the polarising microscope reveals to be anisotropic, and which from analogy with similar systems is assumed to be neat soap. Provided a tube is not cooled sufficiently for curd to separate, this phenomenon is perfectly reversible, and the temperature (Ti) at which the anistropic phase just separates or disappears can be determined with precision, even though the isotropic phase is a gel. The emulsion of anistropic phase in isotropic gel can be kept at a suitable temperature for weeks without change (excepting a slight tendency for the globules to coalesce), although the same tube previously cooled until curd separates, may be kept indefinitely at the same temperature or even slightly above Ti, without the curd dissolving completely, and without the appearance of any anistropic phase.

It is possible to demonstrate this phenomenon even more dramatically in the following manner: three sealed tubes may be prepared each containing the same solution (e.g. sodium oleate 0.22 N_w; sodium chloride 0.32 N_w) and after heating until the contents become homogeneous, the first may be left in this condition, the second cooled until it contains an opaque mass of curd, and the third cooled until curding just commences and then warmed again so that it contains numerous nodules of curd dispersed through a clear gel. These three tubes can then be kept indefinitely at any temperature between Ti and Tc (32° to 36° for the solution suggested) without any apparent change taking place in any of them. If the temperature is reduced to a little below Ti,the first (clear) tube becomes cloudy from separation of neat soap, the second remains opaque with curd, while the third shows nodules of curd dispersed through a cloudy emulsion of neat soap in isotropic gel. The nodules of curd in this third tube show no inclination to increase in size or to redissolve at either temperature in the course of a week or so.

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[1] J. Chem. Soc., 117, 1507 (1920).

Only when the temperature is reduced to the value Td, several degrees below Ti, (25° for the solution suggested) do the curd nodules begin to grow in this tube, and to appear in the first tube, until eventually both tubes become filled with masses of curd like the second tube.

It should be noted that in bulk the neat soap phase in not permanently stable at 25° but separates into curd and isotropic solution, although in the form of small globules it appears to be stable for indefinite periods. This fact may perhaps be related to the relative sizes of these neat soap globules and the curd fibres. In terms of the average diameter of the neat soap globules, the curd fibres appeared to have a length of some 50 times, and a thickness of 1/10 this value. When an emulsion of neat soap in isotropic solution was allowed to cool and curd out on a microscopic slide, the curd fibres appeared to form in the isotropic solution, shooting between the neat soap globules, which gradually redissolved as the isotropic solution became depleted of soap from deposition of curd.

In case any of these findings should be attributed to the presence of less soluble soaps in the sodium oleate employed, a number of the measurements were repeated using sodium oleate made from highly purified oleic acid prepared by Mr. Skellon by the methods described in his recent paper.[1] The results were qualitatively identical, and differed quantitatively only insofar as the temperatures Tc, Ti, Td, were slightly slower in the case of the especially pure sodium oleate. The author wishes to express his thanks to Mr. Skellon for the gift of this oleic acid.

In order to express these observations in terms of isotherms, it is necessary to draw on the phase diagram (Fig. 1) *three* lines delimiting the field of isotropic solutions. The smallest field P Q water apex, is the one first described, comprising solutions in which curd dissolves completely on warming to 25°; the second line C R shows the composition of solutions in equilibrium with neat soap: the third M S indicates the composition of solutions still richer in soap or salt, from which curd just separates at 25°.

Thus the usual isotherm representing the solubility of sodium oleate in salt solutions, is replaced by the area PQSM between the first and third of these lines. Any solution, the composition of which is represented by a point within this area, may be in equilibrium with curd.

In the case of solutions poor in salt the temperature Tc and Td tended to approach one another more closely, and neat soap either did not appear at all on cooling the tube, or appeared as a metastable phase at a temperature below Td. Thus if the isotherms were drawn for a temperature somewhat below 20°, the lines CR and MS would cross.

Unless these phenomena can be shown to be cases of suspended transformation, it can only be concluded that the Phase Rule in its usual form is not applicable to this system. The observations are however not entirely new, nor is this suggestion without precedent. McBain and Langdon[2] observed that in the system sodium palmitate, sodium chloride, water, curd is not

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[1] J. Soc. Chem. Ind., 50, 131T (1930).

[2] J. Chem. Soc., 127, 852 (1925).

deposited until the temperature is reduced about 4° below the temperature Tc at which it dissolved, and that often neat soap appears first as a metastable phase. Previously Laing and McBain[1] had shown that sodium oleate solutions (without salt) could be obtained at suitable temperatures in the three forms of isotropic solution, isotropic gel, and curd, and further that the concentration of the solution admixed with the curd altered slowly with time, as evidenced by the changing conductivity of the system. These authors explained the phenomena by postulating that the solubility and degree of hydration of the curd fibres is a function of their diameter, in the same way that the solubility of a crystalline solid is greater when it is very finely divided. In other words they suggest that for these systems the Phase Rule takes the form of P + F = C + 3, the extra degree of freedom being the diameter of the curd fibres. They nevertheless express the opinion that given sufficient time at a fixed temperature, a soap curd, soap solution, system will reach a definite equilibrium. This is tantamount to saying that the extra degree of freedom is merely a temporary property of the system and that only one diameter of curd fibre (presumably the largest possible), is permanently stable. The present study not only provides more striking illustrations of the necessity for revision of the Phase Rule in connection with soap curd systems, but also calls into question the temporary nature of the extra degree of freedom; the observations recorded above can all be explained

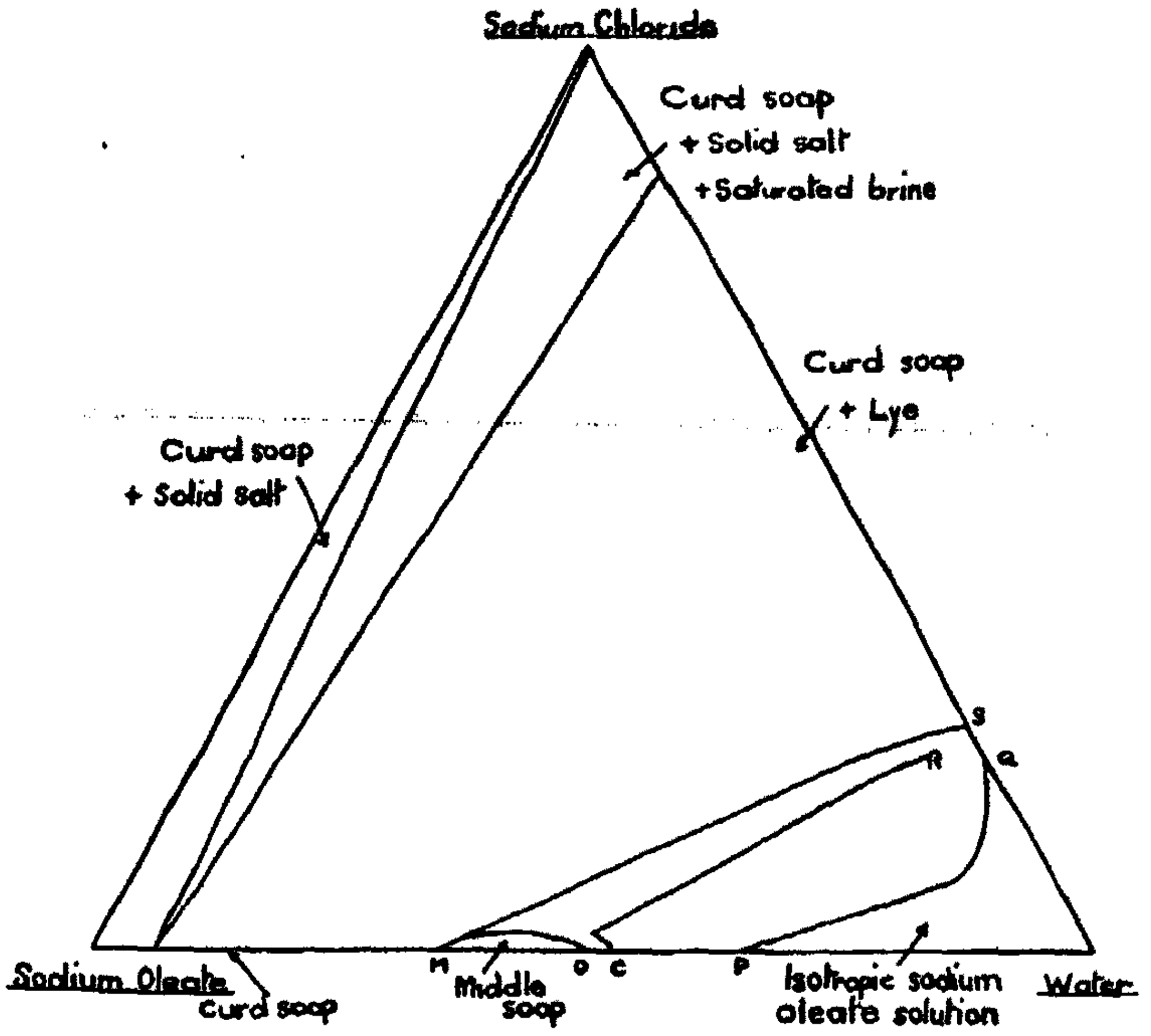

Fig. 1

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[1] J. Chem. Soc., 117, 1507 (1920).

by assuming that the fine curd fibrils have a considerable greater solubility than the coarse fibres. Thus consider a solution which has been allowed to curd out at a low temperature; the curd will be in the form of coarse fibres, and on slowly warming, the last curd fibre will evidently dissolve at the temperature (Tc) at which a solution of this composition is just saturated with respect to the coarse fibres. On cooling again, curd can only be deposited in the form of fine fibrils which subsequently grow; but the solution is not saturated with respect to these fibrils until the temperature is reduced considerably below Tc. Moreover, before this lower temperature is reached the solution may, if the concentrations of sodium oleate and sodium chloride are within certain limits, become saturated with respect to neat soap; since supersaturation with a liquid (or liquid crystal) phase cannot occur, even in soap systems, neat soap promptly separates out at the temperature Ti. At a still lower temperature, for which the symbol Td is used, the solution becomes saturated with respect to the fine curd fibrils. Once these are deposited they can grow and extend without further reduction of temperature, because the solution is already supersaturated with respect to the coarse fibres. Yet the supersaturation which exists between the temperatures T and Td cannot be regarded in the same light as an ordinary suspended crystallisation i.e., as a metastable condition, because if the solution could be seeded with fine curd fibrils, these would not grow but would dissolve, since the solution is not saturated with respect to the fine fibrils. Even if the solution is seeded with the coarse fibres, further deposition of curd does not occur, because this is still dependent on the prior formation of fine fibrils. This fact is illustrated by the third tube in the experiments described above, in which a solution remained permanently in equilibrium with particles of curd over a range of temperature. A sodium oleate system containing curd may probably reach a final equilibrium state *provided the temperature is below Td*, but between Tc and Td the state of the system depends on its previous history, and a condition of "arrested equilibrium" holds indefinitely. Experimentally the temperature Td is difficult to ascertain with precision, because supersaturation readily occurs with respect to the fine curd fibrils. Moreover, since a solution in the neighborhood of the temperature Td is usually cloudy with separated neat soap globules, the soap concentration of the isotropic solution which remains is of necessity lower than that of the solution as a whole, so that the temperature Td at which curd is deposited really represents the temperature at which some solution differing in composition by a small unknown amount from that of the bulk, is in equilibrium with fine curd fibrils.

Neat soap may justly be regarded as a metastable phase at 25° despite its stability in the emulsified state since if the globules could be made to coalesce the mass of neat soap would undoubtably deposit curd. It is possible that the appearance of neat soap may be taken as the equivalent of the separation of curd, but even so it seems impossible to explain the discrepancy between Tc and Ti except by postulating an extra degree of freedom in the system, namely the dependence on fibre diameter of the solubility of soap curd.

Middle Soap

Having established the existence of neat soap as a metastable phase at 25°, it was natural to look for the second anisotropic phase, middle soap, which McBain has found to be common to a number of soaps. It was found that no sodium oleate solution which has curded out will yield middle soap on warming to 25°. Middle soap is stable at higher temperatures however, and some of these solutions remained unchanged on cooling to 25°; when the soap concentration was above a certain limit however, they gradually curded out at 25°. The precise limits of this region on the phase diagram were not determined.

Hydration of Curd

No method is available to determine the hydration of curd when the lye with which it is in equilibrium is a gel, which was the case in this system except when the salt concentration was so high as almost completely to salt out the soap.

The System Sodium Oleate, Water, Ethyl Acetate

The only systems of this type which have previously been investigated in any detail are those in which the organic component is phenol or cresol.[1] The addition of soap progressively increases the mutual solubility of these substances and water, up to the point of complete miscibility; the triangular phase diagrams for these systems therefore show binodal isotherms. These studies are however incomplete, since at higher soap concentrations additional phases such as curd soap would appear, which are not indicated on the published diagrams.

At temperatures above 60°, the system sodium oleate, water, ethyl acetate, behaves in a similar fashion, but at 25° the mutual solubility of ethyl acetate and water is not sufficiently augmented by the soap to render the components completely miscible in any proportions.

The area A B C water apex on the phase diagram (Fig. 2) includes all isotropic sodium oleate solutions containing ethyl acetate. Solutions represented by points on the line A B are saturated with ethyl acetate, and are in equilibrium, as represented by the tie-lines, with ethyl acetate containing traces of water, soap, and fatty acid.

The author has pointed out in a previous publication[2] that the presence of a solvent layer in equilibrium with the soap solution increases the degree of hydrolysis of the latter, by removing fatty acid and so disturbing the hydrolysis equilibrium.[3] In the present study it was essential to ignore this hydrolysis if the number of components was to be limited to four. Fortunately the error so introduced was small.

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[1] Bailey: J. Chem. Soc., 123, 2579 (1923); Weichherz: Kolloid-Z., 49, 158 (1929); Angelescu and Popescu: 51, 247 (1930).

[2] Analyst, 53, 632 (1928).

[3] Holde: Z. Elektrochemie, 16, 436 (1910); also McBain and Buckingham: J. Chem. Soc., 1927, 2867, and the recent criticism of this work by Wellman and Tartar: J. Phys. Chem., 34, 379 (1930).

TABLE I

The System Sodium Oleate, Sodium Chloride, Water

Sodium Oleate	Sodium Chloride	Water	T_c	T_i	T_d (approx.)	Remarks
74.0	0	26.0			>25°	Middle soap, curding at 25°
62.1	0	37.9	>25°		<25°	Middle soap at 25°
49.5	0	50.5		>25°		Middle soap + isotropic at 25°
47.5	0	52.1		25°		
47.1	0	52.9	34°	5°	16-20°	
46.7	0	53.3	32°	—		No anistropic phase separates on cooling
44.5	0	55.5	27.5°	—	16-20°	" " "
41.5	0	58.5	27°	—	16-19°	" " "
37.5	0	62.5	26.5°	—	19°	" " "
32.5	0	67.5	26°	—	19°	" " "
38.6	6.0	55.4		17°	20°-24°	
38.3	6.6	55.1		22.5°	20°-24°	
37.7	8.1	54.2	30°-32°	27°		
27.5	7.9	64.6		12°	20°-24°	
25.8	6.1	68.1		11°		
25.0	13.0	62.0		22°	20°	
24.5	14.3	61.3		25°		
23.5	15.9	60.6	37°	32.5°	20°-25°	
22.3	5.1	72.6	27°	8°	19°-22°	
21.1	4.1	74.8	21°-25°	—	18°	" " "
19.7	19.4	60.9		32°	25°	
15.3	15.2	69.5	32°-36°	<25°		
14.5	20.9	64.6	36°	32°	25°	
14.3	6.6	79.1	28°-30°	8°	19°-21°	
*14.3	22.0	63.7	39.5°	31°	25°-27°	
*14.2	22.4	63.4	40°	32.5°		
14.1	18.7	67.2	32°-36°	27°		
13.4	23.4	63.2		42.5°	>27°	
13.0	22.4	64.6	32°-36°	31°	25°	
*11.2	6.4	82.4	<25°	—	<15°	" " "
10.2	17.0	72.8	32°-36°	<25°		
* 8.1	23.7	68.2	39°			
7.4	21.0	71.6	35°		21°-25°	
5.45	10.2	84.35	28.5°	—	19°	" " "
4.0	14.1	81.9	25.5°	—		" " "
* 3.9	14.8	81.3	27°	—	19°-21°	" " "
3.7	22.6	73.7	40°	36°	20°-25°	
* 2.2	12.2	85.6	21°-24°	—	19°-20°	" " "

* Extra pure sodium oleate.

At the point B, the solution is also saturated with sodium oleate, and a new phase appears. This phase takes the form of a very soft translucent plastic gel, which shows a brilliant play of colours on examination with a polarising microscope. From considerations of its composition and properties, there is no doubt that from the Phase Rule point of view, this liquid crystal phase is correctly designated as neat soap. When it is in equilibrium with isotropic solution and ethyl acetate its composition is necessarily fixed and is represented by the point D on the diagram. Neat soap does not persist as a stable phase at 25° in absence of ethyl acetate, so that the limits for its existence are represented by the area DFG which does not touch the sodium oleate, water, side of the triangle. Along DF, the neat soap is in equilibrium with ethyl acetate, along FG, with curd soap, and along DH, with isotropic sodium oleate solutions. The area FGKJ represents heterogeneous mixtures of neat soap and curd soap, which at F and J are also in equilibrium with ethyl acetate forming an invariant system.

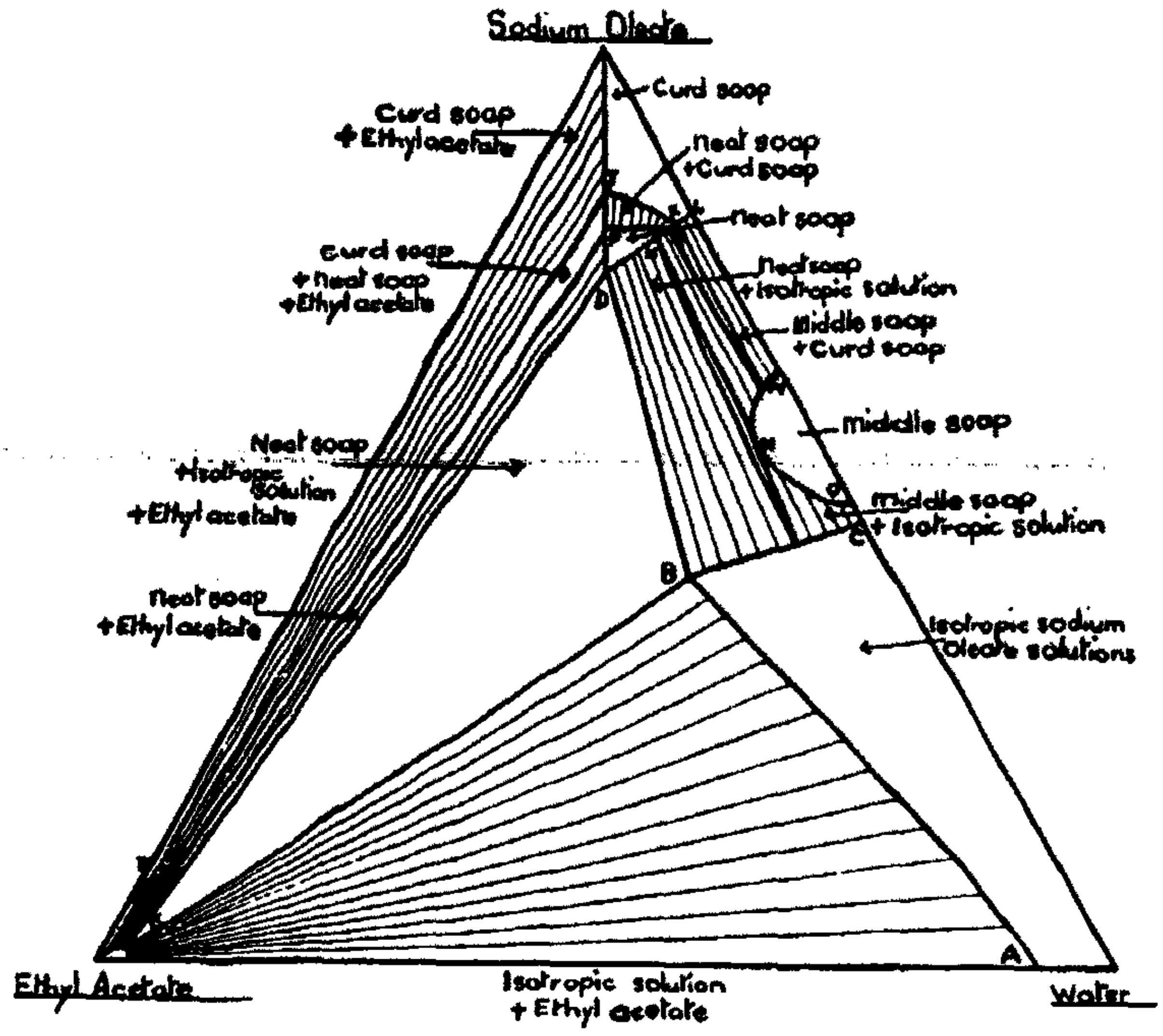

FIG. 2

The area MNO represents approximately the limits for the existence of middle soap. This phase can absorb a little ethyl acetate but breaks down to a mixture of neat soap and isotropic solution before the soap becomes saturated with the ester.

Experimental

The position of the line AB on the phase diagram, and of the tie-lines connecting this with the ethyl acetate corner, were determined as follows:

weighed quantities of a sodium oleate solution of known strength, and of ethyl acetate were shaken together in a separating funnel, and allowed to attain equilibrium and separate in a thermostat at 25°. Ethyl acetate was then estimated in both layers by determining the volume of standard alkali required to saponify the ester. A suitable quantity of the lower layer was run into a flask containing 25 ml of N/2 sodium hydroxide. The flask was immediately restoppered and reweighed, then heated slightly and set aside for about 15 minutes, after which the contents were back-titrated with N/2 hydrochloric acid using phenolphthalein as indicator, sufficient neutral ethyl alcohol being added to make the concentration about 50% in the final solution, to prevent hydrolysis of the soap from obscuring the end-point. About 2 gm of the upper layer were weighed into a flask containing 50 ml of sodium hydroxide, and treated similarly. A larger quantity of the upper layer was evaporated to dryness and the residue weighed to determine the sodium oleate present. The water in the upper layer was estimated by difference. The point B was fixed by measuring the quantity of water required just to dissolve the neat soap in a mixture of isotropic solution, neat soap, and ethyl acetate, of known composition.

The areas near the sodium oleate apex were less easy to delimit accurately. The principal reason for this lay in the instability of the ethyl acetate. It was impossible to heat mixtures in sealed tubes in order to render them homogeneous, because the ethyl acetate was rapidly hydrolysed. For the same reason, it was not permissible to allow mixtures to remain at 25° to attain equilibrium, for longer than a few hours. It was therefore necessary to rely on shaking and stirring at the temperature of the observations in order to mix the components. The examination under the polarising microscope of mixtures of known composition prepared in this manner gave some indication of their nature. The position of the line DL was also fixed approximately by an analytical method, similar to that used by McBain and his colleagues to determine the degree of hydration of soap curd.[1] Sodium chloride was used as the reference substance, the assumption being made that it is not sorbed by the neat or curd soap in the presence of ethyl acetate. Although this assumption may not be true, the error introduced is not likely to be very large, and since it is impossible to eliminate the sources of error mentioned above, other reference substances suggested as more suitable by McBain and Martin and by Laing[2] were not tested.

The further assumption is involved that the degree of hydration of the neat soap is not materially altered by a small concentration of salt in the solution with which it is in equilibrium. A small quantity of sodium chloride solution was added to a soap solution containing less than the saturation concentration of ethyl acetate. After allowing some hours for the attainment of equilibrium, a portion of the isotropic solution was separated from the anisotropic phase (which slowly rose to the top on standing) and analyzed

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[1] McBain and Martin: J. Chem. Soc., 119, 1369; Laing: 1669 (1921); Bennett: 125, 1971 (1924).

