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THE DETERMINATION OF VAPOUR AND LIQUID COMPOSITIONS IN BINARY SYSTEMS

I. Methyl Alcohol-Water

BY J. B. FERGUSON AND W. S. FUNNELL

The composition of the vapour in equilibrium with a binary liquid has been determined experimentally by various methods. Dobson[1] passed an inert gas over the liquid and condensed and analysed the vapour, whilst Rosanoff et al[2] and Sameshima[3] used various modifications of the method in which part of the liquid is distilled off and the composition of both the distillate and residue determined. Cunaeus[4] employed an interferometer method, and with it, preliminary experiments were carried out by Hoover and Glassey[5]. More recently, Calingaert and Hitchcock[6] have devised a method based upon the volume relations of the system at equilibrium.

Although excellent results were obtained by some of these, there appeared to be a need for a method in which the uncertainties with respect to the attainment of equilibrium, and to the assumptions underlying the calculations would largely be eliminated, and in which only small samples would be required.

The perfection of a convenient form of all-glass circulating apparatus by Funnell and Hoover[7] made possible the construction of an apparatus which appears to meet, in some measure, the above requirements, and a description of this apparatus, together with the results obtained by an investigation of the system methyl alcohol-water at 39.90°C. is given in this paper.

Method

1. A weighed sample, of known composition, which need not be air free, was distilled into the apparatus.

2. The vapour was circulated over the liquid until equilibrium was obtained.

3. The pressure of the system at equilibrium was observed.

4. A known volume of the vapour was condensed and weighed.

The results were calculated by the following methods:

I. The weight of the total vapour was found from the weight of the vapour condensed and the weight of the residue was obtained by difference. The composition of the residue was obtained from a total pressure curve and the composition of the vapour was then calculated. This method requires a curve of such a type that the composition can be determined accurately from the total pressure and the only assumption is that the weight of the vapour is directly proportional to the pressure and volume, and inversely to the temperature on the thermodynamic scale. This assumption was used for a correction of only a few percent.

II. From the weight of the condensed vapour, its original volume, temperature and pressure, the composition was calculated, assuming that the mixed vapours form a perfect gaseous solution in so far as their densities are concerned. The total weight of the vapour and the weight of the liquid were obtained as in I and the composition of the liquid calculated. In this case the equilibrium pressure constituted an independent vapour pressure determination.

III. The composition of the liquid was obtained as in I. The number of formula weights in the liquid was found by difference from those in the original sample and in the vapour, making the same assumptions as in II. From this, the weight of the liquid was found and hence the weight of the vapour and its composition. If this method is used alone the vapour need not be condensed and weighed.

In a favourable case all three methods can be used and, if there are no experimental errors, give identical results. In general this may not be possible, but one or other of the methods may be applicable. In cases where it can be assumed that the vapour behaves like a perfect gaseous solution favourable compositions may be experimented with, and the abacus devised by Lash Miller[2] employed to obtain additional results. This abacus indicates whether the results are in accord with the Duhem-Margules equation and makes it possible to extrapolate from experimentally determined values in accordance with this equation which is an approximate form of Gibbs' equation 97 (dt = 0). In still more unfavourable cases the condensed vapour can be analysed by direct chemical or physical methods.

The use of the three methods of calculation affords a check upon the fundamental assumption often made that the vapour is a perfect gaseous solution, but only in so far as density is concerned, since a knowledge of the specific heats and the heats of mixing would also be required to establish completely the validity of the assumption.

Apparatus

The general design of the apparatus is indicated in Fig. 1. During an experiment the liquid came in contact with Pyrex only and the vapour with Pyrex and mercury.

A weighed sample of known composition, contained in a sealed tube, was placed in A, and the apparatus evacuated through stopcocks 1, 8 and 9. Mercury was run through 8 and 9 to fill the outlet tube, and through 3 to seal stopcock 1. The other mercury levels were at the bottom of the U-tubes. After the air thermostats T_2 and T_1 had been brought up to temperature and a zero reading taken, liquid air was placed at the bottom of the small bulb in T_3, the neck of the sample tube was broken off by means of the magnetic hammer, and the sample was completely distilled into the apparatus, as shown by the manometer reading. Mercury was then run through stopcock 4 into the U-tube and air admitted through 1 to force the mercury up into the capillary tube in T_2. The liquid air was removed and cold water run through the copper coil in T_3 until the sample had distilled over into R. Water was

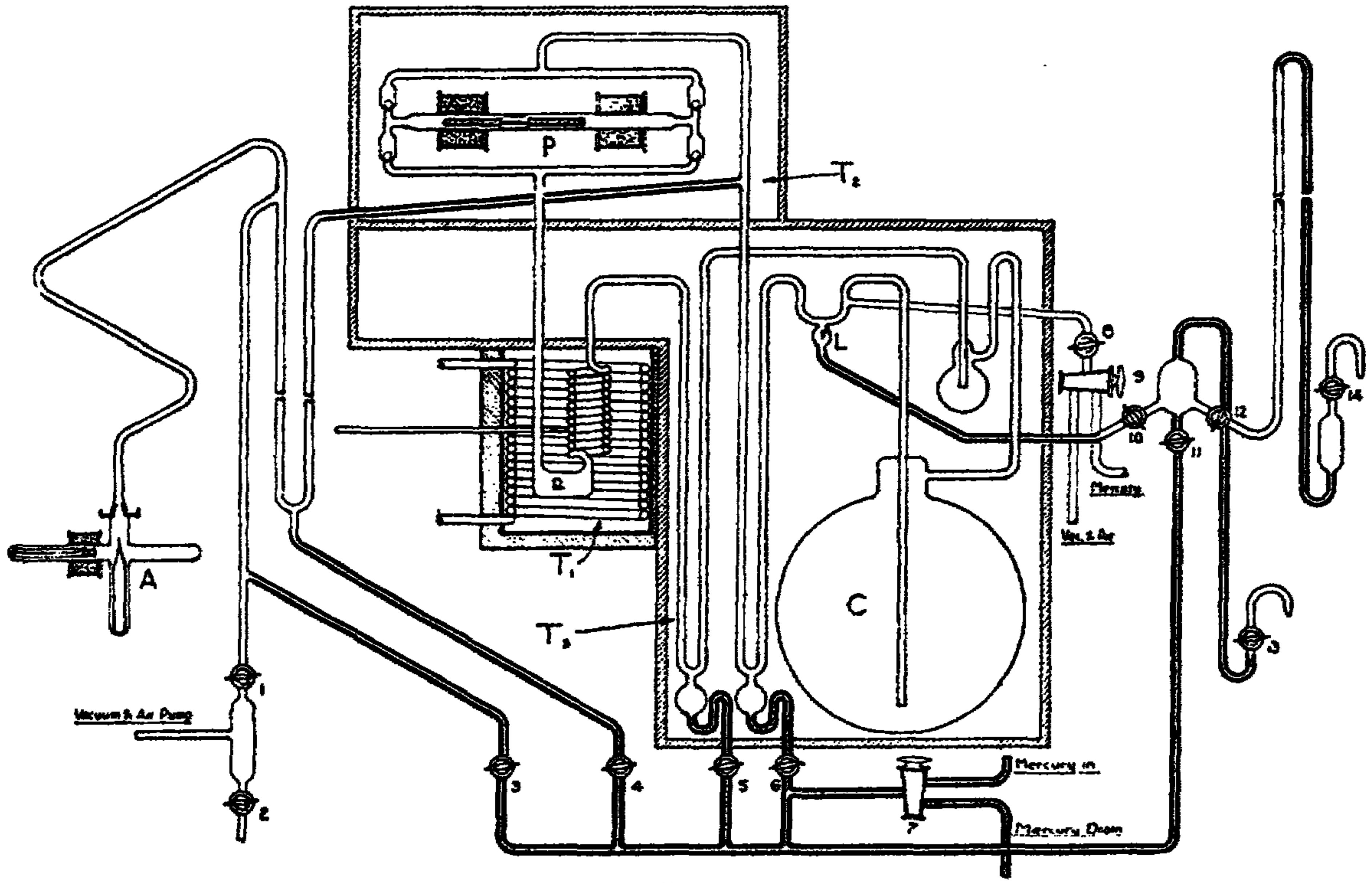

Fig. 1
The Vapour Pressure Apparatus

then pumped from a large thermostat through the coil in T_1 until the desired temperature was reached. This temperature varied ± 0.02 during the experiment, but was maintained at 39.00 ± 0.01 for at least one half hour prior to reading the final pressure. The air thermostat T_3 was maintained at 70°C. and T_4 at 42.5°C.