[2] Loc. cit.

for soap, salt, and ester. The ethyl acetate was estimated by the method described above except that sulphuric acid was used for the titration. Excess acid was then added, the liquid boiled to remove alcohol, and the oleic acid extracted with ether and weighed after evaporation of the ether. The aqueous layer was warmed to remove dissolved ether, neutralised with sodium hydroxide, and titrated with N/10 silver nitrate using potassium chromate as indicator. These analytical data, together with a knowledge of the original composition of the mixture, enable the composition of the neat soap to be calculated. In some cases the mixture of neat soap and isotropic solution which remained was analysed as a check. Further, the concentration of ethyl acetate required to saturate the isotropic solution was known from other experiments, and by making the additional assumption that on satura-

Table II

Composition of Phases in Equilibrium

<table>
<tr><th colspan="3">Lower Layer</th><th colspan="3">Upper Layer</th></tr>
<tr><th>Sodium Oleate</th><th>Water</th><th>Ethyl Acetate</th><th>Sodium Oleate</th><th>Water</th><th>Ethyl Acetate</th></tr>
<tr><td>—</td><td>92.73</td><td>7.27</td><td>—</td><td>2.9</td><td>97.1</td></tr>
<tr><td>8.3</td><td>82.7</td><td>9.0</td><td>1.0</td><td>2.85</td><td>96.15</td></tr>
<tr><td>15.8</td><td>73.2</td><td>11.0</td><td>1.0</td><td>2.7</td><td>96.3</td></tr>
<tr><td>24.6</td><td>61.5</td><td>13.9</td><td></td><td></td><td></td></tr>
<tr><td>27.2</td><td>58.3</td><td>14.5</td><td>1.0</td><td>2.7</td><td>96.3</td></tr>
<tr><td>32.5</td><td>50.4</td><td>17.1</td><td>1.2</td><td>2.8</td><td>96.0</td></tr>
<tr><td>38.5</td><td>42.8</td><td>18.7</td><td></td><td></td><td></td></tr>
<tr><td>39.8</td><td>40.4</td><td>19.8</td><td></td><td></td><td></td></tr>
<tr><td>42.3</td><td>37.3</td><td>20.4</td><td colspan="3" rowspan="2">In equilibrium with ethyl acetate layer and neat soap (point B)</td></tr>
<tr><td>42.2</td><td>37.3</td><td>20.5</td></tr>
<tr><td>77.7</td><td>11.3</td><td>11.0</td><td colspan="3">(Neat soap in equilibrium with ethyl acetate)</td></tr>
<tr><td>80.3</td><td>11.7</td><td>8.0</td><td colspan="3">(hetero. neat soap + curd soap)</td></tr>
<tr><td>74.5</td><td>13.5</td><td>12</td><td colspan="3" rowspan="5">Neat soap in equilibrium with isotropic solution and ethyl acetate (point D)</td></tr>
<tr><td>75.5</td><td>12.5</td><td>12</td></tr>
<tr><td>75.5</td><td>12.5</td><td>12</td></tr>
<tr><td>76</td><td>12</td><td>12</td></tr>
<tr><td>78</td><td>11</td><td>11</td></tr>
<tr><td>80.5</td><td>9.5</td><td>10</td><td colspan="3">Neat soap in equilibrium with curd and ethyl acetate</td></tr>
<tr><td>80.5</td><td>15</td><td>4.5</td><td colspan="3" rowspan="2">Neat soap in equilibrium with isotropic solution (containing Na Cl)</td></tr>
<tr><td>79</td><td>13</td><td>8</td></tr>
<tr><td>60</td><td>36.5</td><td>5.5</td><td colspan="3">Homo. middle soap</td></tr>
<tr><td>58</td><td>36</td><td>6</td><td colspan="3">Middle soap in equilibrium with isotropic solution</td></tr>
<tr><td>57</td><td>35.5</td><td>7.5</td><td colspan="3">Heterogeneous; neat soap + isotropic solution</td></tr>
</table>

tion the ester concentration in the neat soap would increase in the same ratio as in the isotropic solution, it was possible to fix the point D. Fair agreement was obtained between several determinations using different concentrations of ester and salt.

The limits of the middle soap region were determined approximately by dissolving ethyl acetate in sodium oleate solutions of appropriate concentration, and observing the amount which could be added before the mixture became heterogeneous. This was detected by a decrease in viscosity and a change in the appearance of the mixture under the polarising microscope.

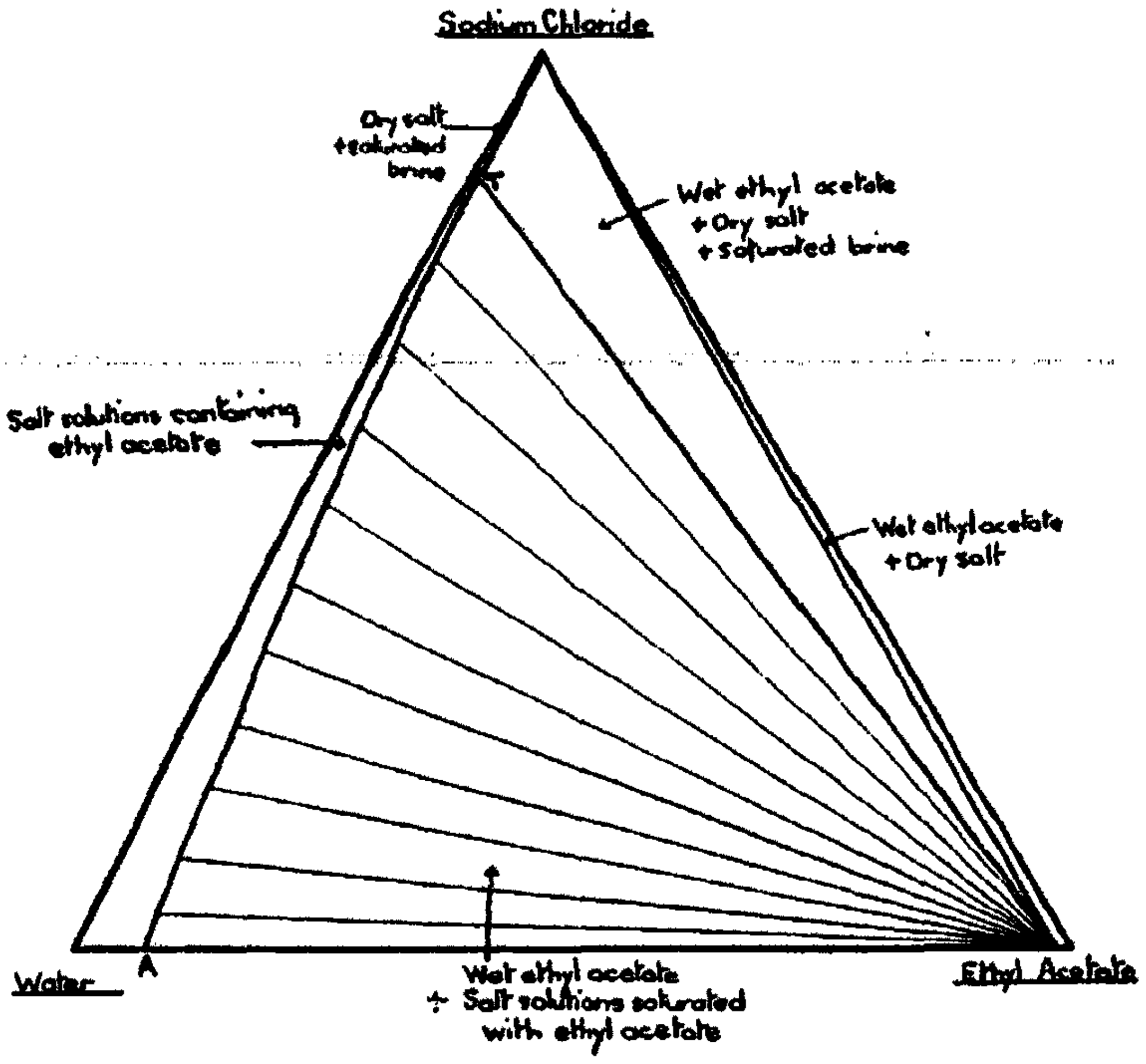

FIG. 3

The System Sodium Oleate, Ethyl Acetate, Sodium Chloride

Sodium oleate and ethyl acetate appear to be almost completely immiscible in the absence of water. The solubility of dry sodium oleate in the dry ester was found to be only 0.005%. It is almost impossible to determine whether the sodium oleate absorbs any of the ester, but the dry powdered soap did not swell or undergo any obvious change even in boiling ethyl acetate. Sodium chloride is completely immiscible with both the other components.

The System Sodium Chloride, Ethyl Acetate, Water

The solubility of ethyl acetate in water is depressed by additions of salt, the ester being "salted out." The solubility of water in ethyl acetate is also slightly decreased by increases in the salt concentration of the aqueous phase with which it is in equilibrium, owing to the dehydrating effect of the salt. These observations are illustrated by the position of the line AT and the tie-lines in Fig. 3. At T the aqueous phase is saturated with salt, which appears as a third phase. The brine and salt are in equilibrium with ethyl acetate containing 1.6% of water, which value therefore indicates the extent to which the wet ester could be "dried" by contact with sodium chloride. The diagram is completed by two very narrow triangles containing tie-lines linking, in the first case, solid salt with ethyl acetate containing less than 1.6% of water, and in the second case, linking solid salt with brine not saturated with ethyl acetate.

Experimental

Weighed quantities of the three components were shaken together in a 100 cc separating funnel immersed in the thermostat until equilibrium was attained. The lower layer was analysed for ethyl acetate as described earlier, except that N/2 sulphuric acid was used for the back-titration, instead of hydrochloric, and the sodium chloride was then estimated as a check in some cases, by titration with N/10 silver nitrate using potassium chromate as indicator. The upper layer was also analysed for ethyl acetate, the water being estimated by difference.

TABLE III

Composition of Layers in Equilibrium

Lower Layer			Upper Layer		
Ethyl Acetate	Sodium Chloride	Water	Ethyl Acetate	Sodium Chloride	Water
7.27	—	92.73	97.1	—	2.9
5.4	19.2	75.4	97.15	—	2.85
3.9	34.7	61.4	97.4	—	2.6
2.25	52.7	45.05			
0.6	76.0	23.4	98.0	—	2.0
0.15	85.75	14.1	98.4	—	1.6
(In equilibrium with solid NaCl)					
—	86.0	14.0			
(In equilibrium with solid NaCl)					

The Quaternary System

When the number of components is increased to four, the equilibria become difficult to describe in words, or to represent on a plane surface. However, the quaternary system presents no phases which have not already been described, and with the aid of the diagrams it is not difficult to construct a mental picture of the three-dimensional tetrahedral diagram within which the system can best be represented. This reconstruction can be made most easily from Fig. 4 which represents the tetrahedron opened out, so that the sides are bent back into the plane of the base.

A number of attempts were made to plot projections of the quaternary diagram, such as the orthogonal projection onto a triangle used by Schreinemakers, the orthogonal projection onto a square used by the same author, and the improvement on this method described by Philipsborn[1] but without exception they produced diagrams too confused to be readily intelligible. The projection used by Jänecke, in which the tetrahedral diagram is projected onto a face triangle by lines radiating from the opposite vertex, proved more useful, and as much of this projection as is practicable has been incorporated into Fig. 4.

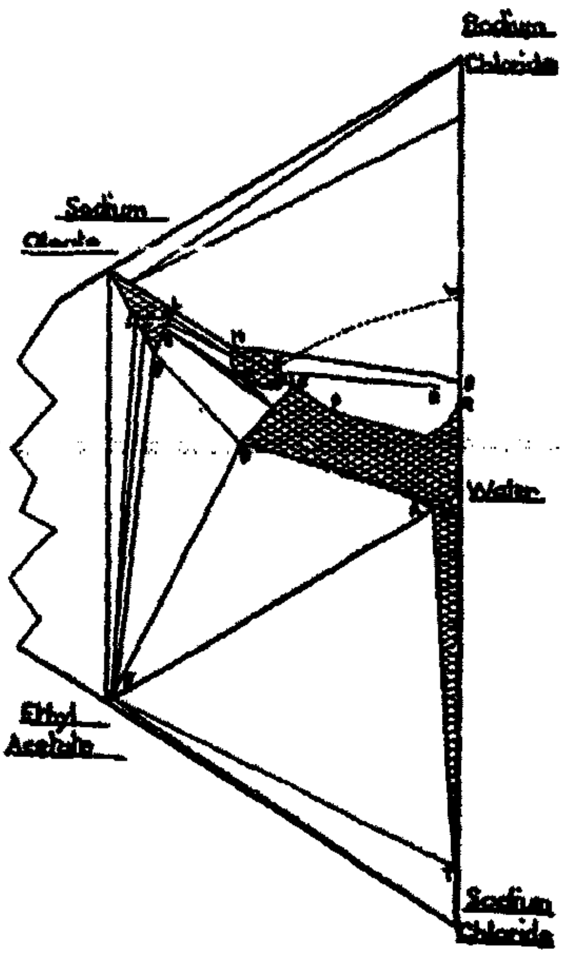

Fig. 4

The principal feature of the quaternary diagram is the figure representing the limits of composition of isotropic sodium oleate solutions, i.e. the extension of the region A, B, C, water apex, in the base triangle. A surprisingly large amount of salt can be dissolved in sodium oleate solutions containing ethyl acetate before the soap is salted out. Similarly many mixtures of curd soap and lye are liquefied to isotropic solution by the addition of ethyl acetate. The figure is characterised by a "ridge" rising from the point B in the base to a point in the line AT close to the salt, water, edge of the tetrahedron.

Projections of this ridge onto both the base triangle and the soap, salt, water, triangle are represented by the lines BU and VW respectively in Fig. 4. One face of the figure, which is almost plane, joins this ridge to the line AB on the base triangle and represents sodium oleate solutions containing salt, in equilibrium with an ethyl acetate layer. A series of tie-lines therefore link this face with points near the ethyl acetate corner. The other face curves away from the ridge, joining it to the line BC on the base and the line CR on the soap, salt, water, face of the tetrahedron. It represents isotropic sodium oleate solutions containing salt and ethyl acetate, in equilibrium with neat soap or curd soap. It is evident that solutions of compositions represented by points along the ridge, must be in equilibrium with both neat soap and ethyl acetate, like the solution represented by the point B on the base triangle. Since, however, the number of components is now four, the presence of three phases in equilibrium does not render the system invariant in composition at the fixed temperature of 25°. The triangle B D E on the base, is therefore multiplied into a series of "tie-triangles" linking together points on the "ridge," points along D F on the neat soap region, and points near the ethyl acetate apex. As one passes up the "ridge" from B, the isotropic solutions

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[1] Thonindustrie Z., 53, 45 (1929).

become progressively poorer in soap and richer in salt until when the line AT is reached, the soap is completely salted out. The phase in equilibrium with this lye (in the presence of an ethyl acetate layer) is, however, still neat soap, so that the series of tie-triangles extend further, linking points along AT to points along DF on the neat soap region and points near the ethyl acetate apex. The limit is reached at the point T where the lye becomes saturated with salt, and solid salt appears as a fourth phase. The system would now be invariant at a fixed temperature, but it also happens that at 25° another phase makes its appearance, namely curd soap. Thus the five phases solid salt, saturated lye (point T), neat soap (point F), curd soap (point J), and ethyl acetate containing traces of water and soap, are in equilibrium, in addition of course to a sixth phase, vapour, which is understood to be present throughout.

Such a system can only exist at a fixed temperature; the quintuple point was difficult to determine exactly, but is certainly within a few degrees of 25°. The equilibrium is represented in the tetrahedral diagram by an irregular solid figure, mixtures represented by points within which separate into five phases of compositions represented by its five apices.

It will be evident that each face of this invariant figure which does not already lie in one of the faces of the tetrahedron, must throw off a series of tie-triangles (just as each tie-triangle throws off tie-lines from its edges). The tie triangles linking ethyl acetate, neat soap, and lye or isotropic solution have already been mentioned. Another series link ethyl acetate, solid salt, and curd soap saturated with ethyl acetate, merging finally into the ethyl acetate, salt, soap, face of the tetrahedron. Other tie-triangles link solid salt, saturated brine, and curd soap not saturated with ethyl acetate, merging finally into the salt, brine, curd, triangle in the salt, soap, water, face of the tetrahedron. Still another series link neat soap and curd soap, (not saturated with ethyl acetate) first with a series of salt solutions, then with soap solutions containing salt and a little ethyl acetate.

Experimental

The experimental methods used in the investigation of the quaternary system are for the greater part similar to those described previously. The compositions of isotropic solutions in equilibrium with both ethyl acetate and neat soap were determined in a few cases by gradually adding sodium chloride solution to an isotropic soap solution mixed with excess ethyl acetate, until neat soap just began to separate at 25°; the isotropic solution was then analysed for salt soap and ester. Subsequently it was found that when an excess of salt was added, the neat soap gradually rose to the surface with the excess ethyl acetate, and a clear sample of the isotropic solution could be withdrawn from the bottom of the vessel for analysis.

TABLE IV

Composition of Phases in Equilibrium

Lower Layer				Upper Layer			
Na $\overline{Ol}$	H_2O	Et $\overline{A}$	Na Cl	Na $\overline{Ol}$	H_2O	Et $\overline{A}$	Na Cl
8.1	51.0	6.7	34.2				
8.5	56.7	7.1	27.7	1.5	2.5	96.0	—
22.8	55.5	12.6	9.1	1.9	2.6	95.5	—
32.4	39.7	16.3	11.6				
35.9	40.0	18.1	6.0				
0.8	52.4	3.1	43.7	In equilibrium with ethyl acetate layer and neat soap "Ridge" of figure.			
5.9	50.3	5.2	38.6				
9.9	48.5	7.4	34.2				
11.9	47.5	8.2	32.4				
21.6	42.5	11.7	24.2				
22.9	41.3	11.8	24.0				
30.5	39.5	15.4	14.6				
2.6	59.2	2.9	35.3	In equilibrium with neat soap			
3.2	57.3	3.6	35.9				
4.2	57.0	4.8	34.0				
5.6	62.9	2.5	29.0				
5.8	55.6	2.6	36.0				
7.2	54.0	3.1	35.7				
7.7	58.0	3.3	31.0				
9.2	56.0	4.0	30.8				
9.7	52.4	4.2	33.7				
12.4	53.6	5.4	28.7				
13.8	52.6	6.0	27.6				
16.8	49.8	7.4	26.0				
18.6	53.3	2.8	25.3				

Equilibrium between isotropic solution and neat soap

	Isotropic solution			Neat soap		
0.7	50.65	0.95	47.7	80.5	15	4.5
—	37.7	1.2	61.1	79	13	8
—	21.0	0.44	78.6	78	11.1	10.9

Discussion

The phenomena observed in studying the system salt, soap, water, which were incidental to the main purpose of these papers, were discussed in the appropriate section. The system soap, water, ethyl acetate, has also been considered from the Phase Rule aspect, but it is now proposed to examine the findings from the point of view of the colloid chemistry of soap solutions.

The nature of the solvent power of sodium oleate solutions for organic liquids was discussed in part 1 of this series where it was shown that the dissolved liquid may be divided into that dissolved by the aqueous dispersion medium, and that dissolved or adsorbed by the colloidal soap.

The data now available render possible a quantitative treatment of the special case where the organic liquid is ethyl acetate.

A solution of sodium oleate saturated with ethyl acetate will again be treated as a two phase system. It will be assumed as a first approximation that the hydration of the colloidal soap is zero, or rather, that the whole of the water in the solution is free to dissolve the normal proportion of ethyl acetate. The difference between this and the total weight of ethyl acetate dissolved indicates the weight of ethyl acetate associated with the soap in the solution; this figure, divided by the weight of the soap, evidently gives a value for the apparent solubility of the ester in sodium oleate—*apparent,* because actually this portion of the ethyl acetate is carried only by the *colloidal* soap. When this calculation is applied to the data in Tables II and IV the apparent solubility value is found to increase as the soap concentration increases, because a greater proportion of the soap is in the colloidal state in the more concentrated solutions. A value for the true solubility of ethyl acetate in colloidal sodium oleate may be obtained by the following expedient: if the apparent solubility values are plotted against the reciprocals of the square roots of the corresponding soap concentrations, a nearly straight line is obtained, which may be extrapolated to zero $\frac{1}{\sqrt{[\text{sodium oleate}]}}$. This obviously corresponds to a hypothetical infinite soap concentration, and the solubility value so obtained may be taken as that of ethyl acetate in colloidal sodium oleate. This value is 1.57 gm of ethyl acetate per gm of sodium oleate, or 5.4 molecules of ethyl acetate per molecule of sodium oleate. This figure divided into the apparent solubility values, gives some indication of the proportions of soap in the colloidal state at various soap concentrations. The results are shown in Table V.

It is interesting to note the effect of adding salt to a sodium oleate solution in presence of ethyl acetate. The total amount of ester dissolved of the soap solution is scarcely affected; it is slightly decreased at low soap concentrations, and slightly increased at higher concentrations. This is illustrated in Fig. 4; the line BA represents the solubility of ethyl acetate in absence of salt, and the line BV which is the projection of the "ridge," represents the solubility in soap solutions containing the maximum of salt.

It must be recalled, however, that the solubility of ethyl acetate in water is depressed by salt, so that when the total ethyl acetate dissolved by a soap solution is separated into the proportion dissolved by the water and the proportion associated with the soap, it is found in every case that the latter value is increased by additions of salt (see Table V). This is to be attributed to an increase in the proportion of soap in the colloidal state, and may be compared with a similar conclusion expressed in Part II as a result of partition coefficient measurements. It may further be noted that although these values for the apparent solubility of ethyl acetate in sodium oleate are higher than any observed in the absence of salt, they never quite reach 1.57, which tends to confirm the conclusion that this value obtained by extrapolation represents correctly the solubility of ethyl acetate in colloidal sodium oleate.

TABLE V

$\{\text{Na } \overline{\text{ol}}\}$ in N_w	$\frac{1}{\sqrt{\{\text{Na } \overline{\text{ol}}\}}}$	$\{\text{Na Cl}\}$ in N_w		$\frac{\text{Excess Et } \bar{\text{A}}}{\text{Na } \overline{\text{ol}}}$	α
0.100	3.16	—		0.98	.625
0.216	2.15	—		1.09	.695
0.400	1.58	—		1.20	.765
0.467	1.465	—		1.21	.77
0.645	1.245	—		1.28	.82
0.900	1.055	—		1.32	.84
0.988	1.005	—		1.38	.88
1.130 (max)	0.94	—		1.36	.87
	0 (by extrapolation)	—		1.57	1.00
0.150	—	0.490	Not saturated Na Cl	1.22	.78
0.159	—	0.671		1.53	.97
0.411	—	0.164		1.25	.80
0.816	—	0.294		1.39	.88
0.898	—	0.150		1.40	.89
0.015	—	0.835	Saturated with Na Cl	0.89	.57
0.117	—	0.770		1.35	.86
0.204	—	0.707		1.52	.97
0.251	—	0.681		1.55	.99
0.555	—	0.580		1.33	.85
0.772	—	0.370		1.39	.88

Generally speaking, the proportion of soap in the colloidal state, calculated as described above, increases progressively with increase in the salt concentration, but insufficient data are available for mathematical treatment. It should be understood that values calculated by this method can only be approximate in view of the assumptions involved, and that they stand in need of confirmation by methods similar to those which have been applied to soap solutions in the absence of organic liquids.

Similar calculations can fruitfully be applied to the system sodium oleate, water, o.cresol, at 20°, studied independently by Bailey[1] and by Angelescu and Popescu.[2] In this case, the triangular phase diagram shows a complete binodal curve (although Angelescu and Popescu investigated only the water-rich section). The solubility of o-cresol in water is less than that of ethyl acetate but high enough to account for an appreciable proportion of the o-cresol dissolved by soap solutions. Allowing for this, values for the apparent

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[1] J. Chem. Soc., **123**, 2579 (1923).

[2] Kolloid-Z., **51**, 247 (1930).

solubility of o-cresol in sodium oleate have been calculated as described above; they increase steadily from 2.0 to 4.1 gm. o-cresol per gm of sodium oleate as the soap concentration increases, showing no tendency to approach a maximum. The reason for this may be that the concentration of soap never becomes very high, the maximum value being less than one third of that attained with ethyl acetate as the third component. A point worthy of attention however is the very high solubility of o-cresol in sodium oleate. At the maximum the value is 4.1 gm. of o-cresol per gm. of sodium oleate, and since a proportion of the soap must be in molecular solution, the true value must be higher. In terms of molecules, each soap molecule is associated on the average with at least 11.5 molecules of o-cresol.

There is no doubt that these solutions have still a colloidal nature, as Angelescu and Popescu have shown by measurements of their viscosities and surface tensions; nor is it possible to regard the cresol as the solvent, for the solutions are in equilibrium with a cresol-rich phase; if therefore the ionic micelle consists as McBain suggests[1] of about ten oleate ions joined together at the hydrocarbon ends of the chains, there seems no escape from the conclusion that each such micelle must be capable of adsorbing over a hundred cresol molecules.

Summary

The four ternary systems and the quaternary system possible with the four components, sodium oleate, sodium chloride, ethyl acetate, and water, at 25°, are described.

The system sodium oleate, sodium chloride, water, is peculiar in that it constitutes an exception to the Phase Rule; an extra degree of freedom is demanded because the solubility of sodium oleate curd fibres is a function of their diameter. Neat soap separates from certain solutions as a metastable phase.

The components sodium oleate, ethyl acetate, and water, yield the six phases:—isotropic sodium oleate solution, middle soap, neat soap, curd soap, wet ethyl acetate, and vapour.

Sodium oleate, sodium chloride, and ethyl acetate are almost completely immiscible.

The mutual solubility of ethyl acetate and water is depressed by additions of sodium chloride up to the point where the salt appears as a third phase.

The quaternary system introduced no new phase; it is noteworthy for an example of an equilibrium between six phases, namely:—neat soap, curd soap, salt, brine, ethyl acetate and vapour.

The nature of the solubility of ethyl acetate in sodium oleate solutions is discussed. It is possible to calculate approximately from the data the proportion of soap in the colloidal state in sodium oleate solutions.

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[1] J. Am. Chem. Soc., 30, 1636 (1928).

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THE PROBLEM OF LIQUID SODIUM-AMALGAMS

(A case for the colloid view)

BY G. R. PARANJPE AND R. M. JOSHI

In a discussion of colloidally disperse structures in metallurgy, Freundlich[1] observes: "It has been pointed out on various sides, with justice, that in the metallurgy of alloys the existence only of true solutions of the components in question or of coarsely disperse system has been assumed, but that no good reason can be seen why colloidally disperse structures should not frequently exist. It is difficult, no doubt, to characterise them, since, as is obvious, almost all our usual methods for proving the existence of the colloidal state fail us." And as an instance of these colloidally disperse structures in iron-carbon alloys he points out after Benedicks[2] that troostite is to be regarded as a colloidal solution of cementite in ferrite.

It was thought, therefore, that it would be interesting to study, in this connection, some of the binary systems in alloys. Recently, much work has appeared on sodium-mercury alloys. And since it is easier to apply colloidal considerations to liquid systems than to solid, it was decided to start with liquid sodium-amalgams in the first instance.

Some General Considerations

Bornemann[3] had pointed out that only the following methods can be employed to determine the composition of these alloys:

(i) The investigation of the thermal diagrams,
(ii) The study of physical properties other than freezing points,
(iii) The preparation and examination of micrographs.

And consequently all the research on this problem has proceeded along these lines. Vanstone[4] studied the problem of liquid as well as solid amalgams of sodium by all these methods. Later, some other physical properties came to be studied by different workers and now sufficient data have been obtained so as to permit of some generalization regarding the structure of the system Na-Hg.

Supposing that the system Na-Hg is a colloid system, it is evident that it can vary in its physical properties in the following among other ways:

(i) total concentration of the disperse phase,
(ii) shape of the colloid particle,
(iii) size of the colloid particle,
(iv) mass of the colloid particle and
(v) charge on the colloid particle.

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[1] "Colloid and Capillary Chemistry," translated by Hatfield, 805 (1922).

[2] Z. physik. Chem., 52, 6 (1905); Kolloid-Z., 7, 290 (1910).

[3] Metallurgie (1919).

[4] Trans. Faraday Soc., 6, 42 (1911); 9, 291 (1914) and other papers.

Considering even these variables, there is room enough for inconsistencies to creep into the results when we examine the system merely from the concentration-change point of view. Variations may be caused by any one or all of the other variables, for they depend largely on the method of preparation and by other conditions which may not always be the same. So far, all the various physical properties that have been examined have been studied only with the concentration of Na as a variable, and there appear to be many inconsistencies in the data obtained by different authors, especially when the same properties have been studied by different workers in different laboratories. Thus, in the data on electrical conductivities, we have four different versions of what happens after the initial decrease with increasing concentration.[1] Hine[2] finds that the conductance of sodium-amalgam passes through a minimum; Vanstone[3] states that the conductivity-concentration curve exhibits a maximum corresponding with $NaHg_2$; D. Bohariwalla and others[4] obtain two discontinuities, one at 0.079% Na and one at 0.272% Na; while Davies and Evans[5] report only one, viz., at 0.272% Na. Experimental inaccuracies certainly could not affect the results to such an extent. The inconsistencies can, however, be easily understood if the colloid hypothesis is assumed, and it is noted that the methods of preparation of the amalgams of different workers were all different. Hine prepared his amalgams by diluting an electrolytically prepared, highly concentrated amalgam; Vanstone by adding mercury to pure, oxide-free sodium; D. Bohariwalla by stopping the electrolysis in the electrolytic method at different stages, i.e. by concentrating dilute amalgams; and Davies and Evans by adding sodium to pure mercury. Thus, according to this hypothesis the method of preparation of an amalgam is a factor of great importance.

Another and a very curious example of how the method of preparation affects the properties of an amalgam has recently been supplied by Willstätter, Seitz and Bumm[6] who point out that amalgams of the same concentration of Na, but prepared in different sorts of vessels such as porcelain dish, or an iron vessel, or a hessian crucible have widely different reducing properties and very different rates of reaction with conductivity water. They, however, attribute it to the impurities coming from the walls of the vessels in which the amalgams are prepared. But this behaviour seems to be strikingly similar to that witnessed in the preparation of Kohlschütter silver sols[7] which differ in their colour and other properties simply because they are prepared in vessels of different glasses. Thus, in order to define an amalgam a mere statement of the concentration of Na does not suffice; the method of preparation at least must be stated.

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[1] Cf. Bornemann and Müller: Metallurgie, 9, 473, 505 (1912).

[2] J. Am. Chem. Soc., 39, 879 (1917).

[3] Trans. Faraday Soc. 9, 291 (1914).

[4] Ind. J. Physics, 4, 147 (1929).

[5] Phil. Mag., (7) 10, 569 (1930).

[6] Ber., 61B, 871-886 (1928).

[7] Z. Elektrochemie, 14, 49 (1908).

Shape and Size of the Particles

Regarding the shape and size of the particles nothing can be said for the present, since no method that could be adapted to study this system has yet been developed. The chief difficulty is that this system is entirely opaque to ordinary light.

Number of Particles in the System

Similarly, we know nothing regarding the number of particles in the system, though it will be perfectly legitimate to imagine an amalgam showing different properties with different proportions of particles of different sizes, though the concentration of the disperse phase is the same.

Charge on the Particles

As regards charge, however, some data are available. Lewis, Adams and Lanmann[1] reported that with the passage of an electric current through a liquid Na-amalgam, sodium always gathers round the anode. Le Blanc and Jäcks[2] confirmed this. But Kremann and co-workers[3] went a stage further and showed that while this is true up to a concentration of 2% Na, at higher concentrations, sodium gathers round the cathode. This, again, is strikingly similar to the change of charge phenomena so often encountered in colloid chemistry.

Theories of the Development of Charge

This raises the question as to how this charge is developed. The explanations so far offered tend generally towards the compound or complex formation view. According to this view a definite compound or a complex of the type of Na_xHg_y is first formed and then is ionised to a certain extent. During the passage of an electric current ordinary electrolysis takes place, sodium going towards one electrode and mercury towards the other. But this explanation, which can be valid only for concentrations higher than 2%, is not quite satisfactory in the case of lower concentrations, for it raises the difficulty as to how sodium which is so electropositive wanders towards the anode, and particularly when it is combined with mercury which is much less electro-positive. This difficulty is got over by some chemists by assuming that the ionisation does not take place as Na_x^- and Hg_y^+ but as $(Na_x Hg_y)^-$ and $Hg_{y_2}^+$. This assumption again is very similar to the assumption of the formation of colloid micellae.

Skaupy[4] has proposed a theory of charge development according to which metals dissolved in mercury are ionised to a considerable extent. His theory, however, cannot directly be applied to the problem in hand without assuming the formation of sodium-mercury complexes as shown by Davies and Evans.[5] The conclusion of Davies and Evans would be acceptable if their amalgams

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[1] J. Am. Chem. Soc., 37, 2656 (1915).

[2] Z. Elektrochemie, 35, 385-416 (1929).

[3] Monatshefte, 46, 515, 529 (1926); 56, 35-65 (1930).

[4] Verhandl. deut. physik. Ges., 16, 156 (1914).

[5] Loc cit.

were prepared by diluting concentrated amalgams but they prepared each of their amalgams by concentrating a dilute one.

But, probably, unaware of Skaupy's work, Lewis, Adams and Lanmann[1] formulated a theory based on Kraus's explanation of the ionisation of Na in liquid ammonia and explained the initial decrease in conductivity on the conductivity-concentration curves as due to large aggregates of mercury atoms gathering round sodium atoms and thus reducing the average mobility of the electrons that take part in the conduction of electricity. This conception of Lewis and co-workers appears to be very similar to the formation of a solutoidal colloid.[2]

Further Confirmation of Lewis's Hypothesis

The assumption of Hg atoms aggregating round Na atoms as nuclei seems to be further supported by Ramsay's observations[3] on the lowering of vapour pressure of mercury by dissolved sodium. He found that the molecular weight of sodium when dissolved in mercury falls with increasing concentration and suggested that this might be due to the formation of a stable alloy of sodium and mercury which acts as a solvent. His suggestion regarding a stable alloy of sodium and mercury, however, cannot be accepted and it is probable that mercury atoms aggregate round the sodium atoms as nuclei.

Non-electro-cratic Nature of the Amalgams

Again, if even a part of the conductivity was electrolytic, as assumed by the previous workers, there should be an increase in the total conductivity on addition of sodium and not the observed decrease which takes place, at least, up to the first discontinuity. Thus the conductivity of the amalgams does not appear to be electrolytic at least, in the ordinary sense of the term. D. Bohariwalla and others[4] have confirmed this to some extent. They measured the conductivity of an amalgam by a direct current method as well as by the induction coil method and found that the values obtained by both these methods were exactly the same. Now, since the conductivity is not electrolytic and there is still the migration of Na towards one electrode or other what was called electrolysis appears to be simply the phenomena of cataphoresis, and the high current densities required to secure the migration show that the system Na-Hg is non-electrolytic. This again is in conformity with the solutoidal or lyophilic nature of the system.

Some Indirect Evidence to support the above Conclusion

There is already some more evidence inherent in the results published from this and other laboratories which points to the same conclusion.

Thus, since Bhatnagar and co-workers[5] found that Na-amalgams are only slightly activated as regards their inter-action with conductivity water

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[1] Loc cit.

[2] Cf. P. P. von Weimarn: Rev. gén. Colloides, 7, 153-158 (1929).

[3] J. Chem. Soc., 1889, 521.

[4] Loc. cit.

[5] J. Ind. Chem. Soc., 1, 263 (1924).

by exposure to ultra-violet light, it would seem that the ultra-violet light does not produce coagulation. Recent work of N. R. Dhar[1] shows that, broadly speaking, the action of light on colloidal solutions consists in flocculating or at least sensitising a lyophobic sol and stabilising a lyophilic sol.

The lowering of surface tension of mercury by the addition of Na observed by F. Schmidt,[2] and later confirmed by our observations on the electrocapillary curves for N $NaNO_3$ against Hg, is also relevant. If the system Na-Hg is assumed to be colloidal it cannot be of a lyophobic type for in such systems the surface tension of a sol does not differ much from that of the dispersion medium, but in lyophilic systems there can be a change in the value of the surface tension of the dispersion medium due to the presence of the disperse phase. Thus the observed lowering of the surface-tension of mercury by the addition of sodium indicates that the system Na-Hg is lyophilic or solutoidal.

The increase in viscosity with increase in Na-concentration observed by Bhave[3] is strikingly similar to the increase in viscosity with increase in gelatine concentration observed in the preparation of gelatine sols which are extremely lyophilic.

Thus it is seen that the available data obtained from the study of electrical conductivity, surface-tension and viscosity together with the other properties discussed support the conclusion that the system Na-Hg is a *Lyophilic Dispersoid System* with Hg as the *Dispersion Medium*, Na the *Disperse Phase* and $(Na_x)Hg_y$ the Colloid Micellae.

Super-fusion and Super-cooling observed by Vanstone

Vanstone[4] determined the F. P.'s of a number of amalgams prepared by adding required quantities of mercury to sodium contained in a tube. He started with pure Na and went on to the other end of the scale on his thermal diagram. At all concentrations he observed persistent super-fusion and super-cooling, which indicates that the F.P. of an amalgam is not definite but extends over a small range of temperature. This, according to the colloid hypothesis can be referred to the presence of a number of different micellae of the type $(Na_x)Hg_y$ —with different values for X and Y.

Arrests in Vanstone's Thermal Diagram

Again, Vanstone obtained arrests at the points of discontinuity, the number and lengths of which differed when he attempted a re-determination of a fairly wide portion of his thermal diagram. Having attributed the discontinuities in the thermal diagram to the stages of formation of different compounds or complexes, he explained the arrests as due to the presence of these compounds in polymorphic forms. Now polymorphism is due to the different

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[1] "Chemical Action of Light" (1930).

[2] Ann. Physik, (4) 39, 1108-1132 (1912).

[3] Thesis, Bombay University (1927).

[4] Loc. cit.

patterns in which molecules arrange themselves. In a similar manner the colloid hypothesis attributes the discontinuities to the sudden appearance of new phases i.e. the formation of different types of micellae with different equilibria with the inter-micellar liquid, and the arrests to the different gel-structures that might be formed during solidification, the variations being due to different rates of cooling.[1]

Uncertain Composition of the Supposed Compounds

In support of this hypothesis, it may be added, that Vanstone does not claim that the compositions of the compounds he mentions can be stated with any certainty. The indefiniteness of the compounds becomes more apparent from Table I which Vanstone himself prepared, and to which we have added the last column and the last item. It is true that some of the compounds mentioned in it are from the solid regions but the whole emphasizes the point that the compositions of these compounds are uncertain and unreliable. This, on the colloid hypothesis, can be referred to the different proportions of the different micellae, while the compositions assigned by Vanstone appear to be the average of the ratios of sodium to mercury in the several micellae.

TABLE I

Compounds found with their formulae	No. of compounds
$NaHg_5$, $NaHg_6$	2[2]
$NaHg_4$	1[3]
$NaHg_5$, $NaHg_6$	2[4]
$NaHg_5$, $NaHg_2$, $NaHg$, Na_3Hg	4[5]
$NaHg_5$, $NaHg_6$, $NaHg_2$, $NaHg$, Na_3Hg	5[6]
$NaHg_4$, $NaHg_2$, $Na_{12}Hg_{13}$, $NaHg$, Na_3Hg_2	5[7]
Na_3Hg, Na_3Hg_2, $NaHg$, Na_7Hg_8, $NaHg_2$, $NaHg_4$	6[8]

The Crystalline Nature exhibited by Vanstone Micrographs

Vanstone's micrographs cannot be cited as an argument against this hypothesis, for the crystalline structures visible therein are not excluded from the broader view of colloids. In some cases it is known that the colloid state is but an intermediate state between molecularly disperse sols and crystalline precipitates. Indeed, with metal-metal sols, especially when they are solidified, flakes with crystalline appearance are to be expected.

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[1] Cf. Freundlich: pp. 613-614.

[2] Berthelot: Ann. Chim. Phys., (5), 18, 442 (1879).

[3] Guntz and Féree: Compt. rend., 131, 182 (1900).

[4] Kerp and Böttger: Z. anorg. Chem., 25, 1 (1901).

[5] Maey: Z. anorg. Chem., 29, 119 (1899).

[6] Kurnakow: Z. anorg. Chem., 23, 434 (1900).

[7] Schuller: Z. anorg. Chem., 40, 385 (1904).

[8] Vanstone: Trans. Faraday Soc., 6, 42 (1911).

Curves for Other Properties

Similar remarks are applicable to all the curves obtained by several workers for different physical properties where maxima, minima and discontinuities are obtained. At maxima and minima, especially when they are flat, the colloid hypothesis assumes that the micellae-inter-micellar liquid equilibria are stable over fairly wide ranges of concentrations and that at abrupt discontinuities they are rather unstable. These equilibria depend largely on the method of preparation of the different amalgams.

Derivations from the Law of Mixtures observed by T. W. Richards

T. W. Richards[1] measured the E.M.F.'s of many concentration cells of liquid Na-amalgams and found that there were considerable deviations from the simple concentration law which holds for true solutions. But, if the system Na-Hg is colloidal, the deviations are to be expected rather than to be treated merely as experimental errors.

Richards also found that the heats of transfer of Na from one amalgam to another calculated by the Helmholtz equation are unusually large. This is not anomalous if the amalgams are colloidal solutions of sodium in mercury.

Change in Viscosity with Time

There is one other phenomenon that can be explained only by the colloid hypothesis. R. V. Barave[2] observed that the viscosity of dilute liquid amalgams of Na decreases with time and that mere mechanical agitation is sufficient to restore the initial values. His results correct up to 1% for two different amalgams are as follows:

TABLE II

Time	For amalgam A	For amalgam B
1st day	0.01906	0.02757
2nd day	0.01744	0.02151
3rd day	0.01626	0.01669
	After shaking on the third day	
	0.01906	0.02760

Thinking that the lowering of viscosity was due possibly to the separation of sodium from the amalgams, he prepared a large quantity of another amalgam and took only a part of it in his viscometer and measured its viscosity from day to day and found similar changes. If sodium was separating, day to day, from the amalgam the initial viscosity of the stored portion which was kept undisturbed for about four days should have been less than the initial value found for the first portion. Actually the initial viscosity of the second portion was if anything greater than that for the first portion. This means that no sodium had separated and that the regaining of the starting

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[1] J. Am. Chem. Soc., **44**, 601 (1922).

[2] Private communication from this laboratory (1928).

value was due to the mechanical agitation the amalgam suffered during its fall into the viscometer. The results of these experiments were as follows:

TABLE III

Time	For amalgam first used	For stored amalgam
1st day	0.01846	0.01887
2nd day	0.01625	0.01699
3rd day	0.01560	0.01539
	On shaking	
	0.01850	0.01885

These results show clearly that without there being any separation of sodium, the viscosity of an amalgam suffers a decrease with time. Woudstra[1] during his coagulation experiments observed a similar decrease in viscosity with time for his silver sols prepared by Wöhler and Muthmann's method. This according to him was due to the coarsening of the colloid particles before complete coagulation occurred. That with the increase in the size of the particles of a sol the viscosity must fall can be seen from v. Smoluchowski's equation.

This deduction has also been confirmed by Odén[2] from his experiments on sulphur sols, which were completely lyophilic.

Thus the lowering of viscosity of an amalgam observed by Barave is to be referred to the gradual coarsening of the colloid particles which occurs during the ageing of lyophilic sols, and the regaining of the initial or higher value by mechanical agitation to the restoration of the original or greater degree of dispersity. This means that together with the concentration of sodium and the method of preparation, the age and the previous history of an amalgam must be stated if the knowledge about it is to be complete.

Scum Formation

Finally there remains to discuss the phenomenon of scum-formation which has been observed even when the amalgams are kept in an inert atmosphere, e.g. pure dry nitrogen. Up to the present this has been regarded as due to the formation of oxide films. We have taken pains to ensure the complete absence of oxygen and we find that the scum-formation still continues. In the light of the colloid hypothesis, we think that the phenomenon is to be referred to the adsorption of the colloid micellae into the surface which takes place according to Gibbs' law. When the concentration of the disperse phase in the surface layer reaches the appropriate value, coagulation takes place with the formation of solid incrustations. This adsorption reaches equilibrium more quickly with lyophobic than with lyophilic sols. Further experiments in this direction are in progress in this laboratory.

Thus from all that has been said it may safely be concluded that liquid sodium amalgams are lyophilic or hydrargyrophilic sols of sodium in mercury.

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[1] Z. physik. Chem., 63, 619 (1908).

[2] "Der kolloide Schwefel," p. 102 et seq.

Our thanks are due to Dr. T. S. Wheeler, Principal of this Institute, for the interest he took in the preparation of this paper and to Dr. Mata Prasad, who so willingly helped us in the course of the discussions.

Summary

1. The considerations of colloid chemistry are applied to the data available on liquid sodium amalgams and it is attempted to show that, unlike the older theories, the colloid hypothesis explains all those results satisfactorily.

2. In the light of this hypothesis it is concluded, (i) that the liquid sodium amalgams are hydrargyrophilic colloidal solutions of sodium in mercury with $(Na_x)Hg_y$ as the colloid micellae, (ii) and that a mere statement of the concentration of an amalgam is not sufficient to define it; the method of preparation, the age and the previous history also must be stated with it.

Physical Laboratory,
Royal Institute of Science,
Bombay.
March 10, 1932.

VARIATIONS IN EXTINCTION COEFFICIENTS DURING THE COURSE OF JELLY FORMATION

BY SATYA PRAKASH

In previous publications[1] from these laboratories, the details of the methods of preparation of various inorganic jellies have been given. We have also investigated the changes in viscosity and hydrogen ion concentrations during the process of jelly formation.[2] In a number of cases, the phenomenon of syneresis has also been studied.[3] Quantitative experiments have also been made regarding the thixotropic behaviour of thorium jellies.[4] The influence of organic substances on the setting of various jellies has also been investigated.[5] On the basis of these results, the mechanism of the formation of jellies has also been advanced, and the views have been applied to explain the nature of the clotting of blood[6] and gelatinisation of serum.[7]

In the present communication, I am recording my observations on the variations of extinction coefficients during the gelation of the following substances:

Thorium arsenate
Stannic arsenate
Stannic phosphate
Mercuri-sulphosalicylic acid
Zirconium molybdate
Zirconium borate
Ceric arsenate
Zirconium hydroxide
Ferric molybdate
Thorium molybdate
Aluminium hydroxide
Ferric hydroxide
Chromic hydroxide

The extinction coefficients were measured by a Nutting's spectrophotometer. The jelly forming mixture was placed in a cell 1 cm. thick. The percentage transmission of light at various stages was calculated from the extinction coefficient data. The results are recorded in the following tables.

Thorium Arsenate Jelly

10 c.c. of thorium nitrate solution, containing 12.035 gm. of the salt in 250 c.c., were mixed with 0.9 c.c. of 18% potassium arsenate solution. The total volume was made up to 12 c.c. by the addition of water. The mixture set to a jelly in the course of 20 minutes. The extinction coefficients were measured in green region (5400 Å).

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[1] Prakash and Dhar: J. Indian Chem. Soc., 6, 587 (1929); 7, 367, 591 (1930).
[2] Prakash and Dhar: J. Indian Chem. Soc., 6, 391 (1929).
[3] J. Indian Chem. Soc., 7, 417 (1930).
[4] Prakash and Biswas: J. Indian Chem. Soc., 8 (1931).
[5] Z. anorg. Chem., 201 (1931).
[6] Prakash and Dhar: J. Phys. Chem., 33, 459 (1929); 35, 629 (1931).
[7] Prakash and Dhar: J. Indian Chem. Soc., 7, 723 (1930).

TABLE I

Time in minutes	Extinction coefficient	% Transmission
0	0.18	66.07
6.5	0.20	63.01
12	0.26	54.95
19	0.33	46.77
Set to a jelly		
30	0.40	39.8
45	0.51	30.88
60	0.65	22.39
75	0.72	19.05
90	0.86	13.8
150	0.90	12.5
22 hours	1.51	3.09

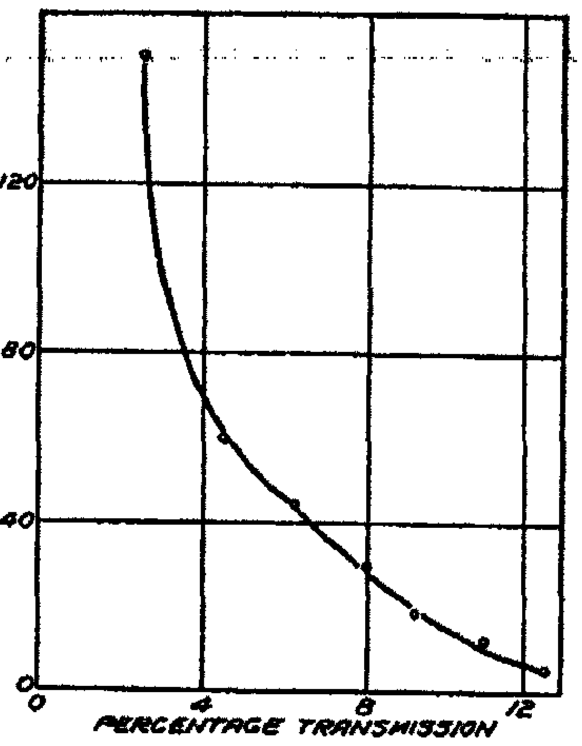

FIG. 1
Thorium Arsenate Jelly (Table I).