The vapour was then circulated over the liquid in the reaction chamber R by means of the pump[*] which was run fairly rapidly at first and then the speed was reduced to a previously determined rate such that the circulation was slow enough for the slightly warmer vapour from T_3 to be cooled by the cooling coil to the temperature of T_1 before reaching the liquid, and no superheating occurred. The pressure usually became constant in less than one hour, but the circulation was continued several hours longer; then the pump P was stopped and the pressure read. Mercury was run through 5 and 6 into the U-tubes, the trapped vapour condensed in the small bulb by means of liquid air and the bulb sealed off. The air thermostats were again brought up to temperature and the pressure of the residual trapped vapour obtained. The ends of the glass tubes attached to the small bulb were warmed, cooled and broken off and the tubes joined by a piece of clean rubber tubing. The bulb was then weighed and clean air drawn through until the weight became constant. Since small traces of mercury distilled into the bulb with the vapour it could not be heated.

The air was then pumped out of the U-tube through 1 until the mercury became level and could be drawn off through 4. The apparatus was then evacuated through 1 until the level of the mercury in the other U-tubes permitted them to be emptied through 5 and 6.

The temperature of the water thermostat was read on a precision mercury thermometer, freshly calibrated at the transition point for sodium sulphate decahydrate (32.384°C.) so that our temperature is according to the I.C.T. scale.

The total volume of the vapour was 3394 cc. and the volume trapped and condensed 3300 cc. The volume of part of the apparatus, consisting of the circulating pump and the various connecting tubes, was determined by measuring the pressure when a known volume of air was introduced, whilst the bulbs were weighed empty and full of distilled water.

The residual pressure after the condensation of the vapour was from 0.5 to 3 mm. mercury. This pressure was caused by the condensation of vapour in the upper part of the condenser and when this happened there was no advantage to be gained by waiting until it distilled into the colder part of the vessel. The temperature of the air bath T_2 was read to 0.5° and of T_2 to 0.1°. The manometer was read to 0.1 mm. and the air introduced with the sample would give rise to a pressure less than this amount.

The effect of the speed of the circulating pump P on the vapour pressure of pure water was observed, and in this way a desirable rate was determined.

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[*] For convenience in operation our commutator was arranged so that the solenoids were alternately unexcited and it was short-circuited prior to starting and stopping the motor.

The System Methyl Alcohol-Water

This system was studied by Wrewsky[8] and his results were apparently confirmed by a preliminary study by Hoover and Glassey[9] and by a more complete study at a lower temperature, 39.76°C. by Bredig and Bayer[10] who also investigated the more dilute solutions. Upon examination, by means of the abacus, Wrewsky's results appear to be subject to some systematic error which increased as the solutions became more dilute and a similar study of those by Bredig and Bayer proves that the vapour compositions for the dilute solutions are inconsistent with those for the more concentrated solutions. In addition, the partial pressures given by Wrewsky indicate that for water, there is first a negative and then a positive deviation from Raoult's law. Since he indicates the same type of deviation for the system ethyl alcohol—water, whilst Dobson[1] found only a positive deviation at a lower temperature, it seems probable that the positive and negative deviation was due to experimental error, particularly when the general properties of methyl alcohol and water are considered. This supposition has been confirmed by our study of the system methyl alcohol-water, and we believe that in the previous work a certain amount of refluxing occurred.

Our materials were distilled water and methyl alcohol from a sealed bottle of Kahlbaum's best grade, purchased in 1912, which a specific gravity determination showed contained 0.22% water. For the water, we obtained a vapour pressure of 55.0 mm. mercury (0°C.) which may be compared with the I.C.T. value of 55.03 mm. and for the methyl alcohol we obtained the value of 260.1 mm. which, by extrapolation, leads to a value of 260.5 mm. for the pure alcohol. The equation of Raikes and Bowen[11] gives 255.1 mm. for the same temperature, but Wrewsky obtained a value of 260.7 mm. and Bredig and Bayer, at a slightly lower temperature (39.76°C.) observed a pressure of 259.8 mm. Minor corrections might alter these results by 1 mm., but they are in good agreement with our determinations. Wrewsky recorded his probable uncertainty as ± 1.1 mm. for his whole series of pressure measurements.

A consideration of the values of the product PV for water vapour and methyl alcohol which are listed in I.C.T.[11] indicates that the densities of these vapours would not deviate appreciably from the theoretical value at

TABLE I

The Calculated and Observed Weights of the Mixed Vapours

Vapour Composition Weight Percent Alcohol	Total Pressure	Observed Weight	Calculated-Observed Weight
60.8	94.2 mm	0.3820 g.	+0.0010 g.
68.8	106.8	0.4580	+0.0014
76.8	126.4	0.5602	+0.0013
82.1	146.6	0.6729	−0.0004
92.2	196.9	0.9670	+0.0011

the temperatures and pressure that we used. This conclusion is supported by the close agreement between the observed weight of the condensed vapour and the calculated weight obtained by method III, using for the formula weight of water 18.02 g., for methyl alcohol 32.04 g., and for the volume of one formula weight of vapour under standard conditions 22410 c.c. Some of these weights are given in Table I.

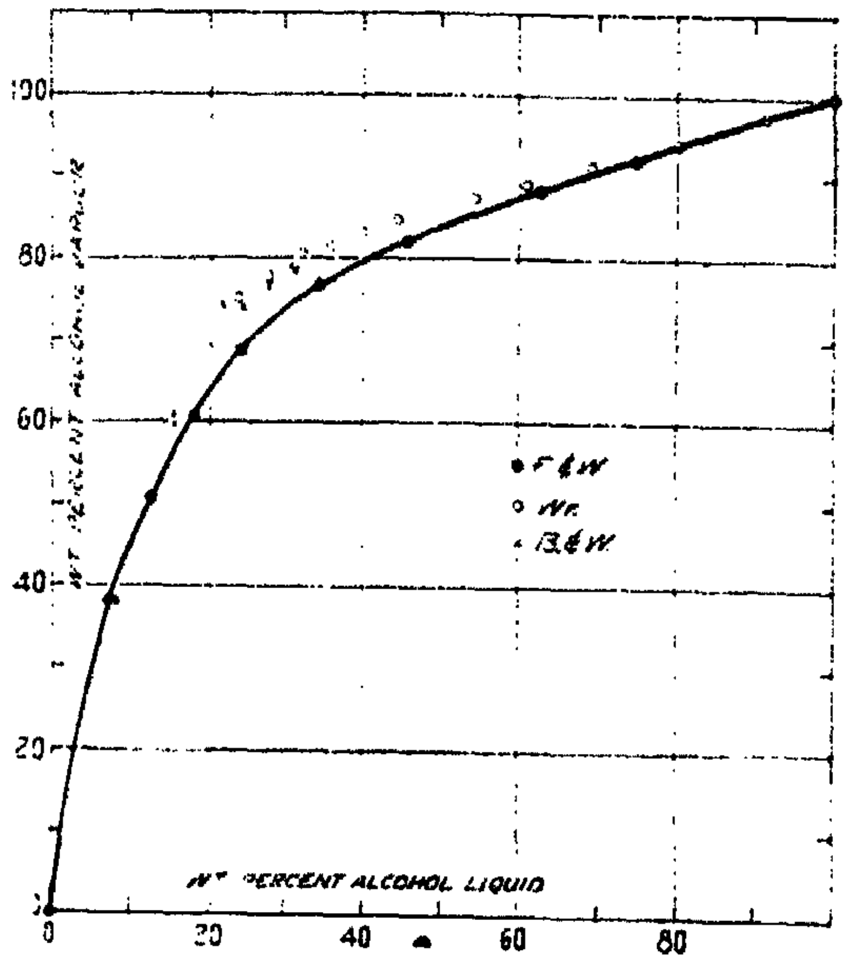

Fig. 2
Vapour and Liquid Composition

TABLE II

The Vapour and Liquid Compositions. Experimental Values.