When the percentage of transmission of light is plotted against time (Fig. 1), a regular curve is obtained. The curve does not break even at the point of setting. The freshly formed jelly transmits as much as 46% of the incident light but becomes more opalescent on ageing.

Stannic Arsenate Jelly

10 c.c. of M/27.2 stannic chloride solution were mixed with 1.3 c.c. 18% potassium arsenate, and the total volume was made up to 12 c.c. A clear transparent solution was obtained which developed opalescence on standing and finally, set to a jelly in 7 minutes. The extinction coefficients were measured in region 5400 Å.

TABLE II

Time	Extinction coefficient	% transmission
39 sec.	0.07	85.1
2 min. 30 sec.	0.17	67.6
3 min. 30 sec.	0.29	40.6
4 min. 30 sec.	0.56	27.6
5 min. 30 sec.	0.93	11.8
6 min. 15 sec.	1.29	5.13
7 min.	1.73	1.86
Set to a jelly		
8 min.	2.33	0.468
9 min.	2.93	0.118
9 min. 40 sec.	4.00	0.01
10 min.	∞	0

The results show that the opacity increases very rapidly. The jelly is not completely opaque at the time of setting and transmits 1.86% of the incident light, but in the course of the next three minutes, it becomes opaque.

Stannic Phosphate Jelly

To 10 c.c. of M/27.2 stannic chloride were added 2 c.c. of 11% potassium phosphate solution. The mixture set to a jelly in the course of 8 minutes. The extinction coefficients were measured in the region 5400 Å.

TABLE III

Time in minutes	Extinction coefficient	% Transmission
1	0.02	95.5
3	0.08	83.2
5	0.16	69.2
7	0.4	39.8
8	0.72	19.05
Set to a jelly		
9	1.14	7.25
10	2.15	0.56
11	∞	0

At the point of setting, the jelly transmits 19% of the incident light, but it becomes completely opaque on standing for another 3 minutes.

Mercuri-sulphosalicylic Acid Jelly

When 10 c.c. of 1% mercuri-sulphosalicylic acid solution are mixed with 1 c.c. of N/2 potassium sulphate, the mixture sets to a jelly in 50 minutes and the freshly formed jelly transmits as much as 68% of the incident light. The opacity does not rapidly increase with time. However, if the jelly is prepared by the addition of a larger quantity of potassium sulphate, the jelly is more opaque at the point of setting and develops marked opalescence on standing. 1.0 c.c. of N-potassium sulphate was added to 10 c.c. of 1% mercuri-sulphosalicylic acid. The mixture set to a jelly in 1 minute. The extinction coefficients were measured in the region 5400 Å.

TABLE IV

Time in minutes	Extinction coefficient	% Transmission
15 sec.	0.49	32.4
Set to a jelly		
2 min.	0.56	27.6
6	0.62	24.0
12	0.67	21.4
35	0.75	17.8
60	0.77	17.0

Zirconium Molybdate Jelly

The zirconium molybdate sol was prepared by dialysing a mixture of zirconium nitrate and potassium molybdate for 5 days. Concentration of the sol was 14.48 gm. zirconium molybdate per litre.

To 10 c.c. of the sol, were added 1.2 c.c. of N/20 potassium chloride and the total volume was made up to 15 c.c. by the addition of water. The mixture set to a jelly in 9 minutes. The absorption was observed in the region 5400 Å.

These observations (Table V) show that a slight opalescence is developed when the sol is coagulated by potassium chloride. We have observed that if potassium sulphate were used as a coagulant, there is no appearance of the opalescence in the jelly.[1]

TABLE V

Time in minutes	Extinction coefficient	% Transmission
1	0.15	70.8
3	0.15	70.8
5	0.15	70.8
9	0.16	69.2
Set to a jelly		
15	0.16	69.2
33	0.19	64.6
90	0.21	61.7
120	0.21	61.7

Zirconium Borate Jelly

The zirconium borate sol was prepared by dialysing a mixture of zirconium nitrate and borax solutions for four days. Concentration of the sol was 24.72 gm. zirconium borate per litre.

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[1] Cf. Prakash and Dhar: J. Indian Chem. Soc., 7, 367 (1930).

10 c.c. of this sol were mixed with 1 c.c. of N-potassium chloride and 1 c.c. of water. The sol set to a jelly in 2½ minutes. The extinction coefficients were measured in the region 5400 Å.

TABLE VI

Time	Extinction coefficient	% Transmission
1 min.	0.04	91.2
1 min. 40 sec.	0.19	64.6
2 min. 30 sec.	0.21	61.7
Set to a jelly		
5 min.	0.21	61.7
7 min.	0.22	60.3
8 min.	0.24	57.5
16 min.	0.27	53.7
30 min.	0.29	51.3

When the sol is coagulated by potassium sulphate instead of potassium chloride, the jelly is quite transparent and does not show marked variations in the extinction coefficients during or after gelation.

Ceric Arsenate Jelly

0.5 c.c. of 18% potassium arsenate solution was mixed with 10 c.c. of 10% ceric ammonium nitrate, containing 30.74 gm. CeO_2 per litre and the total volume was made 11 c.c. by the addition of water. A clear yellow solution was obtained which developed opalescence and finally, set to a jelly in the course of 10 minutes. The extinction coefficients were measured in the region 5400 Å.

TABLE VII

Time in minutes	Extinction coefficient	% Transmission
1	0.20	63.1
2	0.39	40.7
3	0.46	34.7
5	0.74	18.2
8	1.14	7.25
9	1.52	3.02
Set to a jelly		
11	1.82	1.51
13	2.22	0.603
17	2.42	0.380
19	2.62	0.240
21	3.32	0.0479
23	∞	0

It will be seen from these results that the freshly formed jelly transmits about 2.2% of the incident light, but becomes completely opaque in another 13 minutes after setting.

Zirconium Hydroxide Jelly

When sodium acetate is added to zirconium nitrate solution, a clear mixture is obtained which soon develops opalescence and the mixture finally sets to a jelly. To 10 c.c. of zirconium nitrate solution, containing 16.93 gm. of the salt in 250 c.c., were added 1.8 c.c. of 3.84 N sodium acetate and the total volume was made up to 12 c.c. by the addition of water. The mixture set to a jelly in the course of 12 minutes. The absorption was studied in the region 5400 Å.

TABLE VIII

Time in minutes	Extinction coefficient	% Transmission
0.5	0.08	83.2
2.5	0.28	52.5
5.5	0.74	18.2
7.5	1.06	8.71
9.5	1.36	4.36
Set to a jelly		
12.5	1.81	1.55
17	2.56	0.276
23	3.66	0.0219
27	4.0	0.01
30	∞	0

The freshly formed jelly transmits 1.6% of the incident light, but it becomes completely opaque on further standing.

Ferric Molybdate Jelly

To 10 c.c. of 0.929 M ferric chloride were added 5 c.c. of 15% potassium molybdate solution. The mixture was shaken well for 2 minutes, and then filtered. The clean solution set to a jelly in the course of 24 hours. The extinction coefficients were observed in the red region (6500 Å).

TABLE IX

Time in minutes	Extinction coefficient	% Transmission
9	0.82	15.1
35	1.34	4.57
50	1.52	3.02
80	1.82	1.51
110	2.17	0.676
140	2.62	0.240
170	3.02	0.0955
200	3.07	0.0851
260	4.0	0.01
320	∞	0
26 hrs. set to a jelly		

These observations show that much before setting of the jelly, the mixture becomes completely opaque.

Thorium Molybdate Jelly

It has already been shown that the thorium arsenate jelly exhibits marked change in extinction coefficients during and after gelation. Thorium phosphate jellies are perfectly transparent and show only a slight opalescence when preserved for more than 6 months.

Thorium molybdate jelly was prepared by adding 1.4 c.c. of 4.5% potassium molybdate solution to 10 c.c. of thorium nitrate solution containing 12.035 gm. of the salt per 250 c.c. The total volume was made up to 12 c.c. When the solutions were mixed together, the thorium molybdate was thrown down as a white precipitate, which slowly dissolved on shaking. The mixture was shaken for two minutes and the extinction coefficients were taken in the region 5400 Å. The mixture set to a jelly in one hour.

TABLE X

Time in minutes	Extinction coefficient	% Transmission
2.5	0.31	49
4	0.28	52.2
5	0.21	61.7
7	0.18	66.1
11	0.16	69.2
14	0.14	72.5
60	0.14	72.5
Set to a jelly		
90	0.14	72.5
150	0.14	72.5

The fall, in the extinction coefficient in the beginning is due to the fact that thorium molybdate which is thrown down in the form of precipitate is only slowly peptised by the thorium nitrate present in excess. After 12 minutes, there appears to be no change in the extinction coefficients either before or after setting of the jelly.

Aluminium Hydroxide Jelly

The hydroxide jellies were prepared as described in a previous communication.[1] The following solutions were mixed, shaken and filtered:

M/2 aluminium nitrate	4.0 c.c.
3.84 N sodium acetate	2.0 c.c.
2 M ammonium sulphate	2.2 c.c.
4.92 N ammonium	0.8 c.c.

Total volume = 10 c.c. Time of setting = 4½ hours

Extinction coefficients were taken in the region 5400 Å.

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[1] Prakash and Dhar: J. Indian Chem. Soc., 7, 591 (1930).

TABLE XI

Time in minutes	Extinction coefficient	% Transmission
7	0.03	93.3
40	0.03	93.3
85	0.035	92.3
135	0.05	89.1
185	0.33	46.8
205	0.45	35.5
222	0.59	25.7
239	0.77	17.0
260	0.90	12.6
275	0.96	10.95
Set to a jelly		
290	1.05	8.91
317	1.09	8.13
335	1.17	6.76
24 hours	1.61	2.46

It will be seen from these observations that the freshly formed jelly transmits about 11% of the incident light, but the opacity continually increases after setting also, but the jelly does not become completely opaque.

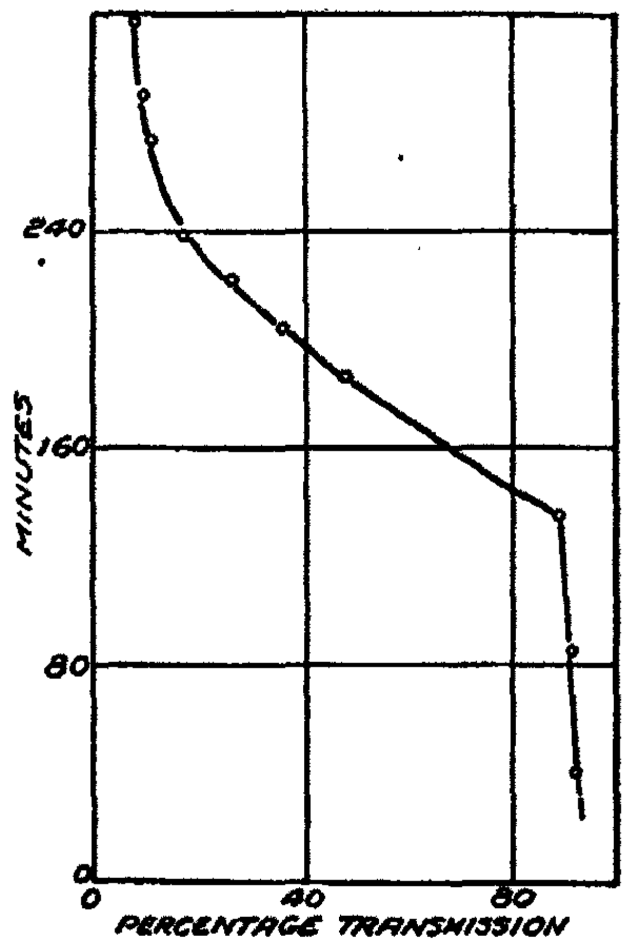

FIG. 2
Aluminum Hydroxide Jelly (Table XI)

When percentage transmission is plotted against time, two definite stages are observed (Fig. 2). For the first 135 minutes, the transparency almost remains constant, but afterwards, a regular steep curve is obtained.

Ferric Hydroxide Jelly

The following solutions were mixed for this jelly:

M/2 ferric chloride	4 c.c.
3.84 N sodium acetate	2.6 c.c.
2 M ammonium sulphate	1.6 .c.c
4.92 N ammonia	0.2 c.c.

Total volume = 10 c.c. Time of setting = 31 hours

Extinction coefficients were studied in the region 6500 Å.

TABLE XII

Time in minutes	Extinction coefficient	% Transmission
4	0.48	33.1
34	0.49	32.4
102	0.51	30.9
224	0.67	21.4
254	0.82	15.1
284	1.12	7.59
314	1.32	4.79
344	1.62	2.40
449	2.12	0.76
525	∞	0
31 hours	Set to a jelly	

The results show that ferric hydroxide jelly becomes completely opaque much before setting.

Chromic Hydroxide Jelly

To 2 c.c. of M/2 chromic chloride solution were added 2.5 c.c. of 3.84 N sodium acetate and 2.5 c.c. of 2 M ammonium sulphate. The mixture was

TABLE XIII

Time	Extinction coefficient	% Transmission
0	0.92	12
4 hours	0.92	12
7 hours	0.92	12
8 hrs. 50 min.	1.40	3.98
10 hr. 15 min.	1.47	3.39
11 hr. 20 min.	1.52	3.02
12 hr.	1.67	2.14
13 hrs.	1.77	1.7
Set to a jelly		
14 hrs.	1.82	1.51
14 hr. 15 min.	1.87	1.35
14 hr. 30 min.	1.92	1.2
24 hr.	∞	0

allowed to stand for one hour, and then, 3.25 c.c. of 4.92 N ammonia were added to it. The total volume was made up to 10 c.c. The mixture set to a jelly in the course of 13½ hours. Extinction coefficients were taken in the region 5500 Å.

From these results, it will be seen that at the point of setting, 1.6% of the light in the region investigated is transmitted, but the jelly becomes completely opaque within 24 hours. When higher concentrations of chromic chloride are taken, the jelly becomes opaque even before setting.

Discussion

The results recorded in the foregoing tables show that the jellies of ferric molybdate and ferric hydroxide become perfectly opaque before their setting, but the jellies of stannic arsenate, stannic phosphate, thorium arsenate, mercuri-sulphosalicylic acid (prepared by coagulating its sol) ceric arsenate, zirconium hydroxide (prepared by mixing zirconium nitrate and sodium acetate), aluminium hydroxide and chromic hydroxide transmit a portion of light when freshly prepared, but the amount of transmission gradually diminishes, as the jellies are allowed to stand for some time. Some of the jellies like stannic arsenate, stannic phosphate, zirconium hydroxide, chromic hydroxide and ceric arsenate become completely opaque sometime after their setting.

The jellies of ferric arsenate, chromium arsenate, ferric phosphate, thorium phosphate, ferric borate, zirconium borate, zirconium molybdate, vanadium pentoxide, and manganese and zinc arsenates do not show any change in extinction coefficients either before or after gelation and they are perfectly transparent.

From these observations, it will be seen that the jellies can be divided into three groups according to their transparency:

(a) Perfectly transparent jellies, which retain their transparency for a long time, e.g., vanadium pentoxide, arsenates of zinc, manganese and iron, thorium phosphate, zirconium molybdate, borate etc.

(b) Jellies opalescent at the point of setting and transmitting only a portion of light, but the opacity increasing with time, and finally, in some cases, becoming perfectly opaque, e.g., the jellies of thorium arsenate, stannic arsenate, phosphate, molybdate, tungstate etc.

(c) Clear sols developing opalescence, and finally, before or at the point of setting, becoming completely opaque, e.g., the jellies of ferric hydroxide, molybdate and tungstate, stannic hydroxide etc.

Very few sols have so far been studied spectrophotometrically, Zsigmondy,[1] Garnett,[2] Mie,[3] Westgren and Reinstötter[4] and Mukherji and Papaconstantinou[5] have studied the colour changes of gold sols during coagulation

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[1] Ann., **301**, 406 (1898).

[2] Phil. Trans., (A) **203**, 285, 402 (1904); **205**, 237 (1906).

[3] Ann. Physik, **25** (iv), 377 (1908).

[4] Z. Physik. Chem., **91**, 750 (1918).

[5] J. Chem. Soc., **117**, 1563 (1920).

and accounted them to the variations in the dimensions of the particles. Miss Roy (now Mrs. S. Dhar)[1] has studied the changes in extinction coefficients of stannic, aluminium, and thorium hydroxides and has observed that the sols exposed to light show a higher extinction coefficient than unexposed sols.

I am of the opinion that the increase in the extinction coefficients is due to the growth of particles. So long as the particles are not much larger in comparison to the wavelength of light, that is, they are in the amicronic or submicronic state, they do not place an obstacle in the path of light. But with the continued growth of particles, the optical discontinuity of the medium is manifested as opalescence or turbidity.

When transparent sols are coagulated by means of electrolytes, the charge on the particles is neutralised by the adsorption of the oppositely charged ions and in the view of Smoluchowski,[2] they tend to agglomerate together through capillary forces or forces of cohesion. As more and more of the particles adhere together, more of the opalescence appears.

From our study of jelly formation, we are led to think, that during the course of jelly formation the uncharged particles develop two tendencies side by side,—the one of agglomeration and the other of hydration. The tendency of hydration begins with the surface hydration and finally merges into the structural hydration. Similar forces of cohesion or the capillary forces which bring about the conglomeration of particles, also cause the adsorption of the solvent medium.

The agglomeration tendency of the particles causes the development of opalescence, while the hydration tendency preserves the transparency of the medium. It appears that the formation of a layer of solvent around the uncharged particles of the sol does not change the extinction coefficients.

In those jellies, where the hydration tendency is much predominant over the agglomeration tendency, no change in the extinction coefficient is expected either before or after gelation. These jellies are quite transparent at the moment of formation and can be preserved as such for a very long time.

When both the tendencies act together, the medium develops opalescence and the depth of opalescence depends upon the extent of predominance of agglomeration tendency over the hydration. So long as the two are in balance, the jellies formed are translucent, and the translucency is maintained for a long time.

In cases, where the agglomeration tendency is stronger than the hydration, and the latter is also exhibited to a marked extent, the changes in extinction coefficients with time are rapid and ultimately the opaque jellies are obtained.

In those sols, where the hydration tendency is negligible in comparison to agglomeration, the particles continually develop opalescence, and the sol may become perfectly opaque also, but it does not give a jelly, and in the end the uncharged particles conglomerate and settle down as a precipitate. These are the hydrophobic sols which exhibit the least change in viscosity during coagulation and are incapable of yielding jellies.

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[1] J. Indian Chem. Soc., 6, 431 (1929).

[2] Z. physik. Chem., 92, 129 (1917).

The two tendencies of the particles much depend upon their specific nature, the nature of the peptiser used, as well as upon the purity of the sol, that is, upon the electrolytes present in the sol in free condition. Thus, under suitable conditions, a hydrophobic sol of high purity and with a favourable peptiser may behave as hydrophilic, and the impure hydrophilic sols behave more or less as hydrophobic, they give rise to opaque jellies or sometimes amorphous precipitates too. It has been observed that the greater the purity of the sol, the more it is capable of developing hydration. Thus, with less pure sols, the jellies obtained are opalescent, while with those sols which have been dialysed for a sufficient time, transparent jellies are obtained. The electrolytes present in the impure sols help in the agglomeration of particles. This fact has been observed in the case of ferric arsenate, ferric phosphate, chromic arsenate and other jellies which are obtained by dialysis.

In the case of zirconium molybdate and zirconium borate jellies, I have observed that more transparent jellies are obtained when coagulation is affected by potassium sulphate than with potassium chloride. From this it appears that a sol may be sufficiently pure for the coagulation affected by bi-valent ions and still it may behave as a less pure sol towards the coagulation with monovalent ions. Gore and Dhar[1] have observed that comparatively impure sols give opalescent coagulum, and this is why the zirconium borate and molybdate sols yield opalescent jellies with chloride ions. However these sols behave as sufficiently pure towards sulphate ions and jellies obtained by these ions are transparent.

It has been observed in many jellies that the transparency goes on decreasing even after the setting of jellies, and no discontinuity in the graph is observed at the point of setting. This fact appears to be in contradiction to the orientation hypothesis of jelly formation, where it is presumed that a jelly is formed by an orderly grouping of the jelly forming units. It seems that jelly formation is a continuous process which begins with the gradual neutralisation of the charge on jelly forming particles with the development of the corresponding amount of hydration, so much so, that the whole of the solvent is surficially or structurally adsorbed by the particles, and is subsequently accompanied by the ageing phenomenon.

On our agglomeration-hydration hypothesis, where a jelly has been supposed to be the limiting case of highly hydrated and viscous mass, the affinity for solvent is gradually diminished as the ageing proceeds, and the tendency to agglomerate is increased. The most transparent jellies as of thorium phosphate, zirconium molybdate, ferric arsenate, etc., also develop slight opalescence when kept for about ten months. In those cases, where the agglomeration tendency is very marked, the opalescence rapidly increases after setting, and the jelly may become completely opaque a few minutes after the setting of the jelly.

It has also been observed in the case of inorganic jellies that the transparency of a jelly can easily be modified by slight alteration of conditions. A sol when coagulated with smaller quantities of electrolytes may give

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[1] J. Indian Chem. Soc., 6, 641 (1929).

perfectly transparent jellies, but when coagulated with slightly higher concentrations, will give opalescent jellies. A jelly may be transparent when coagulated by one sort of ions, but be opalescent when coagulated by other ions. Similarly, a jelly may be transparent when freshly formed, but may become opaque on ageing. In view of these facts, I am of the opinion that even such opaque bodies as blood clot and curds should also be regarded as specific cases of jellies along with the transparent jellies of soaps, gelatin, vanadium pentoxide and arsenates of zinc and manganese. In these opaque jellies the agglomeration tendency has given them the opacity and hydration tendency of the particles the structure of a jelly, and so long as the hydration is there, they cannot be separated from the class of jellies.

Summary

1. The variations in extinction coefficients during the process of jelly formation of the following substances have been investigated and the percentage of light transmitted at different intervals has been calculated: ferric, chromic, aluminium and zirconium hydroxides; thorium, stannic and ceric arsenates; stannic phosphate, thorium, ferric, and zirconium molybdates, zirconium borate and mercuri-sulpho-salicylic acid.

2. The results on extinction coefficient show that the jellies can be divided into three classes according to their transparency: (i) perfectly transparent jellies showing no variation in extinction coefficients during the course of gelation or after the setting of the jelly, (ii) the jellies opalescent at the point of setting but opacity increasing with time, and finally, in some cases, becoming completely opaque, (iii) the jellies obtained from clear sols, but becoming opaque before or at the point of setting.

3. The transparency and opacity of the jellies have been explained on the basis of hydration and agglomeration tendencies of the jelly forming particles. The hydration tendency gives rise to transparency and the growth of particles due to the agglomeration tendency gives opacity. Where the two tendencies are balanced, the translucent jellies are obtained.

4. Where the opacity increases even after the setting of the jelly, it has been observed, that the extinction coefficients vary continuously and there is no marked break in the curve at the point of setting. From this it has been concluded that the process of gelation, setting of the jelly and the subsequent ageing are all continuous.

5. With the sols of zirconium molybdate and borate, it has been shown that when they are coagulated by chloride ions the jellies are opalescent, but when by sulphate ions, the jellies are transparent.

6. The impure sols yield comparatively opaque jellies, because in that case, the agglomeration tendency of the particles is more favoured. The greater the purity of the sol, the greater will be the hydration tendency of the particles.

7. Even very transparent jellies develop slight opalescence on long standing due to the growth of particles, and decrease in the free surface and hydration.

8. It has been stated that the differentiation between jellies, gels, clots or curds on the basis of their transparency is not adequate because one and the same jelly may become opaque or transparent according to the slight alteration of conditions.

In conclusion, the author wishes to express his indebtedness to Prof. N. R. Dhar for his very kind interest and guidance in the work.

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THE EFFECT OF APPLIED VOLTAGE ON ELECTROLYSIS IN THE RESIDUAL CURRENT RANGE*

BY GLENN H. DAMON

The problem of residual currents was first thoroughly investigated by Helmholtz.[1] He concluded from his work that the maintenance of a residual current by applied voltages below the e.m.f. of decomposition of the electrolyte is due to the depolarizing effect of dissolved gases. These gases may be originally present in the solution, or they may be dissolved from the electrodes after electrolysis has begun. Either process readily accounts for a continuous current with no visible liberation of decomposition products.

Other investigators[2] have studied this problem with similar results. Diffusion was found to be one of the principal governing factors, while air dissolved in the electrolyte is of varying importance.

Bigelow[3] made a general investigation of residual currents, but some of his conclusions are based on very meagre data. Bigelow believed that the dissolved gases as well as the ions of the electrolyte were capable of conducting the electric current.

All of the investigators mentioned above carried out their experimental work under very similar conditions. The earliest investigators merely used a Daniell cell as the potential source, while the later investigators used approximately the same voltage. As a Daniell cell gives 1.08 volts, it is well below the e.m.f. of decomposition of H_2SO_4, the usual electrolyte used. Bigelow[3] reports experiments in which he varied the voltage from 0.500 volts to 1.696 volts; but as will be shown later in this paper, the procedure employed would not insure that the cell was in equilibrium at each voltage reported. This procedure tends to invalidate the results obtained.

The investigation reported in this paper was undertaken primarily with the object of determining the effect of applied voltage on the residual current. Several other variable factors which might affect the magnitude of the results were also investigated.

Experimental Procedure

The apparatus used in this investigation is shown in Fig. 1. The container (A) was a vacuum desiccator. A Cenco Hyvac pump was used, and it was found possible to evacuate the desiccator to the vapor pressure of the acid electrolyte used. The smooth platinum electrodes (B) had an area of 5.52 square centimeters each, and the distance between them was 1.8 cm. Whenever possible, electrical connections were made through mercury to eliminate

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* Contribution from the Chemical Laboratory of Michigan College of Mining and Technology, Houghton, Mich.

[1] Helmholtz: Pogg. Ann., **150**, 483 (1873).

[2] Nernst and Merriam: Z. physik. Chem., **53**, 253 (1905); Cottrell: **42**, 385 (1903).

[3] Bigelow: J. Phys. Chem., **6**, 603 (1902); **7**, 327 (1903).

contact resistance. Mercury switches[4] were generally used in place of knife-edge switches to insure reproducible contacts. The impressed voltage was determined to within 0.001 volts by means of a potentiometer. A six-volt storage battery was used as the source of potential. A Leeds and Northrup type P galvanometer was used as a micro ammeter. In the last part of the investigation, a more sensitive type R galvanometer was used. As the results on the two instruments checked satisfactorily, no attempt will be made to differentiate between the results obtained by the two instruments. As employed in this investigation the type P galvanometer was sensitive to 0.009 micro amperes. The type R galvanometer was sensitive to 0.000347 micro amperes. By use of a shunt box (D), it was possible to read currents from 0.009 micro amperes up to 7200 micro amperes. All deflections of the galvanometer were read with a telescope.

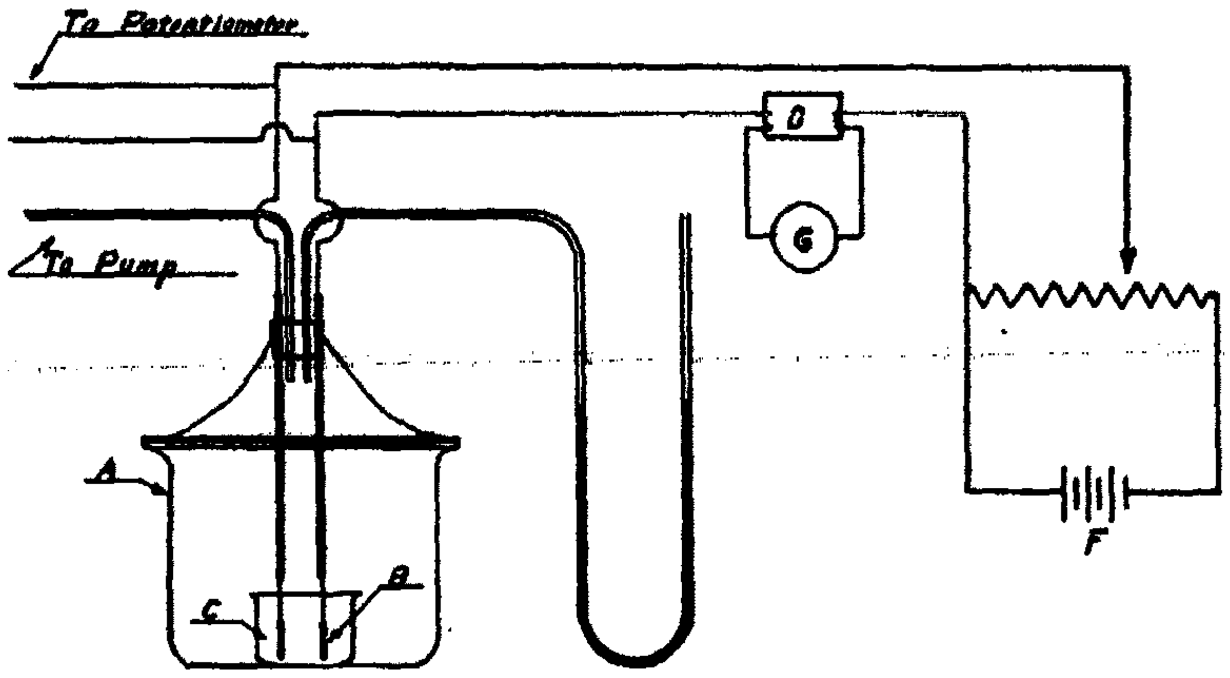

Fig. 1

In the case of all experiments performed in a vacuum, the electrolyte (C) was first boiled and then rapidly cooled before placing in the desiccator. Unless otherwise noted, the apparatus was evacuated for 30 minutes before the switch to the battery was closed; all times given are from the closing of the switch. One-tenth normal H_2SO_4 was used as the electrolyte in all experiments except where the effect of concentration was to be studied. The electrodes were thoroughly washed with distilled water and then heated to incandescence before each run. This last procedure was employed to completely depolarize[5] the electrodes.

Experimental Results

Most of the work reported in this paper was carried out under reduced pressure. The effect of voltage could have been studied at atmospheric pressure, but it was found possible to get much more consistent results in vacuum than in the air. The results in vacuum are believed to be more satisfactory as this procedure almost completely eliminates the variable factor of dissolved at-

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[4] Damon: J. Phys. Chem., 34, 2627 (1930).

[5] Langmuir: J. Am. Chem. Soc., 40, 1361 (1918).

mospheric oxygen. The difference between the residual current in air and in vacuum is shown in Fig. 2, plotted from the data of Table I. Curve 1 shows the results in air and Curve 2 shows the results in vacuum. A constant impressed e.m.f. of 0.200 volts was used in these experiments. Almost identical

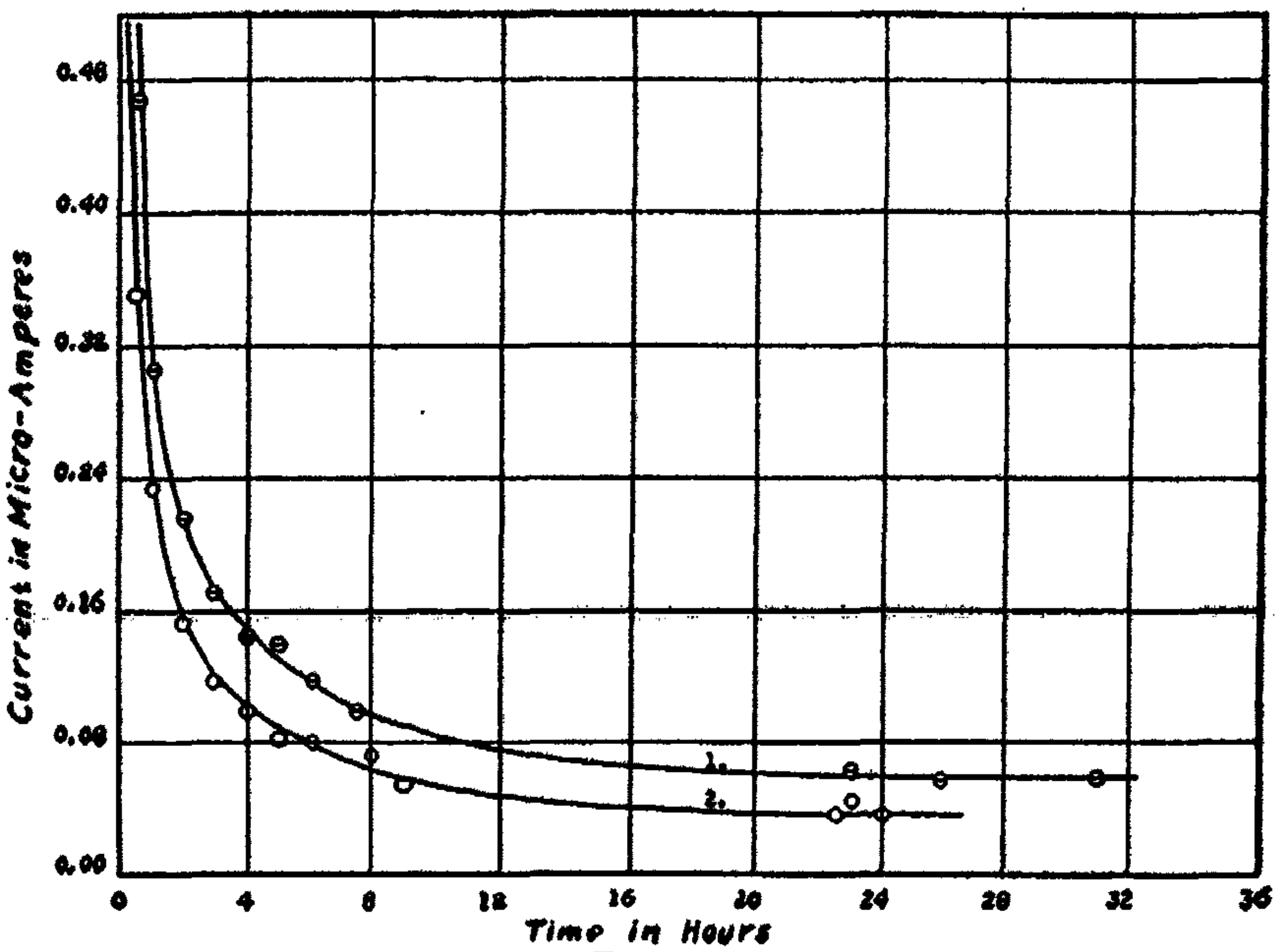

Fig. 2

Relation between Residual Current in Air and in Vacuum

TABLE I

Relation between Residual Current in Air and in Vacuum

Time	I(micro-amperes) in vacuum	I(micro-amperes) in air
½ hr	0.331	0.468
1	0.234	0.306
2	0.153	0.216
4	0.099	0.144
6	0.081	0.117
7½	—	0.099
8	0.072	—
22½	0.036	—
23	0.045	0.063
24	0.036	—
26	—	0.054
31	—	0.054

relationships were found to hold for all work performed at voltages less than 0.75 volts. For higher voltages, the residual current in the presence of air was too variable to make an accurate comparison. This factor is shown more fully in Table III.

The shape of the curves in Fig. 2 are almost identical with those given by Foerster,[6] Bigelow,[3] Helmholtz[1] and others.[2] However, the absolute value of the residual currents shown in Fig. 2 are of an entirely different order of magnitude than those reported by the above investigators. Where they report minimum currents of several micro amperes, Fig. 2 shows a minimum current of 0.036 micro amperes. This enormous difference can not be accounted for merely on the basis of differences in experimental procedure. However, the reason for this difference becomes apparent when we study the effect of applied potential on the residual current.

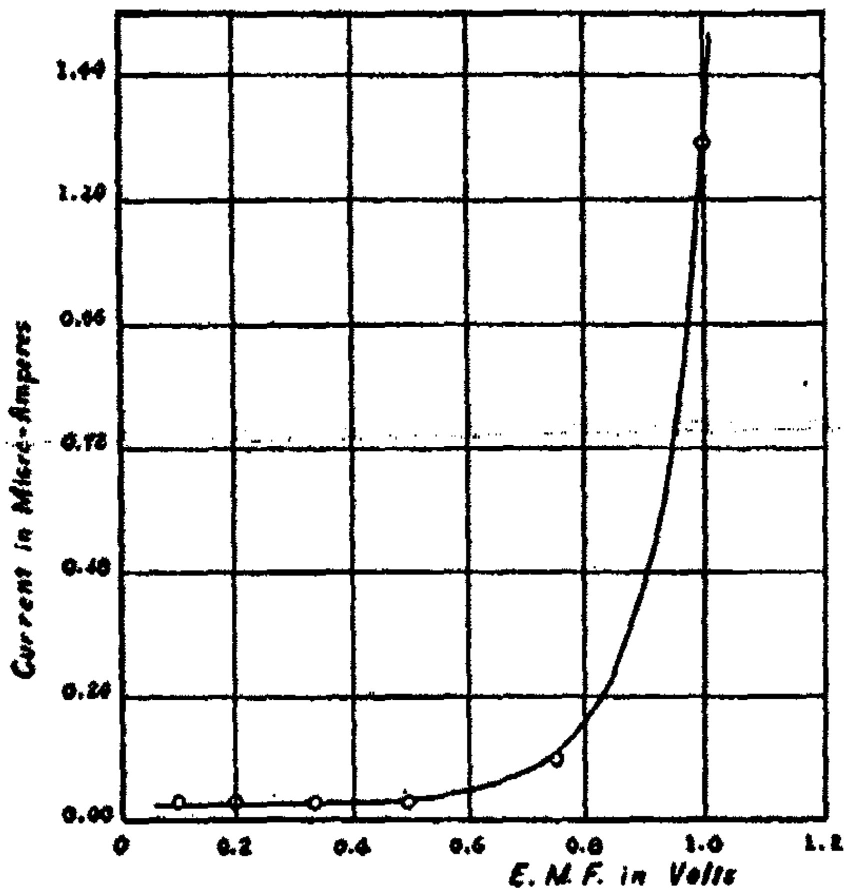

Fig. 3
Relation between E.M.F. and Residual Current

Other investigators[1,2,3] have impressed one volt or more across the electrodes of their cells. Although this voltage is well below the e.m.f. of decomposition of the electrolyte, it does not necessarily follow that the residual current is independent of the voltage. No experiments are reported by the above-mentioned investigators to show the effect of a greatly decreased potential on the residual current.

Table II

Effect of Voltage on the Residual Current

E (Volts)	No. of Runs	Ave. I (micro-amperes)	E (Volts)	No. of Runs	Ave. I (micro-amperes)
0.100	1	0.036	0.500	1	0.036
0.200	2	0.036	0.750	2	0.132
0.335	6	0.036	1.000	2	1.300

Table II and Fig. 3 show (in a summarized form) the effect of different voltages on the residual current. The electrolyte was 0.1 normal H_2SO_4.

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[6] Foerster: "Elektrochemie," 3rd Ed.

All conditions other than voltage were maintained constant as described under procedure. Each point on the curve represents the average value of the residual current at the end of 24 hours. The individual values which go to make up the average values shown were obtained by runs such as reported in Table I. These data were then plotted as shown in Fig. 2 and the value of the residual current at the end of 24 hours was determined from the graph. This procedure successfully eliminated the effect of any fluctuations which might occur at the time of reading.

The reason for running each experiment 24 hours is evident from a study of Fig. 2. During the first 10 or 12 hours, the current is decreasing very rapidly. However, at the end of 24 hours the current has become practically constant. This constant value for the residual current represents an approximate, if not a true equilibrium value. An attempt was made to obtain a curve similar to that in Fig. 3 by substituting short runs of from one to two hours for the 24 hour runs, but the results so obtained would not check for successive determinations. A fresh sample of H_2SO_4, taken from the same stock solution, was used in each determination.

The curve in Fig. 3 has two very noticeable features: (1) the almost constant value of the residual current for voltages lower than 0.75 volts; (2) the enormous increase in the residual current for voltages above 0.75 volts.

It is evident that a fundamental change takes place in the phenomena of residual currents between 0.5 volts and 1.0 volts. This conclusion is also confirmed later in Table III and Fig. 4. Evidently the difference in the magnitude of the currents reported in this paper and those reported by early investigators is due to the voltage. Fig. 3 shows that below 0.5 volts the residual current is practically independent of the applied potential. Above 0.5 volts the current is a function of the applied potential. This would seem to definitely disprove the assumption that any voltage well below the e.m.f. of decomposition could be used in residual current work.

No direct reason can be assigned for the break in the potential-residual current curve. Certainly below 0.5 volts we are dealing only with the problem of residual currents. For the higher potentials, there appear to be other effects superimposed on the residual current phenomena. These superimposed effects are apparently a function of the applied potential. An analogy between these effects and actual electrolysis would suggest a secondary decomposition point for H_2SO_4. This point is apparently very close to one volt, although there is no absolutely sharp break in the curve.

The change in the residual current with voltage might be ascribed as due to the lowering of the decomposition pressure with a decrease in pressure on the electrolyte. Wulff[7] found that the primary decomposition point of H_2SO_4 was not affected by the varying of the pressure from 0.01 atmospheres to 1000 atmospheres. Knobel[8] and also Bircher and Harkins[9] found that the overvoltage is slightly increased by a decrease in the pressure. Since the vapor

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[7] Wulff: Z. physik. Chem., **48**, 87 (1904).

[8] J. Am. Chem. Soc., **46**, 2751 (1924).

[9] J. Am. Chem. Soc., **45**, 2890 (1923).

pressure of the electrolyte used in the experiments reported was always more than 0.01 atmospheres, it is evident that the explanation can not be based on decomposition potentials.

As stated before, more satisfactory results were obtained by working in vacuum than in air. In order to compare this work with that of other workers, a comparison was made between the results in vacuum and in air for several different voltages. In Fig. 4, Curve I shows the change in residual current with voltage when the electrolyte is exposed to the atmosphere. Curve II is the same as Fig. 3 except that it is plotted on a different scale. The ratio of the residual current in air to the residual current in vacuum is shown in Table III. The results shown indicate that air has a greater effect on the residual current for high voltages than for low voltages. The data shown verify the earlier statement that the results are more consistent at low poten-

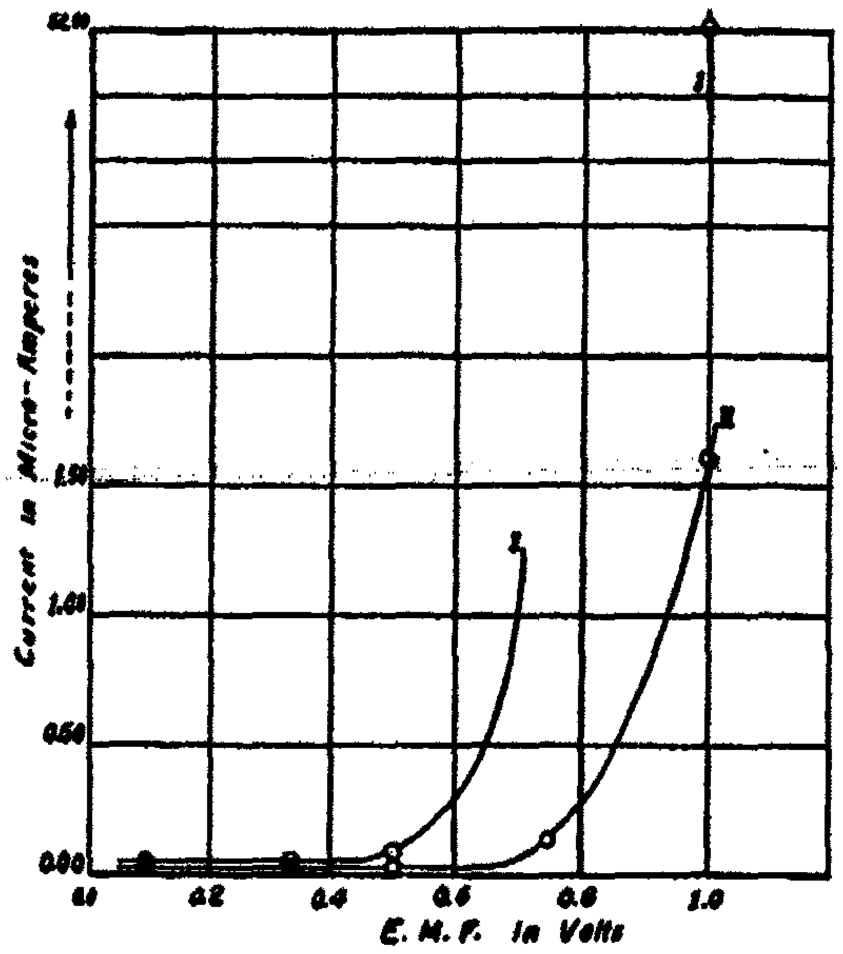

Fig. 4

TABLE III

Time in hours	E = 0.100	E = 0.200	E = 0.335	E = 0.500	E = 1.000
4	2.20	1.44	1.28	3.30	4.13
8	2.10	1.52	1.25	4.08	12.6
12	1.73	1.59	1.30	4.10	14.1
16	1.61	1.60	1.33	3.57	18.0
20	1.56	1.62	1.46	3.00	24.7
24	1.50	1.61	1.66	2.67	33.0
Average	1.78	1.56	1.38	3.45	17.7

tials than at high potentials. The data for the higher voltage scarcely warrant the calculation of an average value, but the ratio at the lower voltages is quite uniform.

Fig. 3 and Fig. 4 certainly lead to the conclusion that there is a fundamental difference in the phenomena at high and at low voltages. It is probable that at the higher voltages there is a decomposition effect superimposed on the true residual current.

The experimental work presented in this paper does not disprove the generally accepted theory of residual currents, but it does show that quantitative data on residual currents can not be obtained with potentials much above 0.50 volts. Quantitative data of previous investigators have included at least one factor other than residual current.

The author wishes to acknowledge his appreciation of the helpful suggestions given by Dr. O. P. Watts, Department of Chemical Engineering, University of Wisconsin, at whose suggestion this work was originally started.

Summary

1. Data are presented to show that the magnitude of the impressed e.m.f. has a marked effect on the magnitude of the residual current.

2. Above 0.5 volts, it is shown that the residual current is a function of the applied potential, while for low voltages the residual current is practically independent of the potential.

3. The relationship between the residual current in air and in vacuum is shown for five different potentials.

INDUCED AND PHOTOCHEMICAL OXIDATIONS AND THEIR IMPORTANCE IN BIOLOGICAL PHENOMENA

BY C. C. PALIT

We have been carrying on for the last 8 or 9 years some work on slow and induced oxidation and have studied their importance in biological phenomenon. In a series of publications[1] from this laboratory, we have emphasised the wide applicability of induced reactions and numerous reducing agents have been used as inductors. Ferrous and cerous salts and sodium sulphite are inductors which have been largely investigated. Numerous organic compounds and food materials have been oxidised simply by passing air at the ordinary temperature through solutions or suspensions of the substances in contact with freshly precipitated ferrous hydroxide or cerous hydroxide which acts as an inductor. Similar results have been obtained with sodium sulphite as inductor. We have induced the oxidation of substances like carbohydrates, fats and nitrogenous substances etc. by air at the ordinary temperature by mixing the above substances with sodium sulphite, ferrous hydroxide, cerous hydroxide and other reducing agents. The slow oxidation of these reducing agents set up the oxidation of carbohydrates, fats and proteins. We have been able to establish that induced oxidations are of general occurrence and that the mechanism of the oxidation can very well be explained.

In order to explain the mechanism[2] of these induced oxidations in the presence of ferrous and cerous salts, the formation of higher oxides like FeO_2 (Manchot[3]) and Ce_2O_6 (Job[4]) has been assumed; and these higher oxides oxidise the difficultly oxidisable substances like the food materials. Our experimental results[5] on the oxidation of sodium formate by air in presence of ferrous and cerous hydroxides lend support to the hypothesis of the intermediate formation of the higher oxides.

From our experimental results[6] on the induced oxidation of glucose by air in presence of ferrous and cerous hydroxides it will be seen that the induction factor—i.e. the ratio of the amount of oxygen taken up by glucose to the amount of oxygen taken up by inductor is as high as 8 or 9. Similar results are also obtained with other reactions. Spoehr also obtained a value as high as 15 for the induction factor. It therefore, appears that the oxidised form of the inductor viz. Fe_2O_5 or CeO_2 etc. is also capable of oxidising the acceptor, thereby regenerating the original inductor. Hence these induced reactions

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[1] Z. anorg. allgem. Chem., 122, 146 (1922); 144, 289 (1925); J. Phys. Chem., 28, 943 (1924); 29, 376, 799 (1925); 30, 939 (1926); 32, 1663 (1928); 36, 711 (1930).