Temp. 39.90° C.

Weight of Sample	Total Pressure Mercury 0°C.	Weight percent alcohol				
		Liquid		Vapour		
		Wrewsky	Ferguson and Funnell	Method I	Method II	Method III
	55.0 mm		0			
0.4140 g.	70.4	7.25				38.36
1.0948	81.0	12.50				50.79
1.6270	94.2	18.20	18.40	60.80	60.22	60.77
1.5650	106.8	24.30	24.50	68.90	68.55	68.80
1.6470	126.4	34.30	34.41	76.95	76.78	76.79
1.5028	140.0	40.00	45.86	82.08	82.24	82.10
1.6225	174.4	62.70				88.03
1.5582	196.0	75.00	74.89	92.21	92.28	92.19
	260.1		99.78			

These weights indicate that the vapours mix without a noticeable change in volume, and support the assumption that the mixed vapours may be considered as a perfect gaseous solution.

The liquid and vapour compositions which we obtained are given in Table II. Wrewsky's liquid compositions were read from a smoothed curve of his total pressures plotted against the weight percent of alcohol.

The agreement between the values for the liquid composition is quite satisfactory and this confirms Wrewsky's values for the total pressures.

Fig. 2 represents what we believe to be the correct values for the vapour compositions plotted against the liquid compositions in weight percent, and our best values are indicated, together with those of Wrewsky and of Bredig and Bayer for their dilute solutions.

TABLE III

Vapour Compositions and Total Pressures. Temperature 39.90°C

Weight percent Alcohol Liquid	Weight percent Alcohol Vapor	Total Pressure mm. Mercury at 0°C.	Weight percent Alcohol Liquid	Weight percent Alcohol Vapor	Total Pressure mm. Mercury at 0°C.
0	0	55.0	40	79.6	136.6
5	30.0	65.2	50	84.0	153.8
10	45.3	77.0	60	87.5	170.0
15	55.7	88.2	70	90.7	187.6
20	63.9	97.7	80	94.0	208.0
25	69.8	108.5	90	97.1	231.0
30	73.7	118.5	100	100	260.5
35	77.0	128.0			

TABLE IV

Partial Pressure. Temperature 39.90°C

Liquid Composition Mole percent Alcohol	Total Pressure	Partial Pressure	
		Alcohol	Water
0	55.0 mm.	0	55.0
5	73.0	20.2	52.8
10	90.5	39.8	50.7
20	119.5	74.4	45.1
30	143.0	101.1	41.9
40	160.5	122.8	37.7
50	176.5	143.7	32.8
60	192.8	165.3	27.5
70	209.0	188.0	21.0
80	225.2	210.4	14.8
90	242.8	235.0	7.8
100	260.5	260.5	0

The interpolated values for the vapour composition and the partial pressures were obtained with the aid of the abacus.* When the abacus is set up, a series of curves can be traced across it, one of which is the solution of the Duhem-Margules equation for the total pressure curve employed. This curve can be identified by one correct experimental determination, and the other determinations, if correct, and the equation applicable, must fall on the same curve. Tested in this manner, our results are consistent, and the curve taken appears to obey the boundary conditions, i.e. $n_1 = 0$, $p'_1 = 0$; $n_1 = 1$, $p'_1 = p_0$. Wrewsky's results, tested in this way, are slightly inconsistent, and the curve on which the values for his weaker solutions lie cannot possibly obey the boundary conditions. There is no curve indicated which can be fitted to the results of Bredig and Bayer, since a line joining the points on the abacus representing their results for the dilute solutions actually cuts across a number of the curves representing possible solutions of Clairault's equation.

Summary

The system methyl alcohol-water has been investigated at 39.90°C. by means of a new type of apparatus which requires only a small sample of material for each determination, and our results, together with those of former investigators, have been critically examined by means of Lash Miller's abacus.

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11 International Critical Tables, Vol. III (1928).

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[*] For general use a longer abacus than the one previously described is required. Our rods were 120 cm. long, 0.38 mm. square and accurately machined. The lines were engraved on the rods which made it possible to work directly on the brass with a grease pencil, instead of on a photograph. They were ruled for every one percent from 10 to 90 and were ruled to the envelope only, to avoid confusing cross-lines. The use of a fine wire attached to a weight, made the interpolation of the slopes quite rapid and accurate.

THE MUTAROTATION OF GALACTOSE

BY THOMAS MARTIN LOWRY AND GILBERT FREEMAN SMITH

In a recent paper[1] on "Consecutive Reactions in the Mutarotation of Glucose and Galactose," Worley and Andrews have produced evidence "that in each case there is an initial divergence from the subsequent uniform unimolecular nature of the change," but that "these divergences... are in agreement with the requirements of an action proceeding in two stages with the formation of an intermediate substance." The initial divergence was detected by working at 0°C, but, since "the velocity of mutarotation for a rise of 10°C is increased 2.8 times for glucose and 2.9 times for galactose," the authors conclude that "at 25° the initial divergence would be completed within the first two minutes after mixing" and that this fact "accounts for the divergence not being detected at 20° or 25° by the polarimetric method."

The conclusion thus reached is in accord with a series of recently-published observations,[2] whereby the unimolecular form of the mutarotation-curves was established "for glucose in aqueous methyl alcohol and for tetramethyl glucose in aqueous pyridine over a wide range of concentrations," including both water and the two almost anhydrous solvents, but without taking into account any observations made during the first few minutes, when deviations from the unimolecular law might be attributed to a lag in the adjustment of temperature. The conclusions of Worley and Andrews in reference to galactose do not agree, however, with the observations which we had already made with this sugar, since the mutarotation-curves for galactose do not conform even approximately to the unimolecular law, but exhibit a drift in the velocity coefficient of perhaps 25%, which can only be eliminated by ignoring all the readings taken during the first 20 minutes at 20°. The deviations are indeed of an entirely different order in the cases of glucose and of galactose, since all the mutarotation curves for galactose which have been plotted during the past forty years (with the exception of the recent observations of Riiber and Minsaas[3] show an unmistakable drift in the velocity-coefficient, whereas no similar drift can be discovered in any of the earlier observations on glucose.

The paper in which we first called attention to these persistent deviations[4] included a complete mathematical analysis of the mutarotation curves of α and β galactose in 5–10% solutions in water at 20°. This analysis showed that the experimental data conform exactly to the equations for *two consecutive unimolecular reactions*[5] as Worley and Andrews suspected on more general

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[1] J. Phys. Chem., 32, 307 (1928).

[2] Lowry: Z. physik. Chem., 130, 125 (1927). "Dynamic Isomerism of the Reducing Sugars."

[3] Ber., 59, 2266 (1926).

[4] J. Chem. Soc., 1928, 666.

[5] Lowry and John: J. Chem. Soc., 97, 2634 (1910).

grounds. It is therefore sufficient to postulate the presence of three sugars α, β and μ in the solution, although the presence of additional sugars cannot be excluded by an analysis of this kind.[1] If, however, we ignore the γ-sugars and make the rather unreasonable assumption that only three sugars are formed in an aqueous solution of galactose, our method of analysis enables us to calculate (i) the proportions of these sugars in the final equilibrium-mixture, (ii) the velocity-coefficients of the four unimolecular actions by which they are converted into one another, and (iii) the approximate rotatory power of the unknown intermediate sugar. The constants thus deduced for galactose at 20° were as follows:

$$\begin{array}{ccccc} \alpha & \underset{0.0404}{\overset{0.0207}{\rightleftharpoons}} & \mu & \underset{0.0788}{\overset{0.0159}{\rightleftharpoons}} & \beta \\ 28.5\% & & 12.0\% & & 59.5\% \\ 173^\circ & & 58^\circ & & 63.5^\circ \end{array}$$

where the figures in the last line are the specific rotatory powers $[\alpha]_{5461}$ of the three sugars.