[2] J. Phys. Chem., 35, 2043 (1931).

[3] Ann., 314, 177 (1899); 325, 93 (1902); 460, 179 (1927).

[4] Job: Ann. Chim. Phys., (7) 20, 207 (1900).

[5] Palit and Dhar: J. Phys. Chem., 34, 711 (1930).

[6] Palit and Dhar: J. Phys. Chem., 29, 799 (1925); 30, 937 (1926).

appear to be partly catalytic in nature but inasmuch as the rate at which the original inductor is regenerated is small as compared with the rate of its oxidation, these reactions belong more to the induced type rather than the catalytic one.

These higher values of the induction factors can be satisfactorily explained from the point of view of the generation of ions in the primary exothermal reaction. Thus for example, a small amount of an inductor is oxidised; some ions will be generated in this exothermal reaction and the ions will activate some molecules of the acceptor or the actor or both. These then will react. This reaction being exothermal will in its turn give rise to more ions which will activate some more molecules of the reactants and so on. Thus the oxidation of a small quantity of the inductor brings about the oxidation of a large amount of the acceptor, that is, the slow oxidation of the reducing agents (inductors) set up the oxidation of carbohydrates, fats, proteins and other food materials.

It is well known that the edible substances like carbohydrates, fats and proteins are very readily oxidised in the body, whereas they are oxidised with difficulty by ordinary laboratory reagents. We have carried on our experiments[1] and have been successfully able to induce in the laboratory the oxidation of edible substances like glucose, starch, milk, butter, egg-white, egg-yellow and also the oxidation of other substances like cholesterol, lecithin, glycerol, etc. at the ordinary temperature by passing a slow stream of air in presence of inductors like sodium sulphite, ferrous hydroxide, cerous hydroxide, etc.

It has also been shown[2] that not only fats but carbohydrates and nitrogenous substances are oxidised by hydrogen peroxide and a ferric salt at 37°, volatile aldehydric or ketonic compounds being formed. We[3] have conclusively proved in a systematic manner that fats, carbohydrates and nitrogenous and other organic substances can be completely oxidised into their main end products, carbon dioxide and water by air with the help of an inductor ferrous or cerous hydroxide or in presence of sunlight at the ordinary temperatures and we have thus been able to imitate successfully the physiological process of oxidation on which animal life depends. It appears, therefore, that the intermediate iron peroxide obtained in the case of hydrogen peroxide and ferric or ferrous salts must be different from that formed with ferrous compounds and oxygen, because the products of oxidation are different in the two cases.

We have also carried on investigations[4] on photochemical oxidation of each of substances investigated in connection with the slow and induced oxidations. It is interesting to note that all these substances—such as glucose, lactose, maltose, starch, glycogen, glycine, urea, glycerol, hippuric, and uric acids, formate, tartrate, stearate, oleate, etc. and complex edible sub-

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[1] J. Phys. Chem., 34, 711 (1930).

[2] J. Ind. Chem. Soc., 6, 617 (1929).

[3] J. Phys. Chem., 34, 711 (1930).

[4] Palit and Dhar: J. Phys. Chem., 32, 1263 (1928); 33, 1897 (1929); 34, 737 (1930); 34, 993 (1930); Z. anorg. allgem. Chem., 191, 150 (1930).

stances such as butter, milk, egg-white, egg-yellow, carbohydrates, etc. can be readily oxidised by passing air through them if they are exposed to sunlight without catalyst or inductor. In each of these cases, complete oxidation to carbon dioxide takes place. Even the most complex substances like butter, milk, egg-white, egg-yellow, lecithin, cholesterol, glycerol, etc. are oxidised quantitatively into carbon dioxide and water.

Our results on induced and photo-chemical oxidation of all the substances investigated conclusively prove the following facts:

Induced Oxidations

1. The oxidation of fats is retarded by carbohydrates or less powerfully by proteins and to a greater extent by a mixture of carbohydrates and proteins.
2. The oxidation of proteins is markedly retarded by carbohydrates and fats.
3. When fats are rapidly oxidised due to the absence of the negative catalyst, glucose, acetone bodies are likely to be generated in the body. Apparently the easily oxidisable carbohydrates which act as negative catalyst in the oxidation of fats are necessary for the complete combustion of fatty food materials; the oxidation of both fats and carbohydrates can go on slowly and simultaneously.

The view that diabetes is due to insufficient oxidation of glucose and fats in the animal body, has been emphasised by us in one of our previous publications.[1] In other words, the disease is caused by want of catalysts or enzymes which in normal health exist in the body and help the oxidation of glucose, fats, etc. It seems pretty certain that disappearance of acetone bodies from diabetic urine due to the injections of insulin is an effect caused by the increased oxidation of glucose in the body. We suggested in one of our publications that insulin extracts of yeast, vitamins, etc. activate the catalysts or the enzymes and consequently act as accelerators in the oxidation of glucose by air in the system. It may be that minute traces of iron or sulphur are present in insulin, extract of yeast, vitamins, etc. and that this iron present in a very reactive state, is the active substance which helps the oxidation of glucose by air. As from our researches, we find that iron is a very important catalytic agent in many oxidation reactions and that iron in some form or other is essential for life and plays an important part in the oxidation reactions in plants and animals. Hence we urge on medical people to treat diabetes by the internal use of iron salts or colloidal iron preparations which will act as an accelerator in the oxidation of glucose and fats by oxygen.

In one of our publications[2] from this laboratory it was suggested that insulin and other allied substances are good reducing agents and are readily oxidised by atmospheric oxygen and the oxidation of these substances induces the oxidation of sugar in the body. We have now been able to substantiate this view by our new sets of oxidation experiments on insulin and glucose.

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[1] Palit and Dhar: J. Phys. Chem., **32**, 1663 (1928); **31**, 1259 (1927).

[2] J. Phys. Chem., **29**, 376 (1925).

For these experiments a definite volume of air freed for carbon dioxide was passed through an aqueous solution of insulin (B.D.H.) kept at 25° and the amount of carbon dioxide obtained by oxidation of insulin was absorbed by standard barium hydroxide solution and estimated as usual. When glucose is added to the insulin solution and the same volume of air is passed through the mixture, glucose is slowly oxidised and this can be shown by estimation of glucose by Fehling's solution, which, however, cannot be reduced by insulin. In this experiment with insulin and glucose, the oxidation of insulin which is readily oxidised by air at ordinary temperature leads to the oxidation of glucose thus corroborating our previous statements.

In several publications,[1] we have emphasised the importance of induced oxidations in understanding the phenomenon of animal metabolism. It has been stated that the readily oxidisable substances like glutathionone and other substances present in muscle and in other parts of the body, are first oxidised by the inhaled oxygen and these oxidations induced the oxidation of food materials. Insulin and other internal secretions also appear to be readily oxidised in the body and these lead to the oxidation of carbohydrates, fats and proteins. It is now well-known that in the treatment of acute diabetes, repeated doses of insulin have to be injected in order to get satisfactory results. Our experiments on the oxidation of insulin by air show that it is used up by the oxidation in the body and thus repeated doses are necessary. Moreover the oxidation of insulin leads to the oxidation of glucose in the body and this explains the decrease of glucose in the diabetic blood and urine on injection of insulin.

(5) Animal life is assumed to depend essentially on the catalytic activity of the enzymes and iron in the animal body. It is likely that in the animal body, there exist readily oxidisable substances such as enzymes containing traces of iron in complex colloidal condition and the oxidation of these substances induce the oxidation of food materials.

(6) In the animal body, the iron in the blood accelerates catalytically the oxidation of food stuff by the peroxide formed in the body from the inhaled oxygen. When there is a deficiency of iron in the blood, the animal becomes anaemic. At this stage any iron salt preferably of colloidal nature taken in the body, will supply the natural deficiency and the necessary amount of oxidation will take place.

(7). We also suggest that fever is an auto-catalytic reaction. The oxidation of substances like starch, sugar, proteins, fats, etc. by oxygen in the animal body is believed to be catalytically accelerated by the parasites or secretions of bacteria. Hence the amount of heat generated in the animal body for unit time is increased and the phenomenon of fever is observed. Moreover like all other chemical changes, the amount of oxidation in the animal body for unit time is also increased by the incipient rise of temperature.

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[1] J. Phys. Chem., 35, 2043 (1931).

(8). From our quantitative experiments[1] on the oxidation of carbohydrates, glycerol, fats and proteins by air in presence of freshly precipitated ferrous and cerous hydroxides and sodium sulphate as inductors, we have shown that the amount of carbon dioxide obtained in these slow oxidations is practically the same as is expected from the point of view that the carbohydrates, glycerol, fats and nitrogenous substances are completely oxidised into carbon dioxide and water by passing air at the ordinary temperature. Similarly Spoehr has obtained considerable amounts of carbon dioxide from the induced oxidation of carbohydrate by air in presence of sodium ferrous and ferric pyro-phosphates. We are of opinion that these results are of importance because these oxidations are of the same type as those taking place in the animal body. Hence we emphasise that in normal health, the food materials taken in the body are completely oxidised into carbon dioxide and water without the formation of intermediate compounds, just as food materials are completely oxidised to carbon dioxide and water when air is passed through their solutions or suspensions in presence of inductors. Intermediate compounds are only formed in the diseased condition of the animal body.

(9) Voit stated "that the metabolism in the body was not proportional to the combustibility of the substances outside the body, but that protein which burns with difficulty outside metabolises with the greatest ease, then carbohydrates, while fat which readily burns outside is the most difficultly combustible in the body." This conclusion was arrived at by Voit from actual feeding experiments on animals. We have obtained quantitative and comparative results[2] on the velocity of oxidation of fats, proteins and carbohydrates by air and thus tried to establish whether fats or carbohydrates are oxidised more readily in the system. Our results show that the order in which they are oxidised in presence of cerous hydroxide are as follows: egg white > egg-yellow > starch > glucose > butter. In presence of cerous hydroxide, the induced oxidation of fats, nitrogenous substances and carbohydrates follows the same order as stated by Voit.

(11) The experimental results[3] show that carbohydrates, proteins, fats and other substances are oxidised in presence of inductors in neutral and alkaline solutions, and the greater the amount of alkali, the greater is the amount of oxidation. Hence we are of opinion that alkaline treatment should prove efficacious in gout, diabetes, beri-beri, rickets and other metabolism diseases, because in presence of even sodium bicarbonate, the amount of oxidation of fats, carbohydrates and nitrogenous substances is greatly increased.

Hence all these results on slow and induced oxidation of fats, nitrogenous substances and carbohydrates occurring either singly or in mixtures by air at ordinary temperature are important, because these oxidations are of the same type as those taking place in the animal body.

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[1] Palit and Dhar: J. Phys. Chem., 34, 711 (1930); and Z. anorg. allgem. Chem., 191, 150 (1930).

[2] Palit and Dhar: J. Phys. Chem., 34, 711 (1930).

[3] Palit and Dhar: J. Phys. Chem., 29, 799 (1925); 30, 939 (1926).

Photochemical Oxidation and Physiological Experiments

(1) Aqueous solutions or suspensions of the following substances have been oxidised by passing air in presence of sunlight:[1] arabinose, cane sugar, galactose, glucose, lactose, laevulose, maltose, starch, glycogen, urea, glycine, α-alanine, hippuric acid, sodium urate, potassium oxalate, sodium formate, sodium tartrate, potassium stearate, potassium oleate, potassium palmitate, lecithin, glycerol, cholesterol, butter, egg-white, egg-yellow and milk. Zinc oxide, uranium nitrate and ferric nitrate act each as a photosensitiser in the oxidation of the above substances and the amount of oxidation of these substances is greater than that in their absence.

(1) Our results[2] also show that the amount of oxidation increases with (i) the intensity of light, (ii) the amount of light falling in the solutions and (iii) the time of exposure.

(2) Dilute solutions of lactic acid, oxalic acid, tartaric acid and citric acid are appreciably oxidised by air in presence of sunlight and the order in which they are oxidised is: oxalic > lactic > tartaric > citric.

(3) In order to find out whether in presence of sunlight the carbohydrates, fats, and nitrogenous substances are oxidised completely to carbon dioxide or other intermediate products are formed, we have estimated the amount of carbon dioxide obtained in these oxidations in potash bulbs. The amount of oxidation of these substances was also, in all cases, estimated by direct analysis. The experimental results[3] show that the amount of oxidation determined from carbon dioxide obtained is practically the same as the oxidation found out from the direct analysis of the carbohydrates, fats and nitrogenous substances remaining unoxidised. Hence in presence of sunlight, different carbohydrates, fats and nitrogenous substances can be completely oxidised by air at the ordinary temperature into their main end products, carbon dioxide and water. No intermediate compounds are formed in these photochemical oxidations. We have thus been able to imitate successfully the physiological processes of oxidations on which animal life depends.

(4) Voit in his necrology of Pettenkofer writes: "that the metabolism in the body was not proportional to the combustibility of the substances outside the body, but protein which burns with difficulty outside metabolises with the greatest ease, then carbohydrates, while fat which readily burns outside is the most difficultly combustible in the body." We have tried to imitate the metabolism taking place in the animal body and have made comparative experiments[4] on the oxidation of butter, egg-white, egg-yellow, starch, glycogen, and glucose by passing air at the ordinary temperature in presence of sunlight. The following results have been obtained:

Egg-yellow	60.9%	oxidised
Egg-white	31.25%	"
Starch	38.2%	"
Butter	31.8%	"
Glucose	13.6%	"

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[1], [2] and [3] Palit and Dhar: J. Phys. Chem., 32, 1263 (1928); 34, 993 (1930); Z. anorg. allgem. Chem., 191, 150 (1930).

[4] J. Phys. Chem., 34, 993 (1930).

It appears therefore, that egg-yellow is the most easily oxidisable substance in presence of light, then come starch, egg-white, and butter, while glucose is the least oxidisable. Hence eggs which metabolise readily in the animal body, are also easily oxidised by air at the ordinary temperature in presence of sunlight.

(5) We have investigated whether the Einstein Law of Photochemical Equivalence is applicable to the photochemical oxidation of carbohydrates, fats and nitrogeneous substances in sunlight. The amount of energy absorbed by solutions of carbohydrates, fats and nitrogenous substances was measured with the help of Boys' radiomicrometer. It is interesting to note that the Einstein Law of Photochemical Equivalence is applicable to the photochemical oxidation of glucose, lactose and α-alanine by air. The law however is not applicable to the photochemical oxidation of glycine by air where about seven molecules react per quantum of light absorbed. These results show that practically colourless one percent aqueous solutions of glucose, lactose, glycine and alanine can absorb light from the sunshine falling on the solutions. This absorption of energy leads to the activation of the molecules and their consequent chemical reaction with oxygen in presence of light. When these solutions are mixed with ferric or uranium nitrate, the absorption of radiation is considerably increased and the amount of oxidation is also increased.

(6) In one of our previous publications,[1] we have shown that appreciable amounts of the compounds of the peroxide type are formed when air is passed through aqueous suspensions of cholesterol, olive oil, butter and many other substances like coconut-oil, castor oil, linseed oil, mustard oil, etc. It has been also observed that olive oil can be retained in that activated or excited state for a sufficient length of time if kept in the dark but this phenomenon was not observed in a marked degree in the case of cholesterol, as it was found to have lost its active or excited state in the course of a few days. Moreover appreciable amounts of glucose have been oxidised by mixing the solution of glucose with the exposed cholesterol, olive oil, butter, and other oils respectively, containing the peroxide compounds. Hence it is believed that the anti-rachitic and beneficial properties of substances not containing the necessary vitamins are due to the presence of peroxide, which help the oxidation of food materials in the animal body. Substances can acquire anti-rachitic properties when exposed to light only in presence of air and light.

In the light of the observations made, we can safely say that when the food materials are exposed to sunlight in presence of air, they take up oxygen forming some peroxide type of compound which can oxidise other food materials when mixed with them. Consequently the addition of the exposed substances to ordinary food stuff facilitates the proper ingestion of food materials and produce efficacious results.

(7) Sunlight and artificial lights have been used with great success in the treatment of tuberculosis, pernicious anaemia, rickets, etc. In some previous

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[1] J. Phys. Chem., 34, 737 (1930); Ind. J. Med. Research, 17, 430, 993 (1929).

publications[1] we have emphasised the importance of sunlight in the treatment of deficiency diseases and we have observed that rickets, osteomalcia, beriberi, pellagra, etc., would have been more common in poor tropical countries like India and China, had not the compensating agent—sunlight—been present. This conclusion had been corroborated by our experiments on the metabolism of animals.

(18) Having investigated the above facts on the efficacy of exposed oils in oxidising other food materials, we have carried on experiments[2] on the metabolism of pigeons and rats using these exposed and unexposed oils. Incidentally we have also investigated the influence of sunlight and small quantities of colloidal iron preparations, juice of several green leafy vegetables, tomato, etc. in the metabolism of pigeons and rats. For this, different lots of pigeons and rats were fed on polished Rangoon rice, which is believed to be entirely devoid of vitamins, for about a month. One lot had plenty of sunlight, whilst the other had very little of it. The lot which had sunshine did not show any sign of polyneuritis whilst the other lot, not having sunshine, developed stomachic troubles first and then acute form of polyneuritis, paralysis and their eyes were highly affected. All the affected pigeons were separated from the rest and kept in sunlight and fed artificially with substances rich in vitamins and containing iron in small doses. They were all finally cured and restored to normal health.

In carrying out feeding experiments upon animals, one cannot but realise that the balance between health and disease, even between life and death, is actually under control. The scales are so sensitive that they have been swayed in one direction or the other by the addition or subtraction of seemingly trifling quantities of certain food stuffs. A growing animal provided with plenty of food can be stunted at will, made to decline almost to the point of death and restored with miraculous suddenness by slight readjustment of the diet.

The experiments on the metabolism of animals were further investigated with different lots of pigeons and rats with the addition of following substances mixed with their diet. (Rangoon rice):

1. Rangoon rice and kept in sunlight, (2) Rangoon rice mixed with juice of green leafy vegetables and kept in diffused light, (3) Rangoon rice mixed with irradiated oil and kept in diffused light, (4) Rangoon rice mixed with unexposed oil and kept in diffused light, (5) Rangoon rice mixed with colloidal iron preparation and kept in diffused light, (6) Rangoon rice mixed with a little quantity of Bajra (Pennisetum typhoideum) and kept in sunlight and (7) Rangoon rice mixed with a little quantity of gram and kept in sunlight. The experiment lasted for a month. Our experimental results show[3] that animals receiving normal diet and sunshine viz. set nos. 6 and 7, keep very

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[1] J. Phys. Chem., 32, 1263 (1928); 33, 1897 (1929); Chemie der Zelle und Gewebe 12, 217, 225, 317 (1925); 13, 209 (1926).

[2] J. Phys. Chem., 32, 737 (1930); Ind. J. Med. Research, 17, 430 (1929).

[3] Palit and Dhar: J. Phys. Chem., 34, 737 (1930); Ind. J. Med. Research, 17, 430 (1929).

good health. Even if the animals do not get any vitaminous food but only sunlight, they keep good health. Of course, the animals which get irradiated oils were much better than those getting iron preparations and unexposed oils, though they were kept in darkness. Still they were getting inferior in general health to those which obtained sunlight but no vitaminous food. Hence it is found that irradiated oils are not efficacious as the vitaminous food or even as sunlight. It is also found that iron in small doses which are present in green leafy vegetables is beneficial to health. Our results also show that iron in larger doses is rather harmful to animals and cannot prevent the attack of polyneuritis. All these experiments confirm our view that sunlight acts as a promoter of oxidation of food materials in the body, and normal food with plenty of sunlight is the best for the maintenance of health. We are of opinion that in presence of sunlight the metabolism of the food materials taken in the system is accelerated and that is how the disease is avoided. We believe that by absorption of sunlight, the body cells are activated and greater amounts of oxidation of carbohydrates, fats and proteins take place than in the absence of sunlight. It seems pretty generally accepted that several diseases are caused by defective metabolism. We are of opinion that in these diseases which are caused by the want of proper metabolism, sunlight or artificial light should be highly efficacious, because as we have proved experimentally that the oxidation of fats, carbohydrates and proteins is greatly accelerated by light.

All our experiments on slow and induced oxidations as well as on photochemical oxidations are imitations of Nature's process of oxidation and throws considerable light on the processes of life phenomenon.

Further work in this line is in progress in these laboratories.

Summary

(1) An explanation for the mechanism of induced oxidation has been suggested.

(2) Carbohydrates, fats, proteins, food materials, and other organic substances have in presence of inductors been oxidised.

(3) The oxidation of fats is retarded by carbohydrates or less powerfully by proteins and to a greater extent by a mixture of proteins and carbohydrates. Also the oxidation of proteins is markedly retarded by fats and carbohydrates.

(4) The view, that diabetes is due to insufficient oxidation of glucose and fats in the body, has been corroborated by our experimental evidence on the oxidation of insulin, which go to prove that the oxidation of insulin leads to oxidation of glucose in the body. This explains the decrease of glucose in and disappearance of acetone bodies from, the diabetic blood and urine on injection of insulin.

(5) Iron in the blood accelerates catalytically the oxidation of food materials. The iron preferably of colloidal nature, when taken into the system, will supply the natural deficiency and the necessary amount of

oxidation will take place, thus showing the efficiency of the iron preparations in deficiency and metabolism diseases. An explanation that fever is an autocatalytic reaction has also been suggested.

(6) Experimental results on the estimation of carbon dioxide prove that carbohydrates, fats, proteins, and other organic substances are oxidised by air at the ordinary temperature in presence of inductor chiefly to carbon-dioxide and not to any intermediate products.

(7) Comparative experiments on the induced oxidation of fats, carbohydrates, and proteins show that in presence of inductor, the order of oxidation is the same as that obtained by Voit, the eminent physiologist.

(8) An explanation of the internal use of alkali and alkaline carbonates has been suggested based on the increased oxidation of food materials by air in presence of alkali. The alkaline treatment should prove efficacious in gout, diabetes, beri-beri, rickets and other metabolism diseases.

(9) Aqueous solutions or suspensions of the following substances have been oxidised by passing air in presence of sunlight: arabinose, cane sugar, galactose, glucose, lactose, laevulose, maltose, starch, glycogen, urea, glycerine, α-alanine, hippuric acid, sodium urate, potassium stearate, potassium oleate, potassium palmitate, potassium oxalate, sodium formate, sodium tartrate, lecithin, cholesterol, butter, milk, egg-white, egg-yellow, and dilute solutions of citric, tartaric and lactic acids. Zinc oxide, uranium nitrate and ferric nitrate act as a powerful photosensitiser in the above oxidations and in their presence the amount of oxidation in each case is greater than in their absence. Our experimental results show that the amount of oxidation increases with (a) the intensity of light, (b) the amount of light falling on the solutions, and (c) the time of exposure.

(10) Experimental results on the estimation of carbon dioxide prove that carbohydrates, fats, proteins, food materials, cholestrol, lecithin etc. are oxidised by air in presence of sunlight chiefly to carbon dioxide and not to any intermediate product.

(11) Comparative experiments show that order in which the food materials are oxidised in presence of sunlight is as follows: egg-yellow > starch > egg-white > butter > glucose.

(12) The Einstein Law of Photochemical Equivalence is approximately applicable to the photochemical oxidations of glucose, lactose and alanine by air.

(13) Experimental results show that appreciable amounts of the compounds of the peroxide type are formed when air is passed through aqueous suspensions of cholesterol, butter, olive, coconut, mustard, castor, and linseed oils and some carbohydrates. These peroxides have been estimated by the amount of iodine liberated by them from an acid solution of potassium iodide. Moreover appreciable amounts of glucose have been oxidised by mixing the solution of glucose with the exposed substances containing the peroxide compound. Hence it is believed that the anti-rachitic and beneficial properties of substances not containing the necessary vitamins are due to the presence of peroxides which help the oxidation of food materials in the animal body.

(14) From the experiments on metabolism of animals, we have proved that sunlight is the best preventive for disease like polyneuritis, beri-beri, rickets, etc. Olive oil exposed to sunlight and air comes on close second, whereas iron and unexposed oils are harmful to animals. The natural food with plenty of sunlight seems to be the best kind of diet for the maintenance of health. In tropical countries, many deficiency diseases are avoided due to sunlight. Hence sunlight and other kinds of artificial lights prove efficacious in this treatment of diseases specially of metabolic origin.

(15) These results (induced and photochemical oxidations) are very important, because these oxidations are of the same type as those taking place in the animal body. The experiments in this investigation are in reality imitations of Nature's process of oxidation of food materials in the animal body.

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August 27, 1931.

SOLUBILITY OF SUCCINIC ACID IN BINARY MIXTURES

BY WILDER D. BANCROFT AND F. J. C. BUTLER

Many cases are known of a maximum solubility of a solid in some mixture of two consolute liquids.[1] Holleman and Antusch consider the possible explanations for aqueous alcohol to be: the formation of alcohol hydrates in solution; the formation of complex molecules of the solute in solution; the formation of a compound between solvent and solute. There is no evidence for the existence of alcohol hydrates in solution. If this is the sole cause of the abnormality, the position of the maximum must be independent of the temperature. While the absolute amount of the hypothetical compound will vary with the temperature, the percentage composition at which there is a maximum formation of the compound at any temperature will be independent of the temperature.

We have made a study of the behavior of succinic acid, substituting mass concentrations for the volume concentration used by Herz and Knoch. At 20° they found the maximum solubility at about 35% by weight of water; we find it at about 45% by weight at 40°. Seidell found that the position of maximum solubility of acetanilide in aqueous alcohol was displaced by change of temperature. In these two cases there is therefore no justification in assuming that a compound of acetone and water or of alcohol and water plays any important part. This is what one would have expected anyway from the partial pressure curves of aqueous acetone and aqueous alcohol. There is no evidence from these of any appreciable amount of any hydrate being formed.

There is no evidence for the existence of any appreciable amounts in solution of any compound between succinic acid and water or acetone though the non-existence of such compounds has not been proved. Nobody has even made an attempt to show how the maximum solubility of succinic acid in aqueous acetone could be accounted for on the assumption of polymerization or depolymerization of succinic acid. The explanations suggested by Holleman and Antusch seem therefore to be inadequate.

There is one other factor that has not yet received adequate consideration, namely reversible polymerization and depolymerization of either or both of the solvents. If succinic acid is more or less soluble in monomolecular water than in polymolecular water, the solvent action of the water will change with changing concentration of the water.

Experiments were made on the solubility of succinic acid in binary mixtures of methyl, ethyl and propyl alcohols. The data are shown graphically in Fig. 1. The solubility curves are so near straight lines that any variation from them

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[1] Cf. Holleman and Antusch: Rec. Trav. chim., **13**, 277 (1894); Herz and Knoch: Z. anorg. Chem., **41**, 315 (1904); **45**, 262; **46**, 193 (1905); Seidell: J. Am. Chem. Soc., **29**, 1088 (1907); Dehn: **39**, 1399 (1917); Highfield: Trans. Faraday Soc., **22**, 57 (1926); Disselkamp: Z. physik. Chem., **123**, 99 (1926); Angelescu and Dumitrescu: **132**, 217 (1928); Wilson and Wright: J. Chem. Soc., **1928**, 3111; Duff: **1931**, 881, 1196.

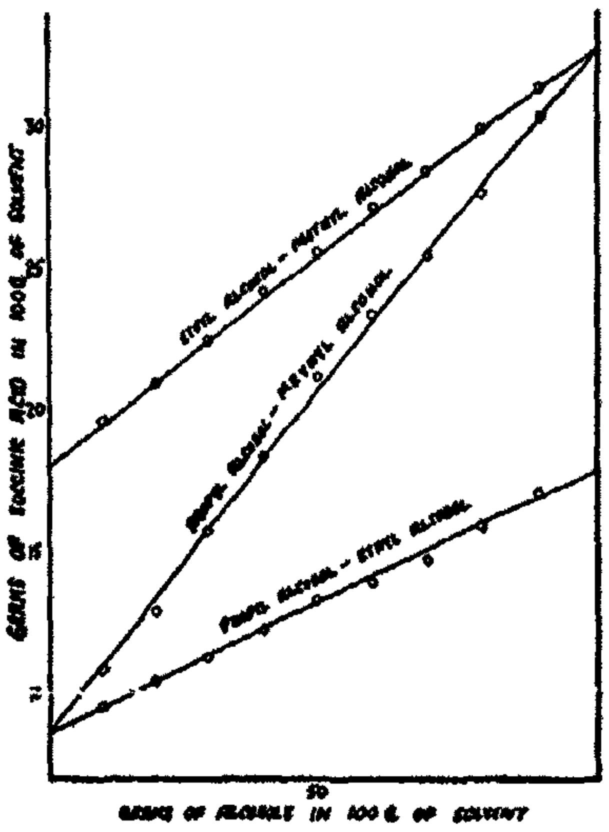

Fig. 1

can be disregarded for the time being. In terms of our hypothesis this means that there is practically no change in solubility of succinic acid with changing polymerization of the alcohols.

Similar data for water with acetone, methyl alcohol, ethyl alcohol, and propyl alcohol are shown graphically in Fig. 2. In all cases there is a maximum solubility and this maximum solubility was predicted from the experiments of Herz and Knoch with aqueous acetone. It seemed probable that other acids of the same type would behave similarly and in Fig. 3 are given the data for adipic acid for water with acetone, methyl alcohol and ethyl alcohol at 40°. In each of the three cases there is a maximum solubility as expected. As might also have been expected there is less of a maximum relatively with aqueous methyl alcohol than with the other pairs of liquids because the relative effect ascribed to monomolecular water will be less the greater the solubility in the organic liquid.

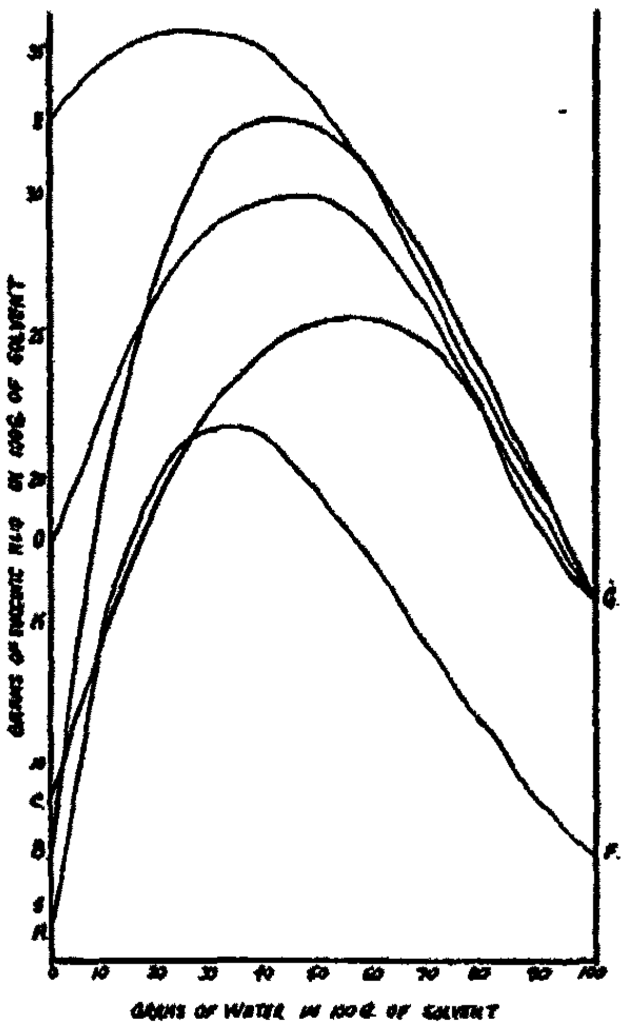

Fig. 2

AF:—Aqueous acetone at 20°
BG:—Aqueous acetone at 40°
CG:—Aqueous propyl alcohol at 40°
DG:—Aqueous ethyl alcohol at 40°
EG:—Aqueous methyl alcohol at 40°

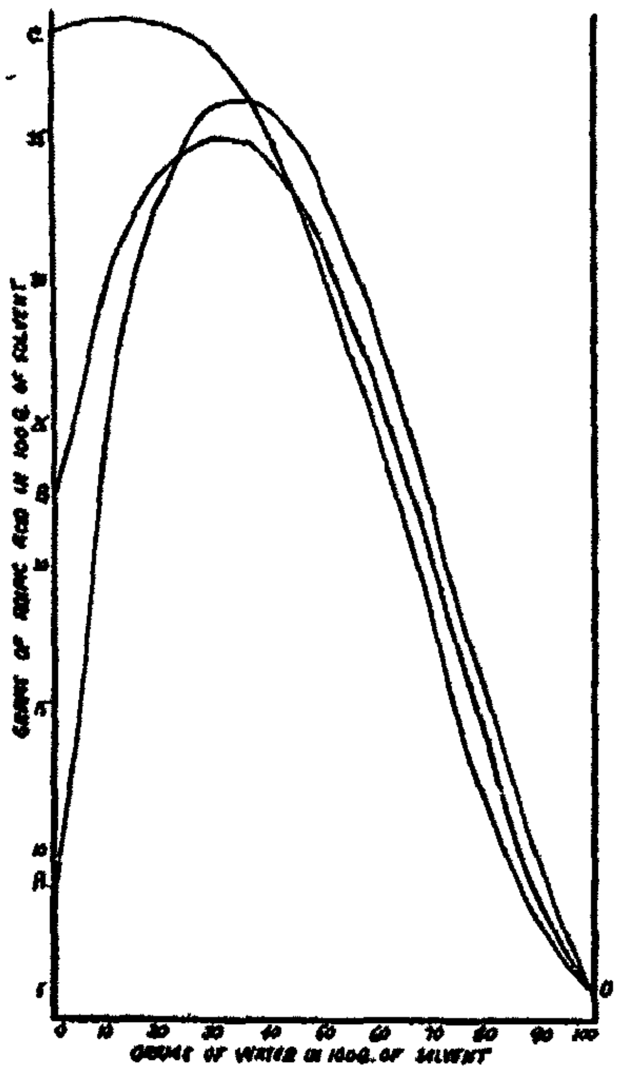

Fig. 3

AD:—Aqueous acetone at 40°
BD:—Aqueous ethyl alcohol at 40°
CD:—Aqueous methyl alcohol at 40°

If we make the explicit assumption that the solubility due to an alcohol is a linear function of the concentration in the aqueous alcohol mixtures, just as it has been shown to be in the mixtures of two alcohols, the difference between the calculated value for the alcohol and the found value for the mixture represents the assumed solubility of succinic acid in the water. By recalculating to the basis of one hundred grams of water, we get the data given in Table I.

TABLE I

M = weight percentage of methyl alcohol in aqueous alcohol.
E = weight percentage of ethyl alcohol in aqueous alcohol.
P = weight percentage of propyl alcohol in aqueous alcohol.
x = calculated grams of succinic acid per hundred grams water.
Temperature, 40°.

M	x	E	x	P	x
0	15.7	0	15.7	0	15.7
10	19.8	10	18.5	10	20.5
20	21.0	20	23.9	20	26.1
30	24.8	30	29.5	30	31.5
40	29.2	40	35.0	40	36.9
50	34.1	50	41.8	50	42.2
60	38.7	60	47.4	60	48.0
70	43.0	70	53.7	70	54.5
80	48.1	80	59.8	80	60.9
90	52.1	90	62.0	90	66.2

TABLE II

M = weight percentage of methyl alcohol in aqueous alcohol.
E = weight percentage of ethyl alcohol in aqueous alcohol.
x = calculated grams adipic acid per hundred grams water.
Temperature, 40°.

M	x	M	x	E	x	E	x
0	5.2	50	21.5	0	5.2	50	41.9
10	4.1	60	28.9	10	6.6	60	51.4
20	4.8	70	36.7	20	11.5	70	63.7
30	8.3	80	40.9	30	19.4	80	76.9
40	14.6	90	42.8	40	28.3	90	94.5

In each case there is a smooth curve with increasing apparent effectiveness as the concentration of the water in the mixture of the two liquids becomes less. Since water is monomolecular in dilute solutions, this means that the apparent solubility of succinic acid in monomolecular water at 40° is approxmately four times as great as in pure water at the same temperature. This cannot be the whole truth, however, because the solubilities do not extrapolate to the same value in the three cases. There is therefore another factor to be taken into account and we cannot at present state what that factor is. We may point out empirically that the apparent solubility in water comes out lowest in the alcohol in which succinic acid is most soluble. Succinic acid is about twice as soluble in methyl alcohol as in ethyl alcohol and about four times as in propyl alcohol.

A similar result is obtained for adipic acid as shown in Table II.

The general relations are much the same as with succinic acid, but the change in apparent solubility is much greater and the difference between the end values is much greater.

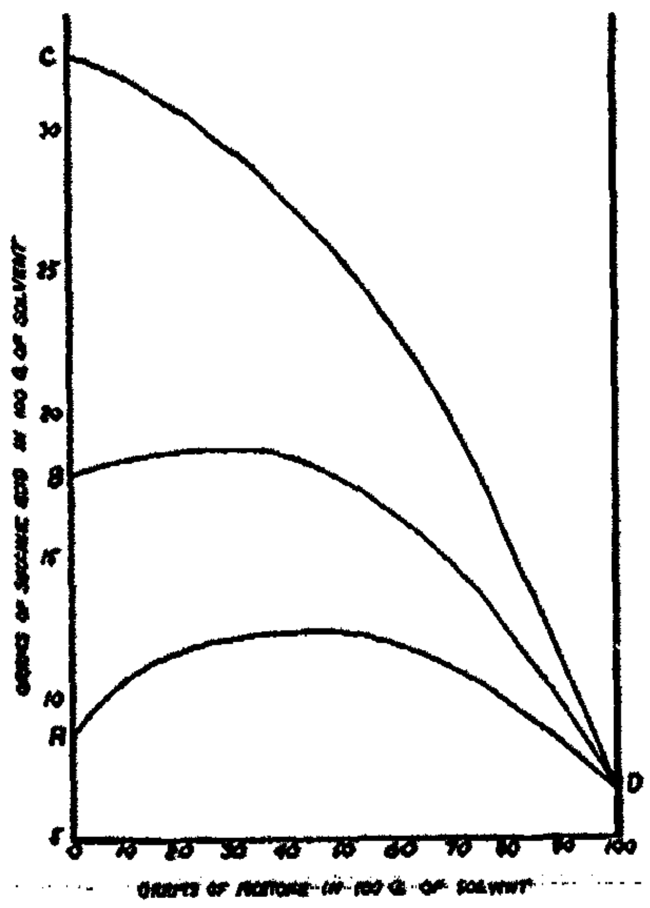

Fig. 4
AD:—Acetone-propyl alcohol at 40°
BD:—Acetone-ethyl alcohol at 40°
CD:—Acetone-methyl alcohol at 40°

Data for the solubility of succinic acid in mixtures of acetone with methyl alcohol, ethyl alcohol and propyl alcohol are shown graphically in Fig. 4. There is a maximum solubility in acetone and propyl alcohol and in acetone and ethyl alcohol; but none in acetone and methyl alcohol. In terms of our hypothesis this means that there is a change in the solubility of succinic acid with changing polymerization of acetone. If we assume that the solubilities due to the alcohols are linear functions of the concentration, the apparent solubilities in acetone are given in Table III.

The apparent solubility of succinic acid in monomolecular acetone at 40° is approximately four times that in pure acetone at the same temperature. The apparent solubility is greatest in the propyl alcohol solutions in which

Table III

M = weight percentage of methyl alcohol in alcoholic acetone.
E = weight percentage of ethyl alcohol in alcoholic acetone.
P = weight percentage of propyl alcohol in alcoholic acetone.
x = calculated grams succinic acid per hundred grams acetone.
Temperature, 40°.

M	x	E	x	P	x
0	6.60	0	6.60	0	6.60
10	8.89	10	8.52	10	8.21
20	11.31	20	10.52	20	10.04
30	13.63	30	13.10	30	12.03
40	16.27	40	15.37	40	13.95
50	18.22	50	17.64	50	15.92
60	19.57	60	19.70	60	17.85
70	21.77	70	20.70	70	20.53
80	22.90	80	21.45	80	23.35
90	24.60	90	22.50	90	28.70

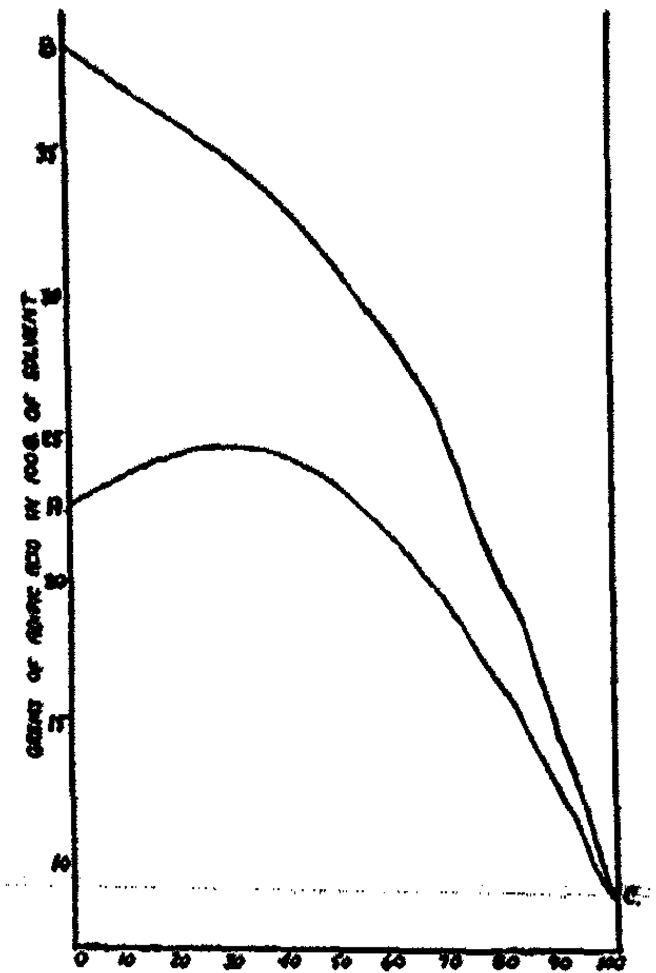

Fig. 5

AC:—Acetone-ethyl alcohol at 40°
BC:—Acetone-methyl alcohol at 40°

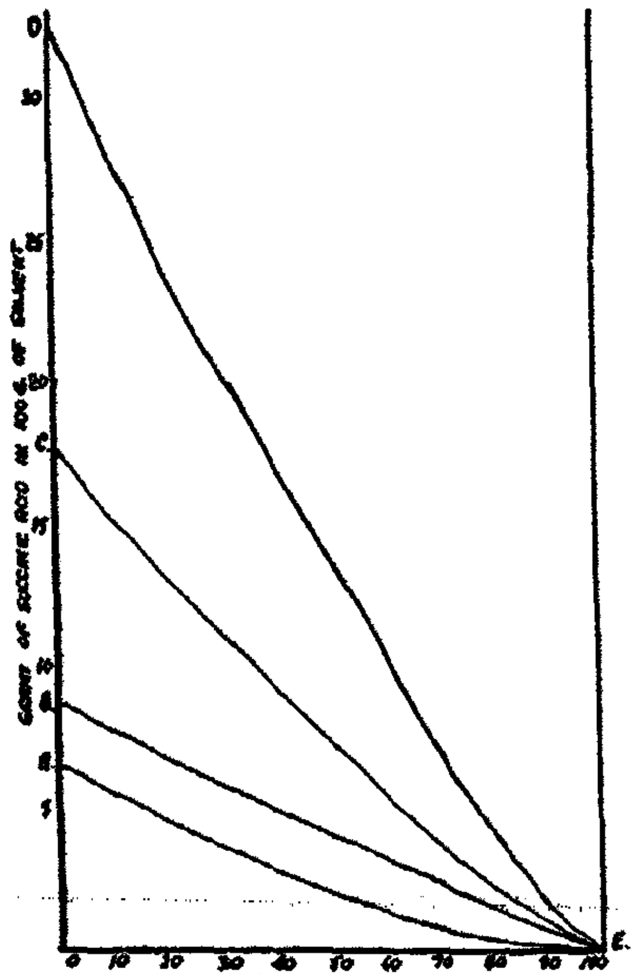

Fig. 6

AE:—CCl_4-acetone at 40°
BE:—CCl_4-propyl alcohol at 40°
CE:—CCl_4-ethyl alcohol at 40°
DE:—CCl_4-methyl alcohol at 40°

the solubility of succinic acid is the least; but it is least in the ethyl alcohol solutions and not in the methyl alcohol solutions, as was the case in the aqueous solutions. No explanation is offered for this discrepancy.

The solubility data for adipic acid in mixtures of acetone with methyl alcohol and with ethyl alcohol at 40° are shown graphically in Fig. 5. There is a maximum solubility in the ethyl alcohol solutions and no maximum in the methyl alcohol solutions. This is qualitatively identical with what was found with succinic acid. The calculated data for the apparent solubilities of adipic acid in acetone are given in Table IV.

The apparent solubility of adipic acid in monomolecular acetone at 40° is three to four times the solubility in pure acetone at that temperature. The

Table IV

M = weight percentage of methyl alcohol in alcoholic acetone.
E = weight percentage of ethyl alcohol in alcoholic acetone.
x = calculated grams adipic acid per hundred grams acetone.
Temperature, 40°.

M	x	M	x	E	x	E	x
0	8.71	50	23.22	0	8.71	50	24.08
10	11.94	60	24.83	10	11.74	60	28.05
20	16.00	70	26.07	20	14.98	70	29.53
30	19.00	80	26.50	30	17.96	80	31.55
40	22.65	90	25.80	40	21.05	90	32.90

higher apparent solubility occurs in the ethyl alcohol solutions and adipic acid is less soluble in ethyl alcohol than in methyl alcohol.

Succinic acid is practically insoluble in carbon tetrachloride. Data for the solubility in mixtures of carbon tetrachloride with acetone, methyl alcohol, ethyl alcohol, and propyl alcohol at 40° are shown graphically in Fig. 6. All the curves are slightly concave as seen from above. This is not surprising because carbon tetrachloride would tend to precipitate succinic acid from solution in an alcohol and succinic acid would increase the partial pressure of carbon tetrachloride in an alcoholic solution. This would give a curve which would be concave as seen from above.

The general results of this investigation are as follows:

1. In binary mixtures of methyl alcohol, ethyl alcohol, and propyl alcohol, the solubilities of succinic acid are practically linear functions of the concentrations of the solvent.

2. With binary mixtures of water and the alcohols, water and acetone, and acetone and the alcohols, the solubility curves for succinic acid and for adipic acid, so far as determined are convex as seen from above.

3. There are no maxima in the solubility curves for succinic acid and adipic acid in mixtures of acetone and methyl alcohol. There is a maximum solubility in each of the other curves which are convex when seen from above.

4. The solubility curves for succinic acid in binary mixtures of carbon tetrachloride with acetone, methyl alcohol, ethyl alcohol, and propyl alcohol, are concave as seen from above. The solubility of succinic acid in carbon tetrachloride is practically negligible.

5. If a maximum solubility is due solely to the formation of a definite chemical compound between the two liquids, the concentration at which the maximum solubility occurs must be independent of the temperature.

6. With acetone-water mixtures and succinic acid the concentration showing maximum solubility changes with varying temperature. The existence of a hypothetical hydrate of acetone cannot therefore be the sole factor and is probably not an important factor in causing the maximum solubility in this system.

7. Since the solubility curves of succinic acid in binary mixtures of methyl ethyl, and propyl alcohols are very nearly straight lines, we must assume that the solubility of succinic acid does not vary much with varying polymerization of the alcohols.

8. From the existing data it seems probable that succinic acid and adipic acid are more soluble in depolymerized water and acetone than in the polymerized liquids.

9. Since the calculated values for the apparent solubility of succinic and adipic acids in depolymerized water and acetone vary with the nature of the other liquid, there must be still another factor to be taken into account.

10. In all cases but one the apparent solubility of succinic or adipic acid in depolymerized water or acetone comes out higher the less soluble the organic acid is in the other liquid. No explanation is offered for this.

Cornell University.

NOTE ON H. B. WEISER'S AND W. O. MILLIGAN'S PAPER ON THE TRANSFORMATION FROM ROSE TO GREEN MANGANOUS SULFIDE

BY GEORG LANDESEN

In the issue for August of this journal Weiser and Milligan[1] published some investigations on the question mentioned, referring there to the first of two of our papers dealing with the same phenomenon[2] which, however, is done partly in such a peculiar way, that it calls for some remarks in defense.