In the present communication we have described a simplified process of analysis, whereby the empirical formulae of these more complex mutarotation curves can be deduced almost as readily as in the more familiar cases in which the curves conform to the unimolecular law. This method has then been applied in order to determine whether the velocity-coefficients are influenced by the concentration of the sugar in the solution. The new measurements which were made for this purpose show that this effect, if it exists, is too small to be detected on the scale of accuracy now available; the mutarotation-process therefore possesses the property, which is characteristic of unimolecular reactions in general, that the velocity-coefficients are independent of the concentration, at least to a first approximation. On the other hand, by analysing a series of data for the mutarotation of α and β galactose at 0.8°, we have been able to determine the influence of temperature on the coefficients of the equations, and to deduce a precise value for the temperature coefficient of one of the principal functions. The observations made at the

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[1] It has often been supposed (see for instance, Baker, Ingold and Thorpe: J. Chem. Soc., 125, 277 (1924)), that, if a mutarotation-curve obeys the unimolecular law, the third form of the sugar can only be a minor constituent of the equilibrium-mixture. A more complete mathematical analysis shows that this deduction is incorrect, since two consecutive reversible unimolecular actions give rise to unimolecular mutarotation curves whenever $k_1 = k_2$, $k_3 = k_4$ and $\alpha + \beta = 2\mu$ (Smith and Lowry: *loc. cit.*, p. 671). This statement is true for all values of the relevant constants, and is therefore valid even if the intermediate sugar is the principal product of isomeric change. A similar error is made by Worley and Andrews, *when they cite the absence of mutarotation in a synthetic mixture of α and β* glucose of suitable composition (which we had already established by our own experiments, see Cohen Festband, p. 144, footnote) as evidence that "if an intermediate substance is formed, the rate of its transformation into α and β glucose must be very much greater than that of its formation." This deduction is again incorrect, since mathematical analysis shows that if the preceding conditions are fulfilled, there are, as we pointed out, "no theoretical reasons for supposing that the formation of an equilibrium-proportion of the aldehydic sugar, at the expense of α and β sugars, could give rise to mutarotation in such a solution."

freezing-point also enabled us to compare the equilibrium-percentage of the α-sugar as calculated from our equations (which is entirely different from that deduced by Riiber and Minsaas) with the percentage deduced from measurements of the initial and final solubilities of the sugar in water at 0°.

Throughout this investigation we have used the method of analysis which is illustrated in Fig. 1. In this diagram, the experimental mutarotation curves for α and β-galactose are represented by the lines AF and CF. Analysis shows that the changes of rotatory-power for either sugar can be represented as the sum of two exponential terms. The mutarotation-curves can therefore be reproduced by plotting the algebraic sum of the ordinates of a simple unimolecular curve BF or DF, of *long* period, and of a unimolecular curve of *short* period, the ordinates of which are represented by the vertical lines which form the shaded areas of the diagram. In order to analyse the experimental data, it is therefore only necessary to extrapolate the unimolecular curves FG and FH back to zero time, in order to fix the position of the points B and D; the magnitude of the second exponential term can then be deduced from the differences between the observed curves AG, CH,

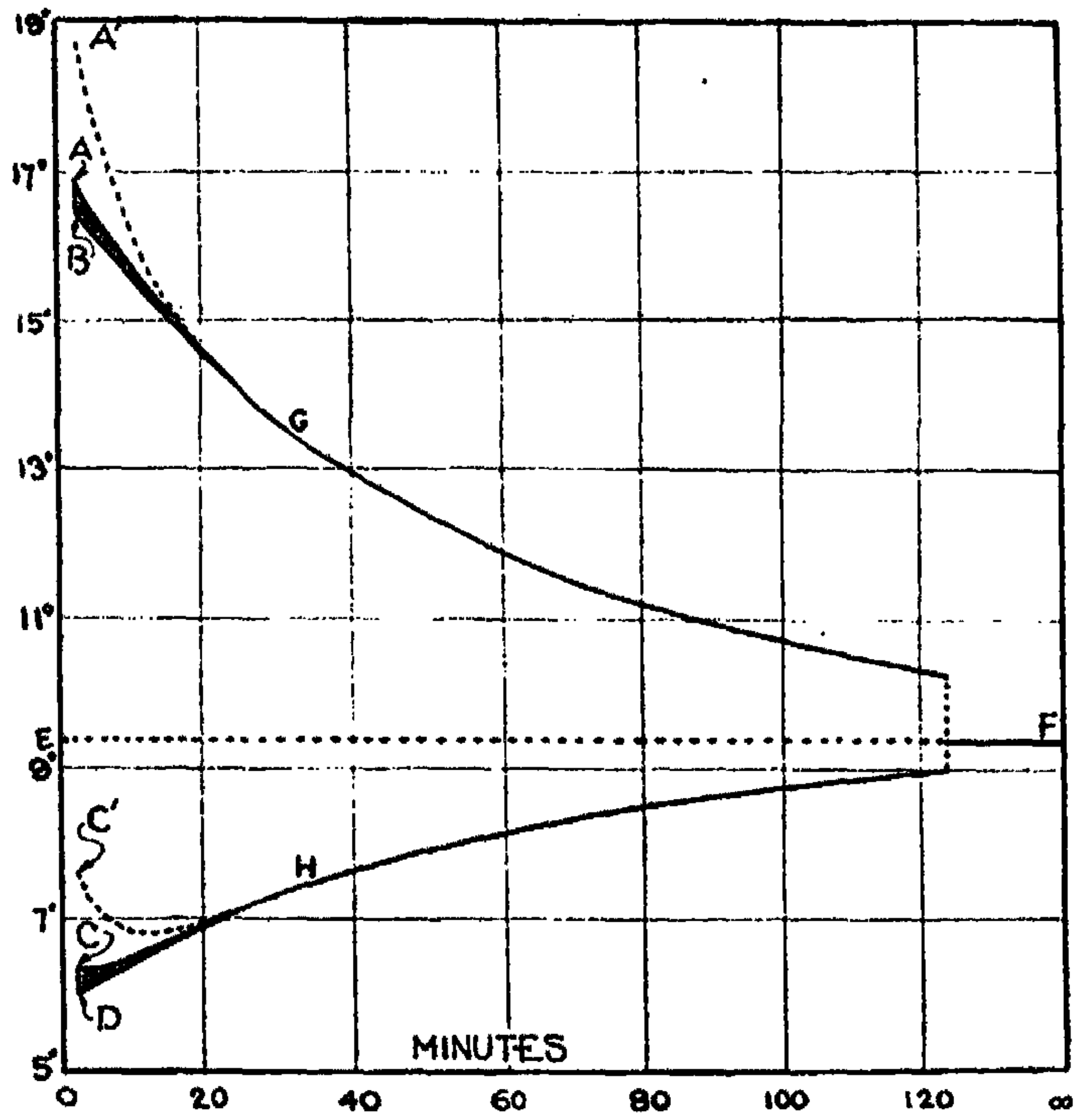

Fig. 1

Graphical analysis of the mutarotation curves for α- and β-Galactose in water at 20°. (The broken lines A′F, C′F show the effect of increasing five-fold the magnitude of the small short-period exponential term.)

and the extrapolated unimolecular curves BG, DH. In practice, it is found that, when extrapolated to zero time, the later readings give uniform values for the rotations at B and D, the magnitude of which can therefore be deduced from the average of a considerable number of independent observations. When the points G and H are reached, the extrapolated values begin to increase towards the limiting values A and C. The residual rotations, represented by the shaded areas in Fig. 1, can, however, be analysed as if they were independent unimolecular curves, in order to give the index of the short-period exponential. In this way, it is a simple matter to deduce the constants of the empirical equations

$$\Theta_\alpha = A_1e^{-m_1t} + B_1e^{-m_2t} + C. \quad \Theta_\beta = A_2e^{-m_1t} + B_2e^{-m_2t} + C.$$

As usual, however, when dealing with experimental data, certain practical limitations are encountered. In the present instance, the weakest feature of the analysis is the extreme sensitiveness of the exponent m_2 of the short-period term which is responsible for a maximum change of rotation of only about 1° to the effects of small variations in the value of the exponent m_1 of the much larger long-period term. Whilst, therefore, it is easy to fix the value of the principal exponent m_1 within about 1%, the values for the exponent m_2 of the small term can be varied by perhaps 25% by making minor adjustments in the value of m_1. The ultimate effect, in the case of galactose, is that, whilst the equilibrium-proportion of the *α*-sugar remains fixed at about 29%, even when the constants of the *empirical equations* are varied somewhat widely, much larger variations are found in the distribution of the balance of 71% between the *μ* and *β* sugars. The rotatory power deduced for the unknown *μ*-sugar is also extremely sensitive to variations in the constants of the equations.

The values of the two exponents deduced by *the preceding process* from the new data recorded in the present paper are summarised in Table I. It will be seen that the principal exponent varies only from 0.0184 to 0.0193

TABLE I

Exponents of Empirical Equations for the Mutarotation of *α* and *β* galactose

Sugar	Concentration	Temperature	m_1	m_2
α-Galactose	8%	0.8°	0.00216	0.037
β- "	10%	"	0.00216	0.037
α-Galactose	2½%	20°	0.0185	0.18
β- "	2½%	"	0.0192	0.26
α- "	7%	"	0.0184	0.18
β- "	7.7%	"	0.0192	0.26
α- "	13%	"	0.0190	0.25
α- "	15%	"	0.0186	0.18
β- "	15%	"	0.0193	0.25
			0.0189	0.22

for a temperature of 20°, but that three series of data for α-galactose at $2\frac{1}{2}$, 7 and 15% concentrations, which gave an average value $m_1 = 0.0185$, gave for m_2 the value 0.18, whilst the three corresponding series for β-galactose, for which $m_1 = 0.0192$, gave the value $m_2 = 0.26$; a similar value $m_2 = 0.25$ was given by the series for a 13% solution of α-galactose, for which the value of m_1 was 0.0190.

These data show clearly that the values of the two exponents are independent of the concentration of the sugar, within the limits of experimental error; and there is no reason to suppose that there is any real difference between the values for α and β-galactose, since the second exponent is the same for 13% α-galactose and for 15% β-galactose. On the other hand, a definite contrast can be drawn between the constants deduced for 8% α and 10% β galactose at 0.8°C and the constants already deduced for α and β-galactose at 20°C, as follows:—

$$\text{At } 20^\circ \left\{\begin{array}{l} \Theta_\alpha = 14.30e^{-0.0185t} + 1.40e^{-0.146t} + 18.8 \\ \Theta_\beta = \ \ 7.13e^{-0.0188t} + 1.03e^{-0.14t} \ \ + 18.8 \end{array}\right\} \begin{array}{l} k_1 = 0.0207 \ k_3 = 0.0159 \\ k_2 = 0.0494 \ k_4 = 0.788 \end{array}$$

$$\text{At } 0.8^\circ \left\{\begin{array}{l} \Theta_\alpha = 14.66e^{-0.00216t} + 0.62e^{-0.037t} + 19.75 \\ \Theta_\beta = \ \ 6.93e^{-0.00216t} + 0.46e^{-0.037t} + 19.75 \end{array}\right\} \begin{array}{l} k_1 = 0.00239 \ k_3 = 0.00180 \\ k_2 = 0.01344 \ k_4 = 0.2163 \end{array}$$

$$\begin{array}{l} \text{At } 20^\circ \ \alpha : \mu : \beta = 28.5 : 12.0 : 59.5 \ [\alpha] = 173^\circ, [\mu] = 58^\circ, [\beta] = 68.5^\circ \\ \text{At } 0.8^\circ \alpha : \mu : \beta = 30.0 : 5.5 : 64.6 \ \ [\alpha] = 175^\circ, [\mu] = 61^\circ, [\beta] = 66.4^\circ \end{array}$$

The temperature-coefficient of the principal exponent is given by these data as 0.0188/0.00216 for range of 19.2°, or a ratio of almost exactly 9 for 20°, or 3 for 10°C.

In making this comparison we have not considered it necessary to calculate fresh values for the constants at 20°, although the values of m_2 deduced by the simpler graphical method of analysis are higher than that deduced previously by a more complex mathematical analysis of the initial stages of mutarotation. The difference between these values is indeed perhaps a measure of the inaccuracy of the assumptions that must be made in order to carry out a mathematical analysis of data which conform so closely to the requirements of a three-sugar system. The values set out above are, however, inherently probable, at least as a first approximation, since they conform to the condition that the rotatory power of the intermediate μ-sugar must be nearly equal to that of β-galactose, as is indicated by the horizontal start of the mutarotation curve for the latter sugar, moreover, they indicate that the optical rotatory power of the unknown sugar is affected by changes of temperature only to the same small extent as are the directly-observed rotations of the α and β sugars.

The data set out above show that the proportions of α-galactose in the final equilibrium is not affected appreciably by small variations in the constants of the curves selected for analysis, and is, moreover, almost independent of temperature, whereas the proportions of the β and μ sugars are at the same time more variable and less trustworthy. It is, however, precisely at this point that our percentages differ most profoundly from the values deduced by Riiber and Minsaas, who give the ratio $\alpha : \mu : \beta = 6.61 : 27.35 : 60.04$ at 20°, where only the β-value agrees with our own, whilst the α-value is very much lower. Since, however, the α-sugar is the stable phase, it is possible to determine the percentage which persists in the final equilibrium by measuring its solubility in water before and after equilibrium has been attained, in accordance with a method developed for this purpose[1] in 1904 and applied in the same year to aqueous-alcoholic solutions of glucose and galactose.[2] These two sugars are too soluble to give trustworthy results when using water at ordinary temperatures, but the solubility in aqueous-alcoholic mixtures of various compositions showed that the proportion of α-galactose diminished from about 50% in anhydrous methyl alcohol to 35% in propyl alcohol containing 37 per cent of water. *In the present experiments* the solubility was reduced by making measurements at the freezing-point, where the calculated proportion of the α-sugar is 30% as contrasted with about 28% at 20°.

Some difficulty was experienced in finding the correct minimum solubility of the unchanged α-sugar, but after several trials a concordant value $\alpha_{5461} = 8.4°$, was obtained for the (final) rotatory power of the saturated solution when warmed up to 20° in the polarimeter tube. After a condition of equilibrium has been attained by prolonged stirring of the sugar with water at 0°, the corresponding reading was 22.6°. The proportion of the α-sugar in the final equilibrium-mixture is therefore $8.4/22.6 = 37\%$, on the assumption that its solubility in water is not affected by the presence of the α and β sugars. These measurements show immediately that the inherently-improbable ratio deduced by Riiber and Minsaas must be wrong, and that the higher percentage given by our own analysis is substantially correct. The difference between 30% and 37% can be taken as a measure of the errors introduced by the two assumptions (i) that the solubility of the α-sugar in grams per 100 cc. of solution is not affected by the presence of the products of isomeric change, and (ii) that only 3 sugars are concerned in determining the form of the mutarotation curves.

Experimental

Preparation of Materials. The α-galactose was recrystallized successively from acetic acid and ethyl alcohol. β-galactose was prepared by the method of Hudson and Yanovsky[3] and gave an initial specific rotation $[\alpha]_{5461} = 63.5°$, which was not reduced by several successive extractions with 80% alcohol.

Observations of Mutarotation. The galactose was weighed into a 20 cc. graduated flask and the reaction started by the addition of water at the requisite temperature. No accurate adjustment of the volume was attempted, since it was necessary to introduce the solution into the polarimeter tube very quickly in order to observe the rotation of the solution during the first two or three minutes. For this purpose the solutions were transferred

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[1] Lowry and Robertson: J. Chem. Soc., **85**, 1541 (1904).

[2] Lowry: J. Chem. Soc., **85**, 1551 (1904).

[3] J. Am. Chem. Soc., **39**, 1022 (1917).