Weiser and Milligan assert repeatedly that our calculated results do not follow from our reported observations. These assertions are apparently proved by reproducing part of our Table I[3] under the heading of "Table V" on p. 2338 of their paper. This table is accompanied by some calculations that lead Weiser and Milligan to results which differ from those obtained by us. To the reader, however, the true cause of these differences remains hidden, because Weiser and Milligan pass over in silence our statement on the "concentrations of standard solutions" ("Gehalte der Ständigen Lösungen") which we have stated on p. 110 immediately before Table I. There is to be found e.g. a detailed statement of the concentration of the hydrochloric acid which was used for titrations mostly in tenfold dilutions, here as well as in the following Tables II to VI. In headings and headlines of these for the sake of brevity, and on account of proximity to normality resp. 0.1 of normality the concentrations are marked as n/10-HCl-solution for instance. If in the calculations account is taken of this statement of concentration of the hydrochloric acid and its contents of NH_4SH- and NH_3-solutions per cc as stated in the first and second columns of the tables referred to, then it is evident that the calculated figures cited in these tables are correctly deduced from the reported observations.

To correct but one of the examples calculated by Weiser and Milligan, the apprehended value 14.16 (in *the second column* of Table I) is obtained by, first, keeping in mind that the quantity of ammonia (0.017 gr in 10 cc of the residue of filtration) equivalent to manganese which was poured into the reaction mixture equals to 0.017 . 10/0.0207 = 8.21 cc if expressed in cc of the tenfold diluted hydrochloric acid mentioned above. In the second place, the quantity of ammonia contained in 10 cc of the reaction mixture, i.e. in 2.5 cc of NH_4SH solution, is equivalent to 8.95 . 2.5 = 22.37 cc of the same tenfold diluted solution of hydrochloric acid, by the first column of Table I. The difference of these two values leads to 22.37 − 8.21 = 14.16, i.e. the apprehended value.

Did the circumstance that the reported titrations (in the second column of Table I of our paper, p. 111, under "gef.") gave a higher value than the value 12.37 as calculated by Weiser and Milligan really not suggest to them

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[1] J. Phys. Chem., 35, 2330-44 (1931).

[2] A. Mickwitz und G. Landesen: Z. anorg. allgem. Chem., 131, 101 (1923); the other paper being: G. Landesen: 193, 277 (1930).

[3] Z. anorg. allgem. Chem., 131, 110-111 (1923).

that the cause of their differing values might lie with them? The same applies to all remaining calculations done by Weiser and Milligan to control our figures; and their thoughtless objections are thereby annihilated by themselves.

At the very beginning of their paper on p. 2330 (before and after "(1)", and near the bottom of this page), Weiser and Milligan intimate by unskillful wording in quoting us that we too have proved and concluded that the rose manganous sulfide does not turn green when precipitated by alkali sulfide. In connection therewith they then describe experiments which prove under certain conditions the contrary. But Weiser and Milligan ought to know from our paper that on this subject no investigations were done by us, nor any conclusions drawn.[4] How misleading their representation is, is shown plainly by the fact that the abstractor of Weiser and Milligan's paper in the "Zentralblatt (1931 II p. 2440) begins with the statement that we have "established" this fact.

Finally, the statement on p. 2335 saying that we have denied the influence of the rate of mixing on the rate of transformation to the green modification as recognised by Fischer, is not correct. When Fischer's statements on this subject are compared,[5] it is not quite possible to speak of a recognition of this influence. Accordingly, treating the literature on the subject on p. 102 of our paper, we have indicated that Fischer's many contradictory statements do not allow any definite conclusion on this influence which seems not to be essential if other definitive conditions are observed.

Inorganic Chemistry Laboratory
of University, Tartu-Dorpat,
April 11, 1932.

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[4] W. M. Fischer, however, whose paper is repeatedly referred to by Weiser and Milligan, but which they seem not to be acquainted with, has made investigations and has drawn definite conclusions on this subject; cf. J. Russ. Phys.-Chem. Soc., **46**, chem. section pp. 1496 to 1500, and 1484 (1914).

[5] Cf. pp. 1485 to 1490, 1492 to 1493 and 1508 to 1510 of his paper under (4).

NEW BOOKS

Annual Review of Biochemistry. *Edited by James Murray Luck. Vol. I. 23 × 16 cm; pp. vii + 724. Stanford University, Stanford University Press, 1932. Price: $5.00.* "It is not without significance that the last few years have witnessed the inception of new journals, of interest to chemists, at no less a rate than one every two weeks. . . . It is the exceptional individual who succeeds in reading an appreciable portion of the papers outside the confines of his own restricted field of research. The Annual Review of Biochemistry will present from year to year reviews of the current developments in from twenty-five to thirty of the major fields of interest," p. v.

The articles and authors are: permeability, R. Höber; the rôle of water in the structure and properties of protoplasm, R. A. Gortner; biological oxidations and reductions, R. Wurmser; enzymes, E. Waldschmidt-Leitz; the chemistry of acyclic constituents of natural fats and oils, R. J. Anderson; the chemistry of the sterols, bile acids, and other cyclic constituents of natural fats and oils, A. Windaus; the chemistry of the lipins, I. Smedley-MacLean; the chemistry of the amino acids and the proteins, C. L. A. Schmidt; the chemistry and metabolism of the compounds of sulfur, H. B. Lewis; the chemistry and metabolism of the compounds of phosphorus, H. D. Kay; the chemistry of the carbohydrates and the glucosides, P. A. Levene and A. L. Raymond; carbohydrate metabolism, P. A. Shaffer and Ethel Ronzoni; fat metabolism, W. R. Bloor; the metabolism of proteins and amino acids, J. M. Luck; nutrition, A. H. Smith; vitamins, L. H. Harris; the hormones, D. L. Thomson and J. B. Collip; the chemistry of muscle, J. K. Parnas; liver and bile, J. L. Bollman and F. C. Mann; the metabolism of brain and nerve, E. G. Holmes; chemical embryology, Joseph Needham; the chemistry of the animal pigments, Hans Fischer and F. Neumann; plant pigments, A. E. Mirsky and M. L. Anson; the terpenes, saponines, and closely related compounds, L. Rusicka; the nitrogenous constituents of green plants, H. B. Vickery; mineral nutrition of plants, D. R. Hoagland; the chemistry of the bacteria, M. Stephenson; immunochemistry, Michael Heidelberger; the biochemistry of the fungi, N. N. Iwanoff.

"Mammals and teleosts are characterized by low figures [for the time of hemolysis,] elasmobranchs and amphibia by high values; reptiles give hemolytic times somewhat higher than mammals, and the birds show a peculiar behavior inasmuch as the value for the chicken is high, while those of the pigeon and duck are low. . . . In mammals permeability to urea is much greater than to ethylene glycol; the reverse is true for elasmobranchs and teleosts. Reptiles resemble mammals; birds and amphibia approach the fishes. The comparison between urea and glycerol gave similar results. The penetrating faculty of urea exceeded by far that of glycerol in the case of mammalian cells, and to a somewhat smaller degree in reptiles and the frogs, while the permeability of the two substances is about the same in fishes," p. 2.

"Lepeschkin has published new experiments regarding the influence of light upon cell-permeability. He investigated the speed of penetration of methylene blue into the leaves of *Elodea* with a colorimetric method especially worked out for *Elodea*. The permeability increases in the light and decreases in the dark. It may be objected: (1) that the difference in coloring may be produced by a change in the adsorption of the dye in light—but dead cells adsorb dyes with equal velocity in the light and in the dark; or (2) the affinity of the cell sap may be increased by the illumination—but also the amount of dye adsorbed by the cell is the same in light and dark. By shading a part of the leaf by means of a strip of tin-foil it can be demonstrated that the increase of permeability does not spread to neighboring cells. The greater the change of the illumination—in positive and negative direction—the greater is the change of permeability; this can be explained by the supposition that there exist in the cells substances essential for permeability, destroyed by light and restored in the dark; therefore, the more products of the decomposition the protoplasm contains, the more rapidly the restoration proceeds, and conversely. The rays most active are those with a wave-length of 320 to 420 $m\mu$," p. 16.

"In the case of gelatin all of the water which would freeze was frozen when the temperature was lowered to -6°C. and no additional water froze even when the temperature was lowered to -50°C.," p. 23.

"McQuarrie has made the important discovery that at least certain types of epilepsy appear to be due to disturbed water relationships and that when water is withheld from the patient the patient becomes free from seizures and may remain entirely free from seizures providing that the water intake is reduced to a minimum. A sudden increase in the water intake or the parenteral administration of a solution of the pituitary or the anti-diuretic hormone of the hypophysis produces a positive water balance in such 'dehydrated' patients and a corresponding recurrence of the seizures. If, however, sufficient urea is added to the ingested water, the seizures do not develop," p. 32.

"Harding and Harris report that in order to produce convulsive spasms in dogs the retention of water must exceed 60 cc. of kg. of body weight and that, while the administration of 10 percent NaCl solution will cause recovery, the administration of hypertonic urea solutions is relatively ineffective. These authors express doubt that the convulsions of epilepsy and eclampsia are due to water intoxication even though they may be accompanied by a positive water balance," p. 35.

"Frog skin shows a differential directional osmosis which is reversed as one passes the isoelectric point," p. 44.

"It is shown by the recent researches of Meyerhof and Lohmann on the extract from muscles of cold-blooded animals, that during the esterification of the phosphate which precedes the scission of glucose into lactic acid the adenyl-pyrophosphate, which is the coenzyme of this transformation, undergoes scission. The resynthesis of phosphagen in anaerobiosis is rendered possible by the energy of scission of this adenyl-pyrophosphoric acid, while the energy of formation of the lactic acid serves to reconstitute the decomposed pyrophosphate. Under conditions of aerobiosis the chain of energy-transfer, which makes possible the resynthesis of glycogen from the lactic acid, and in part of the phosphagen, is still longer, and is yet incompletely known," p. 56.

"Bamann and Laeverenz have shown that in splitting racemic esters of the mandelic acid group by liver esterase, a reversal of the optical selectivity can be obtained by adding strychnine; the rotatory direction of the more quickly saponified component of the racemate was found to be different with and without strychnine. Later researches have developed this observation. The change in steric specificity under the influence of the alkaloid has proved, within the limits tested, to be independent of the degree of purity of the enzyme from the accidental and separable concomitant materials of the enzyme preparations; there seems to be a reaction of the strychnine with the enzyme itself," p. 71.

"Oparin and Kurssanow have reported on the important observation of an enzymatic synthesis of cane sugar. Having found that the transformation of γ-fructose $<2,5>$ present in cane sugar into β-fructose $<2,6>$ which takes place after its hydrolysis, is retarded by phosphorylating the cane sugar, they succeeded by simultaneous action of saccharase and phosphatase on solutions of invert sugar in the presence of phosphate, in obtaining a synthetic sugar identical with cane sugar," p. 80.

According to Lohmann the presence of magnesium ion as well as of co-zymase is necessary for fermentation by dry yeast. The conjoint action of the magnesium is responsible for the partial process of glucose-phosphorylation since the activity of the phosphatase can, it is well known, be much increased by magnesium ion," p. 82.

"Rosenfeld found from feeding experiments on hens that lecithin could be formed in the body if phosphorus and fatty acids were supplied. When glycine was added to a basal diet containing ether-extracted casein, starch, sugar, stearic acid, and salts, the quantity of lecithin formed in the body was much increased. Rosenfeld therefore regards glycine as a forerunner of lecithin," p. 137.

"Recent studies on the colloidal properties of lecithin have been especially concerned with two questions, (a) the mutually antagonistic effect of solutions of lecithin and cholesterol; and (b) the effect of the addition of lecithin on the precipitation of serum proteins. Theorell and Widström have confirmed the antagonistic action of lecithin and cholesterol on the haemolysis of red blood corpuscles," p. 139.

"In 1920, Meigs, Blatherwick, and Cary described experiments on the mammary gland which seemed to offer conclusive evidence that milk fat was derived from phospholipins, for the blood left the gland richer in inorganic phosphate and poorer in phospholipin in comparable amount. Jost has now brought forward further evidence in support of the view previously advocated by Leathes that the phospholipins act as intermediate substances in fat metabolism," p. 144.

"It is strongly suspected that they [Bancroft and Barnett] have not taken into account all of the factors which must be considered in the reactions which they were studying," p. 164.

"A very interesting dismutation of glyceric aldehyde was observed by Strain and Spoehr. These authors found that glyceric aldehyde is readily converted by organic amines into methyglyoxal which was identified as its *m*-nitrobenzoyl osazone. The reagent was added to the reaction mixture and the osazone settled out in course of the reaction. Glyceric aldehyde does not form an insoluble osazone. Dihydroxyacetone does not undergo dismutation under the same conditions," p. 227.

"The chief result of the new facts is the removal of lactic acid from the central rôle it has long been supposed to occupy, wherein the energy of its formation was the source of the work of contraction. With the demonstration by Lundsgaard that frog muscle when poisoned with iodo- or bromo-acetic acid contracts normally for a time without formation of lactic acid, Meyerhof and Hill were at last forced to agree with the contention of Embden, reiterated since 1924 (Lehnartz), that a part—and now all—of the lactate is formed after the contraction is over. So all the fine balance sheets heretofore thought to demonstrate a quantitative time-energy relation between the initial heat of contraction and lactic-acid formation from glycogen must now be set aside. The idea of a chemical coupling of the various reactions set off by stimulation, never very clearly defined but always implied, now seems impossible since the reactions are separate in time, and Meyerhof now regards the relations as only energetically coupled through cellular activity. Hahn (1931) has criticized this concept," p. 248.

Adrenalin retards the adsorption of sugar by the peripheral tissues and continuous injection of adrenalin with glucose virtually abolishes sugar oxidation as indicated by the R.Q., p. 253.

"The relation of cholesterol to water balance with its effect in epilepsy and other conditions has received attention. Robinson, Brain and Kay found that in the preconvulsive period in epileptics the cholesterol level in both blood and plasma falls and the seizure takes place at or almost at the lower point in the curve. Incidentally they find that the blood cholesterol is reduced in normal individuals by exercise but comes back promptly. They mention that it is low at the menstrual period, which corresponds to the times of most frequent epileptic attacks," p. 290.

"Mattick and Buchwald found that the cholesterol is higher in plasma than in whole blood in 85 percent of cancer patients. In 80 percent of normal it is higher in whole blood," p. 291.

"Apparently the herbivorous animal forms milk fat largely from carbohydrate and has difficulty in using the fat of the food directly for that purpose, while the carnivorous animal can use food and stored fat directly," p. 293.

"Frogs poisoned by injection of 40 mg. of iodoacetic acid or bromoacetic acid become completely rigid after one hour; but if their sciatic plexus be severed before poisoning, the limbs will appear normal after one hour, while the innervated extremities will be rigid. When nerve-muscle preparations from such frog limbs are stimulated, 60 to 100 twitches are produced, which could not be told from normal contractions by their mechanical, thermal, and electrical [Henriques and Lundsgaard] responses (Stage I). Then, the contractions become weaker, and a contracture begins to appear (Stage II), finally the twitches come to an end, and contracture develops rapidly; after a few minutes the muscle is in full rigor (Stage III). *During all these changes no lactic acid is produced in the muscle, either during the periods of activity or when rigor develops.* This is the portentous discovery by Einar Lundsgaard," p. 443.

"We must assume now, with Lundsgaard, that the cleavage of phosphocreatine is the primary change in the normal contraction, as it is the primary and final change in the anaërobic twitch of the iodoacetic muscles; and that this change is followed, in the normal muscle, by restitution of phosphocreatine, depending on the chemical changes of the anaërobic recovery, viz., lactic-acid formation from glycogen and the splitting off of phosphate from the pyronucleotides," p. 445.

"By X-ray investigation, Hopff and Susich have established the identity of the hydrocarbons of balata and gutta-percha, which differ from caoutchouc hydrocarbon. Stillwell and Clark, as well as Hauser and Susich, have observed two modifications of gutta-percha hydrocarbon, having a transition point at 68°," p. 605.

"The rôle of phosphate in lactic fermentations by *Bact. casei* has now been further elucidated (Virtanen and Tikka). It appears that, whereas live cultures of the organism change glucose to lactic acid quantitatively (glucose→hexose monophosphoric ester ["Robison" ester]→lactic acid [100 percent], with dried preparations of the organism 50 percent only of lactic acid is obtained, the remaining 50 percent being found as phosphoric esters," p. 642.

"As may be seen from the works mentioned above, the theories of organic acid formation have entered the stage of vast generalization. The obtaining of succinic, fumaric, and citric acids from acetic acid and alcohol shows definitely that we may accept a uniform schema of sugar metabolism for yeast, as well as for mould fungi, in which, after the breakdown of the sugar has been carried to acetaldehyde, in some cases (yeast) ethyl alcohol is formed, in other cases (through acetic acid or through ethyl alcohol) compound organic acids, such as succinic, fumaric, citric, and other acids, appear. The comprehension of the origin of these acids, as well as of their frequent simultaneous presence, a fact pointing to their common origin, is considerably facilitated. Two courses adopted in research have proved productive; the first, alteration of the cultural conditions (pH, concentration of sugar, amount of nitrogen), with the formation, by the same fungus species, of certain acids and the suppression of others; the second, the study of the various fungi, as well as of their races, with considerable differences in the nature of the acids being formed. The comparison of all data obtained from the two lines of investigation will afford a clear picture of the genesis of organic acids in fungi," p. 689. *Wilder D. Bancroft*

Industrial Chemical Calculations. *By O. A. Hougen and K. M. Watson. 23 × 16 cm; pp. vii + 502. New York: John Wiley and Sons. London: Chapman and Hall, 1931. Price: 28 shillings.* Any manufacturing process in which a material is subjected to a change of physical state or chemical composition properly belongs to the domain of chemical engineering. A chemical engineering process possesses two aspects: an internal or chemical aspect, in which it is displayed as a reaction between certain molecules or ions exhibiting definite quantitative stoichiometric and energy relationships, and an external or engineering aspect in which it appears as an assemblage of special plant units and equipment that are necessary to contain the reaction mass and provide scope for its physical or chemical transformation.

The present book deals with the application of physico-chemical principles to what might be called the "internal design" of a process—the control of a process by a nice adjustment of composition and of pressure and temperature. In so far as chemical engineering is concerned with the control of chemical reactions and physical changes on a large scale, it is very largely applied physical chemistry.

The present book contains much more than is apparent from the title. It is concerned essentially with the application of physico-chemical principles to the control of chemical reactions and physical changes under industrial conditions. The method of presentation adopted throughout the book is admirably clear and logical. Each subject is introduced with a good account of the underlying theory. The industrial conditions to which the theory is to be applied are described and the methods by which the theory can be applied to the solution of definite problems are demonstrated. To each section is appended a list of well-arranged problems, possessing an authentic industrial flavour, for a student to work out for himself.

After a preliminary discussion of the use of the molal method of calculating the quantities of reaction materials and the way in which these quantities change as a result of chemical interaction, the authors proceed to give a very good account of the kinetic theory of gases, and show how the theory can be applied to the calculation of the volume and density of gases at high pressures and the heating effects resulting from compression and expansion. Further calculations deal with the way in which the composition of a gas mixture changes as a result of chemical reaction.

Succeeding chapters deal in a similar way with evaporation and condensation, with solution and crystallisation, with specific heats and latent heats, with heats of reaction and heats of solution, and more particularly with the thermochemistry of combustion.

Two chapters deal very fully with the preparation of quantitative balances of the materials and energy used in a chemical process. This portion of the book is very well illustrated by a detailed analysis of both materials and heat balances for such typical industrial processes as those of the gas producer, the coal-fired boiler furnace, the gas-fired kiln, the sulphuric acid plant considered section by section and also in its entirety, and the blast furnace. An excellent chapter deals with the calculation of distillation equilibria. The final chapter is devoted to problems involving reaction equilibria.

The book is of the greatest possible value to every student of physical chemistry. It is unfortunate that this subject is often taught by specialists who do not appreciate its industrial significance and utility, particularly as so large a proportion of their students will depend for their livelihood upon applied rather than theoretical physical chemistry. The use of this book, along with the ordinary textbooks of physical chemistry, would do a great deal to "lend an air of verisimilitude" to what is apt at times to be "a somewhat bald and unconvincing narrative."

To the student of chemical engineering, the book is indispensable; in so far as his work is applied physical chemistry, he must be thoroughly familiar with the principles and methods that are so well described in it. Every industrial chemical process is at heart a series of physical and chemical reactions, and, unless he understands the physical chemistry of the process, he is unlikely to be able to deal successfully with the engineering aspect of it.

W. E. Gibbs.

25A

Glastechnische Tabellen: physikalische und chemische Konstanten der Gläser. *Edited by Wilhelm Eitel, Marcello Pirani and Karl Scheel. 28 × 20 cm; pp. xii + 714. Berlin: Julius Springer, 1932. Price: paper 145 marks: bound 149.80 marks.* The publication of Hovestadts' "Jena Glass" at the beginning of the century brought into a single compass practically all the data on the physical properties of glass known at that time; and the work of Schott, Winkelmann and others associated with the Jena school was responsible for the bulk of those data. It was a proud record to be associated with an industrial concern. From that time onwards, however, for more than a decade, little new fundamental work on glass appeared save that on general theory inspired by G. Tammann. Even in Germany no institution of advanced learning realised what an opportunity there lay in the study of glasses as a field for systematic investigation. It was left to 1915 for a University in England to embrace this opportunity. Moreover the War stimulated efforts in glass making in a number of countries, efforts which, in America, Japan and Russia as well as in this country were supported by much valuable research work. In 1916 the Society of Glass Technology was founded; in 1917 a Glass Division of the American Ceramic Society; the Deutsche Glastechnische Gesellschaft was founded in 1923. The activities of all these bodies backed by a number of research institutions have developed a distinct science of Glass Technology. Especially in England and Germany has enthusiasm run high. On the literary side, in the compilation of text-books and summaries of knowledge the German workers have been particularly active. The work under review, which owes its appearance in large measure to the support of the Deutsche Glastechnische Gesellschaft, is the result of one of the most ambitious of these literary projects. It is an attempt to combine with the older data the out-pouring of the past fifteen years and to summarise in a single volume all the known physical and chemical data concerning glasses. Such a summary must be regarded as of value, beyond the immediate service to the glass manufacturer; for glass is to the chemist and physicist a material of fundamental importance, though not always used in the past with due regard to its limitations. With this work of reference available chemists and physicists should be able to obtain a clearer understanding of the service which glass can give and what it cannot give.

The book comprises some 726 pages and consists of a preface, recounting the origin and reason for the book, an introduction explaining the plan of arrangement, and a one page note to the reader explaining how he may utilise the book in designing a glass for a specific purpose.

The systematic portion of the book is divided into three parts. Part I, comprising 88 pages, deals with the properties of the individual oxides such as silica, boric oxide, arsenious oxide, and so on, utilised for all types of glasses, and the phase equilibria in systems of 2, 3, 4 or more of such oxides. The equilibrium diagrams are reproduced in all essential detail together with tables showing the phases present at different temperatures and in some cases drawings of the crystal forms which are deposited. In all cases the latest equilibrium diagrams are given but with selected references to the most important of the older literature. Part II, comprising 536 pages, reproduces in tabular form and in many instances diagrammatically, occasionally also photographically, the records of all modern measurements which have been made on the physical properties of glasses including viscosity, surface tension, internal stress, annealing and softening temperatures, density, elasticity, compressibility, tensile strength, hardness, brittleness, permeability to gas, gas absorption and evolution, thermal expansion, specific heat, heat conductivity, dielectric constant, electrostriction, impact strength, electro-motive force, magnetic susceptibility, refractive index, photo-elasticity, Kerr's constant, Verdet's constant, spectral transmission, U. V. transmission, ultra-red transmission, general transmission, light diffusion, chemical durability and devitrification.

The collation of all these results has been done very well. One sees from them not only what information is available, but also the gaps which remain to be filled and they, therefore, indicate useful fields for further work. The comprehensive section on the durability of glass serves to illustrate both the tremendous diversity of methods which have been employed, and also the very great need for the standardisation of methods so that the results of different investigators can be usefully compared with one another.

The composition of the glasses is not given in Part II, as this would involve needless repetition in many cases. A reference is given in each case, however, to the section in Part III where the composition of any particular glass can be found. In Part III all the glasses which have been referred to in Part II are systematically classified according to their chemical composition. Included is a reference also to organic glasses which in recent years have been studied in connection with the theory of the vitreous state by quite a number of workers.

The whole work has been done uncommonly well. In a systematic examination of the volume the writer has found little or nothing to criticise. The type is beautifully clear and the numerous diagrams, some 900, are not only clear but in some cases appear to better advantage than in the original papers. The work reflects very great credit on the editors, and on the seventeen collaborators who have worked through the very large amount of modern literature.

We may reasonably anticipate that Glastechnische Tabellen will constitute the standard work of reference for all those who are interested in the physical properties of glasses.

W. E. S. Turner