TABLE II

Mutarotation of α-Galactose in Water at 20°

13 gm/100 cc. $\Theta_\alpha = 19.56e^{-0.0190t} + 2.27e^{-.025t} + 24.61$

Time	A_1	k	m_1	$A_1e^{-m_1t}$		$B_1e^{-m_2t}$		C		$\Theta\alpha$ (calc.)	$\Theta\alpha$(obs)	$\Theta\alpha$(O-C)
4.27	20.42			18.03	+	0.78	+	24.61	=	43.42	43.43	+0.01
4.90	20.28	0.0293		17.82	+	0.65	+	24.61	=	43.08	43.09	+0.01
5.42	20.20	0.0282		17.64_5	+	0.58	+	24.61	=	42.83_5	42.83	-0.00_5
6.07	20.11	0.0273		17.43	+	0.50	+	24.61	=	42.54	42.53	−0.01
6.72	20.01	0.0268		17.21	+	0.42	+	24.61	=	42.24	42.24	0.00
7.68	19.92	0.0261		16.90	+	0.33	+	24.61	=	41.84	41.83	−0.01
8.68	19.83	0.0255		15.59	+	0.26	+	24.61	=	41.46	41.43	−0.03
10.50	19.74	0.0244		16.02	+	0.16	+	24.61	=	40.79	40.78	−0.01
12.63	19.68	0.0239		15.38	+	0.10	+	24.61	=	40.09	40.09	0.00
14.72	19.60	0.0229		14.78	+	0.06	+	24.61	=	39.45	39.43	−0.02
17.15	19.60	0.0222		14.12	+	0.03	+	24.61	=	38.76	38.76	0.00
20.23	19.56	0.0217		13.31	+	0.01	+	24.61	=	37.93	27.95	+0.02
24.28	19.60	0.0212		12.29	+	0.005	+	24.61	=	36.91	36.93	+0.02
29.90	19.53	0.0207		11.08	+	—	+	24.61	=	35.69	35.69	0.00
33.55	19.53	0.0205		10.34		—	+	24.61	=	34.95	34.95	−0.02
37.48	19.57	0.0203		9.59_5		—	+	24.61	=	34.20_5	34.21	0.00
41.37	19.50	0.0202		8.91		—	+	24.61	=	33.52	33.49_5	-0.02_5
46.53	19.56	0.0200	0.0184	8.08		—	+	24.61	=	32.69	32.69	-0.02_5
56.13	19.52	0.0199	0.0189	6.73		—	+	24.61	=	31.34	31.33	0.00
61.30	19.51	0.0198	0.0187	6.10		—	+	24.61	=	30.71	30.70	−0.01
68.28	19.47	0.0197	0.0191	5.34		—	+	24.61	=	29.95	29.93	−0.02
80.52	19.45	0.0196	0.0190	4.23_5		—	+	24.61	=	28.84_5	28.84	-0.05_5
89.97	19.47	0.0196	0.0190	3.54		—	+	24.61	=	28.15	28.13_5	−0.015
97.60	(19.39)	0.0196	0.0191	3.06		—	+	24.61	=	27.67	27.64	−0.03
107.35	19.53	0.0194	0.0190	2.54		—	+	24.61	=	27.15	27.15	0.00
125.08	19.61	0.0193	0.0189	1.81_5		—	+	24.61	=	26.42_5	26.43	$+0.00_5$
∞	19.56										24.61	

to a 2 or 4 dcm, jacketed, polarimeter tube, through which water was pumped from a bath at constant temperature. In experiments at the freezing-point, cold water was circulated round the tube from a bath containing a mixture of ice and water; condensation of moisture was prevented by blowing a slow current of dry air directly on to the cold end-plates of the tube.

The data for a 13% solution of α-galactose at 20° are given in Table II, together with the numbers used in deducing the calculated rotations. Thus the extrapolated values of A_1 are given in column 2. Column 3 shows the values of the unimolecular velocity-coefficient, k_1, calculated in the ordinary way, whilst column 4 shows the values of the unimolecular coefficient, m_1, when the first half of the reaction was neglected and the coefficients were

TABLE III

Mutarotation of Galactose in Water at 20°

(a) 2½% α-Galactose

$\Theta_\alpha = 7.27e^{-.0186t} + .75e^{-.180t} + 9.51$

Time	θ cal.	θ obs.	Diff. (O-C)
2.68	16.89	16.89	0.00
3.25	16.77	16.77	0.00
3.93	16.64	16.64	0.00
4.60	16.51	16.51	0.00
5.53	16.35	16.36	+0.01
6.68	16.17	16.17	0.00
8.45	15.89	15.89	0.00
10.75	15.57	15.57	0.00
13.07	15.29	15.28	−0.01
16.12	14.94	14.92	−0.02
19.07	14.64	14.64	0.00
22.10	14.35	14.33_5	−0.01
25.80	14.03	14.01	−0.02
26.38	13.97	13.97	0.00
32.78	13.48	13.47	−0.01
38.20	13.10	13.09	−0.01
43.27	12.77	12.76	−0.01
50.38	12.37	12.38	+0.01
58.00	11.99_5	12.01	$+0.01_5$
71.25	11.46	11.44	−0.02
83.80	11.05	11.07	+0.02
98.08	10.68	10.69	+0.01
123.93	10.24	10.25	+0.01
135.53	10.10	10.10	0.00
∞	9.51	9.51	0.00

(b) 2½% β-Galactose

$\Theta_\beta = 3.51e^{-.0186t} + .48e^{-.180t} + 9.32$

Time	θ cal.	θ obs.	Diff. (O-C)
2.08	6.27	6.30	+0.03
2.65	6.28	6.27	−0.01
3.18	6.28	6.29	+0.01
3.68	6.29	6.28	−0.01
4.23	6.30	6.29	−0.01
4.68	6.31	6.30	−0.01
5.13	6.32	6.32	0.00
5.68	6.33	6.33	0.00
6.55	6.36	6.34	−0.02
7.75	6.40	6.39	−0.01
9.68	6.47	6.45	−0.02
11.75	6.55	6.53	−0.02
13.83	6.64	6.63	−0.01
16.60	6.76	6.75	−0.01
19.52	6.88	6.87	0.00
22.50	6.99	6.99	0.00
25.83	7.14	7.14	0.00
29.05	7.27	7.27	0.00
34.05	7.45	7.44	−0.01
37.30	7.50	7.50	0.00
42.30	7.71_5	7.72	0.00_5
48.12	7.88	7.88	0.00
54.25	8.03	8.04	+0.01
60.82	8.18	8.18	0.00
68.57	8.33	8.34	+0.01
87.12	8.62	8.61	−0.01
101.63	8.78	8.78	0.00
121.05	8.95	8.94	−0.01

TABLE III (Continued)

Mutarotation of Galactose in Water at 20°

(c) 7% α-Galactose

$\Theta_\alpha = 21.30e^{-0.0184t} + 2.20e^{-.182t} + 27.12$

Time	θ cal.	θ obs.	Diff. (O − C)
4.20	47.86	47.86	0.00
5.00	47.43	47.40	−0.03
5.97	46.94	46.93	−0.01
7.38	46.29	46.32	+0.03
8.75	45.70	45.70	0.00
10.18	45.12_5	45.12	-0.00_5
12.22	44.37_5	44.36_5	−0.01
14.25	43.63	43.65	+0.02
16.45	42.97	42.98	−0.01
17.30	42.71	42.70	−0.01
19.93	41.94	41.93	−0.01
23.43	40.99	41.00	+0.01
28.23	39.80	39.80	0.00
32.33	38.87	38.87	0.00
37.63	37.80	37.77	−0.03
43.28	36.72_5	36.72_5	0.00
52.47	35.23	35.23	0.00
59.10	34.30	34.30	0.00
66.72	33.37	33.34_5	-0.02_5
74.23	32.55	32.54	−0.01
84.28	31.64	31.62	−0.02
106.08	30.14_5	30.15	$+0.00_5$
119.35	29.49	29.51	+0.02
135.25	28.88	28.92	+0.04
150.10	28.47	28.50	+0.03
∞	27.12	27.12	0.00

(d) 7.2% β-Galactose

$\Theta_\beta = 5.57e^{-0.0192t} + .84e^{-.260t} + 14.57$

Time	θ cal.	θ obs.	Diff. (O − C)
1.60	9.72	9.71	−0.01
2.07	9.71	9.72	+0.01
2.42	9.70	9.71	+0.01
2.68	9.70	9.71	+0.01
2.98	9.70	9.70	0.00
3.30	9.70	9.68	−0.02
3.58	9.69	9.69	0.00
3.97	9.71	9.69	−0.02
4.27	9.71_5	9.71	-0.00_5
4.55	9.72	9.72	0.00
4.95	9.74	9.72	−0.02
5.25	9.75	9.73	−0.02
5.62	9.76	9.75	−0.01
6.00	9.78	9.78	0.00
6.55	9.81	9.80	−0.01
7.10	9.84	9.83	−0.01
7.83	9.89	9.87	−0.02
8.50	9.93	9.92	−0.01
9.48	10.00	9.99	−0.01
10.62	10.08	10.07	−0.01
12.32	10.21	10.19	−0.02
13.15	10.27	10.27	0.00
14.03	10.33	10.33	0.00
14.85	10.40	10.39	−0.01
16.50	10.52	10.52	0.00
18.53	10.67	10.67	0.00
21.30	10.87	10.87	0.00
24.77	11.11	11.10	−0.01
26.53	11.22	11.22	0.00
30.50	11.47	11.47	0.00
35.47	11.75	11.76	+0.01
38.03	11.89	11.90	+0.01
44.18	12.18_5	12.19	$+0.00_5$
48.22	12.36	12.36	0.00
52.35	12.53	12.53	0.00
62.70	12.89	12.89	0.00
67.67	13.05	13.06	+0.01
72.32	13.18	13.18	0.00
88.12	13.54	13.53	−0.01
98.43	13.73	13.72	−0.01
112.67	13.93	13.90	−0.03
∞	14.57	14.57	0.00

TABLE III (Continued)

Mutarotation of Galactose in Water at 20°

(e) 13% α-Galactose

$\theta_\alpha = 19.21e^{-0.0186t} + 2.05e^{-.135t} + 24.84$

(f) 15% β-Galactose

$\theta_\beta = 10.68e^{-0.0193t} + 1.66e^{-0.250t} + 28.20$

Time	θ cal.	θ obs.	Diff. (O−C)	Time	θ cal.	θ obs.	Diff. (O−C)
5.08	43.12	43.11	−0.01	1.70	18.96	18.97	+0.01
5.75	42.82	42.79	−0.03	2.27	18.92	18.95	+0.03
6.35	42.55	42.52	−0.03	2.75	18.92	18.93	+0.01
8.30	41.74	41.74	0.00	3.28	18.91	18.94	+0.03
9.97	41.11	41.10	−0.01	3.67	18.92	18.92	0.00
11.97	40.44	40.45	+0.01	4.55	18.95	18.97	+0.02
13.27	40.03	40.04	+0.01	5.38	19.00	19.02	+0.02
15.42	39.38	39.39	+0.01	6.27	19.09	19.09	0.00
17.97	38.75	38.75	0.00	7.62	19.22	19.22	0.00
19.50	38.26	38.28	+0.02	9.40	19.45	19.45	0.00
21.85	37.68	37.70	+0.02	11.87	19.79	19.78	−0.01
24.75	36.98	37.01	+0.03	14.47	20.15	20.15	0.00
32.00	35.33	35.35	+0.02	17.58	20.61	10.60	−0.01
35.07	34.86	34.86	0.00	21.22	21.12	21.08	−0.04
41.58	33.71	33.71	0.00	25.00	21.61	21.61	0.00
45.08	32.99	33.01	+0.02	29.00	22.10	22.09	−0.01
47.07	32.85	32.87	+0.02	33.77	22.63	22.63	0.00
51.32	32.24	32.27	+0.03	38.95	23.17	23.17	0.00
57.90	31.38	31.39	+0.01	45.87	23.80	23.80	0.00
59.50	31.20	31.20	0.00	53.90	24.43	22.43	0.00
64.50	30.62	30.61	−0.01	62.75	25.00	25.09	−0.09
74.32	29.60	29.60	0.00	73.73	25.63	25.63	0.00
85.00	28.75	28.74	−0.01	83.17	26.06	26.04	−0.02
100.10	27.83	27.84	+0.01	92.85	26.42	26.42	0.00
118.35	26.96	26.94	−0.02	103.53	26.75	26.75	0.00
136.38	26.36	26.37	+0.01	120.02	27.15	27.17	+0.02
∞	24.84	24.84	0.00	∞	28.20	28.20	0.00

deduced from the observations made at 41 minutes and onwards. The next three columns show the partial rotations calculated from the three terms of the equation, namely the long-period term (col. 5), the short-period term (col. 6) and the constant term (col. 7); the sum of the three terms is given in column 8, and the differences between the calculated rotations of column 8 and the observed rotations of column 9 are given in column 10.

The data for the mutarotation of 2½%, 7% and 13% solutions of α-galactose and for 2½%, 7.7% and 15% solutions of β-galactose at 20° are summarised in Table III. The equation that fits the mutarotation curve is given at the head of each series of data, and the differences between the calculated and observed values are shown in the ordinary way. In Table IV similar data are given for 10% solutions of α and β-galactose at 0.8°C.

TABLE IV

Mutarotation of Galactose in Water at 0.8°C

(a) 10% α-Galactose

$$\theta_\alpha = 14.66e^{-.000216t} + 0.62e^{-0.037t} + 19.75$$

Time	θ cal.	θ obs.	Diff. (O − C)
10	34.53	34.56	+0.03
13	34.38	34.43	+0.05
17	34.21	34.24	+0.03
22	34.00	34.02	+0.02
27	33.82	33.81	−0.01
32	33.62	33.60	−0.02
37	33.45	33.46	+0.01
42	33.27	33.26	−0.01
47	33.11	333.06	−0.05
56	32.82	32.77	+0.05
64	32.58	32.53	−0.05
72	32.34	32.33	−0.01
82	32.05	32.06	+0.01
94	31.74	31.70	−0.04
111	31.30	31.23	−0.07
130	30.82	30.82	0.00
153	30.29	30.28	−0.01
183	29.62	29.60	−0.02
232	28.63	28.63	0.00
253	28.24	28.24	0.00
297	27.47	27.50	+0.03
330	26.94	26.95	+0.01
370	26.34	26.34	0.00
[410	25.80	25.89]	
459	25.19	25.22	+0.03
476	25.00	25.03	+0.03
520	24.52	24.55	+0.03
550	25.22	24.24	+0.02
580	23.94	23.99	+0.05
631	23.50	23.53	+0.03
∞	19.75	19.75	0.00

(b) 10% β-Galactose

$$\theta_\beta = 6.93e^{-.000210t} + 0.46e^{-0.037t} + 19.75$$

Time	θ cal.	θ obs.	Diff. (O − C)
2.13	13.29	13.31	+0.02
3.05	13.28	13.31	+0.03
3.72	13.28	13.32	+0.04
4.93	13.27	13.32	+0.05
5.75	13.27	13.31	+0.94
6.72	13.28	13.31	+0.03
8.17	13.28	13.31	+0.03
9.65	13.28	13.30	+0.02
11.25	13.30	13.30	0.00
12.67	13.30	13.31	+0.01
14.48	13.30	13.31	+0.01
17.42	13.32	13.32	0.00
21.83	13.35	13.33	−0.02
23.70	13.37	13.36	−0.01
26.68	13.38	13.38	0.00
32	13.43	13.41	−0.02
40	13.49	13.48	−0.01
50	13.60	13.58	−0.02
65	13.77	13.75	−0.02
90	14.06	14.04	−0.02
110	14.30	14.28	−0.02
125	14.46	14.46	0.00
180	15.05	15.06	+0.01
200	15.25	15.26	+0.01
220	15.44	15.45	+0.01
240	15.62	15.63	+0.01
283	15.99	16.02	+0.03
325	16.32	16.33	+0.01
360	16.57	16.59	+0.02
391	16.77	16.78	+0.01
415	16.92	16.92	0.00
460	17.19	17.22	+0.03
505	17.42	17.44	+0.02
547	17.68	17.65	−0.03
593	17.83	17.84	+0.01
626	17.96	17.97	+0.01
∞	19.75	19.75	0.00

Measurements of Solubility. The saturated solutions were prepared by stirring the finely-powdered sugar (100 or 150 grams) with distilled water (150 or 200 cc.) in a bottle surrounded by melting ice. After stirring for not less than five minutes, 20 cc. of the solution were removed by means of a glass filter, and the rotation observed as soon as the solution had been warmed to 20°. A trace of ammonia was then added, and the equilibrium-rotation was observed; the concentration of the solution could then be deduced by comparison with the corresponding rotations of solutions of α-galactose of known strength. In order to determine the solubility of α-galactose in water, it was essential to use a sample which had been freed from all traces of β-galactose. For this purpose the finely-powdered sugar was stirred with water at 0° for about 10 minutes, and then drained as rapidly as possible. The residue had a lower solubility than the initial sample, but this was not reduced substantially by repeating the process.

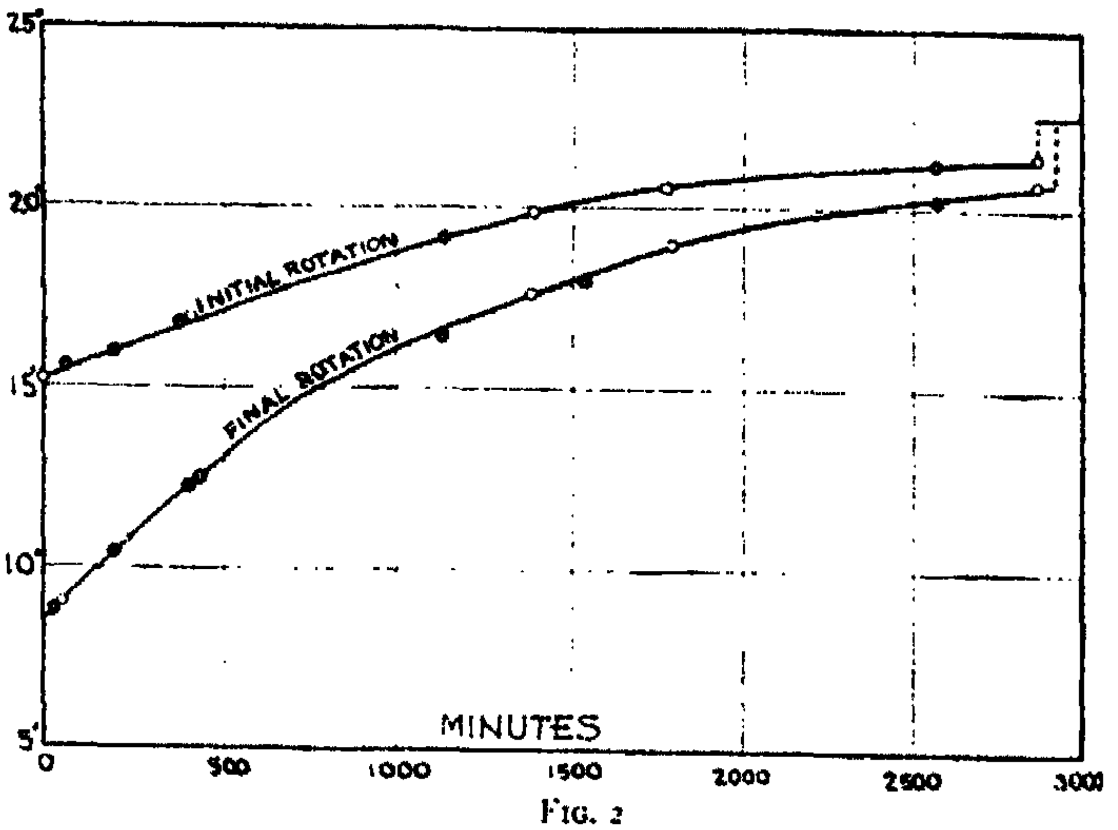

Fig. 2
Rotary Powers at 20° of Saturated Solutions of α-Galactose in Water at 0°.

The results obtained with two different samples of α-galactose before and after repeated extraction with ice-cold water are shown in Table V. The minimum rotation, $\alpha_{5461} = 8.4°$ in a 2 dm tube at 20°, is identical for both samples, and is probably correct within a few tenths of a degree, since almost the whole of the purification was effected in the first extraction, and the values recorded subsequently (8.0 to 8.4) appear to depend almost as much on the speed with which the process of purification was carried through, as on the number of times it was repeated. The final rotation, $\alpha_{5461} = 22.6°$, of the two samples, after saturation during a period several days, are also in close agreement with one another, and the ratio $8.4/22.6 = 37\%$ therefore appears to be substantially correct.

The experimental data for these two samples are set out in Fig. 2, where the upper curve shows the initial rotatory power of a series of cold saturated solutions immediately after warming up to 20°, whilst the lower curve shows the final rotations of these solutions. The two curves approach one another and become coincident when equilibrium is attained.

TABLE V

Rotatory Power at 20° of Saturated Solutions of α-Galactose in Water at 0°C

		Initial	Final
(1)	Sample A.	9.5°	
	Stirred with water	8.6	
	Stirred twice with water	8.4	22.55°
(2)	Sample B	9.65	
	Stirred once with water	8.9	
	Stirred twice with water	8.9	
	Stirred three times with water	8.6	
	Stirred four times with water	8.4	22.63°

Summary

(a) An account is given is a simplified method of analysing the complex mutarotation curves of α and β galactose.

(b) On the assumption that only 3 sugars are present in the equilibrium-mixture, the percentage of α-galactose is found to be about 30% both at 20° and at 0°C.

(c) The general correctness of this proportion (as contrasted with the 6.6% estimated by Riiber and Minsaas) has been shown by measurements of the solubility of α-galactose in water at 0°, which give an uncorrected proportion of 37% of the α-sugar in the equilibrium-mixture.

Laboratory of Physical Chemistry,
The University,
Cambridge, England.
June 7, 1928.

A STUDY OF THE REACTION BETWEEN NITRIC OXIDE AND HYDROGEN SULPHIDE*

BY J. A. PIERCE

Introduction

The only direct references to a reaction between hydrogen sulphide and nitric oxide without the aid of an electric spark may be found in two brief sentences in Gmelin-Kraut.[1] Thomson is here quoted as saying that hydrogen sulphide reacts with nitric oxide in a few hours to form a small amount of nitrous oxide and ammonium sulphide. LeConte is credited with replying that they do not react with one another.

In taking up an investigation of a possible reaction between nitric oxide and hydrogen sulphide we had, then, on one hand the contradictory statements of two chemists who labored in what has been aptly called the retort age of chemistry. On the other hand we had the unlimited field of the theories of present day chemistry to draw upon and convince us that such a reaction was theoretically possible. The instability of both nitric oxide and hydrogen sulphide from the thermodynamic point of view was, in itself, sufficient. Previous work in this Laboratory by Hasche and Patrick[2] on the nitric oxide-oxygen reaction convinced us that there was much potential resemblance between that reaction and the possible one between nitric oxide and hydrogen sulphide.

Our reasons for carrying on this work were, then:

(1) To determine whether or not nitric oxide reacts with hydrogen sulphide, and (a) If it does, to determine qualitatively the resultants of the reaction.

(2) To study the mechanism of the reaction: to determine whether it is an homogeneous gaseous reaction or one affected by the wall of the reaction chamber or by an added catalyst such as silica gel.

(3) Hinshelwood and Green[3] believe that, in reactions affecting nitric oxide, two molecules of nitric oxide always enter into the reaction. We wished to test the validity of this theory, and determine, if possible, a general explanation of the mechanism of reactions of this type.

(4) It is known that very few reactions possess a negative temperature coefficient. Practically all of those known have nitric oxide as one of the reactants. We wished to determine whether or not hydrogen sulphide shared with bromine, chlorine, oxygen and hydrogen this same peculiarity.

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* Contribution from the Chemistry Laboratory of the Johns Hopkins University. Constructed from part of a dissertation presented by J. A. Pierce to the Board of University Studies of the Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy. This work was suggested by Doctors W. A. Patrick and J. C. W. Frazer and carried out under their personal supervision.

[1] "Handbuch der anorganischen Chemie," II, 256 (1907).

[2] J. Am. Chem. Soc., 47, 1207 (1925).

[3] J. Chem. Soc., 1926, 730.

(5) Our preliminary qualitative work showed us quite clearly that the reaction between nitric oxide and hydrogen sulphide was not reversible and, from theoretical aspects, could not be reversible—that it should go to completion. However, we found a rapid drop in the rate of the reaction and a state of equilibrium rather difficult to explain on any grounds other than that of inhibition by one of the resultants. We wished to investigate this as fully as possible.

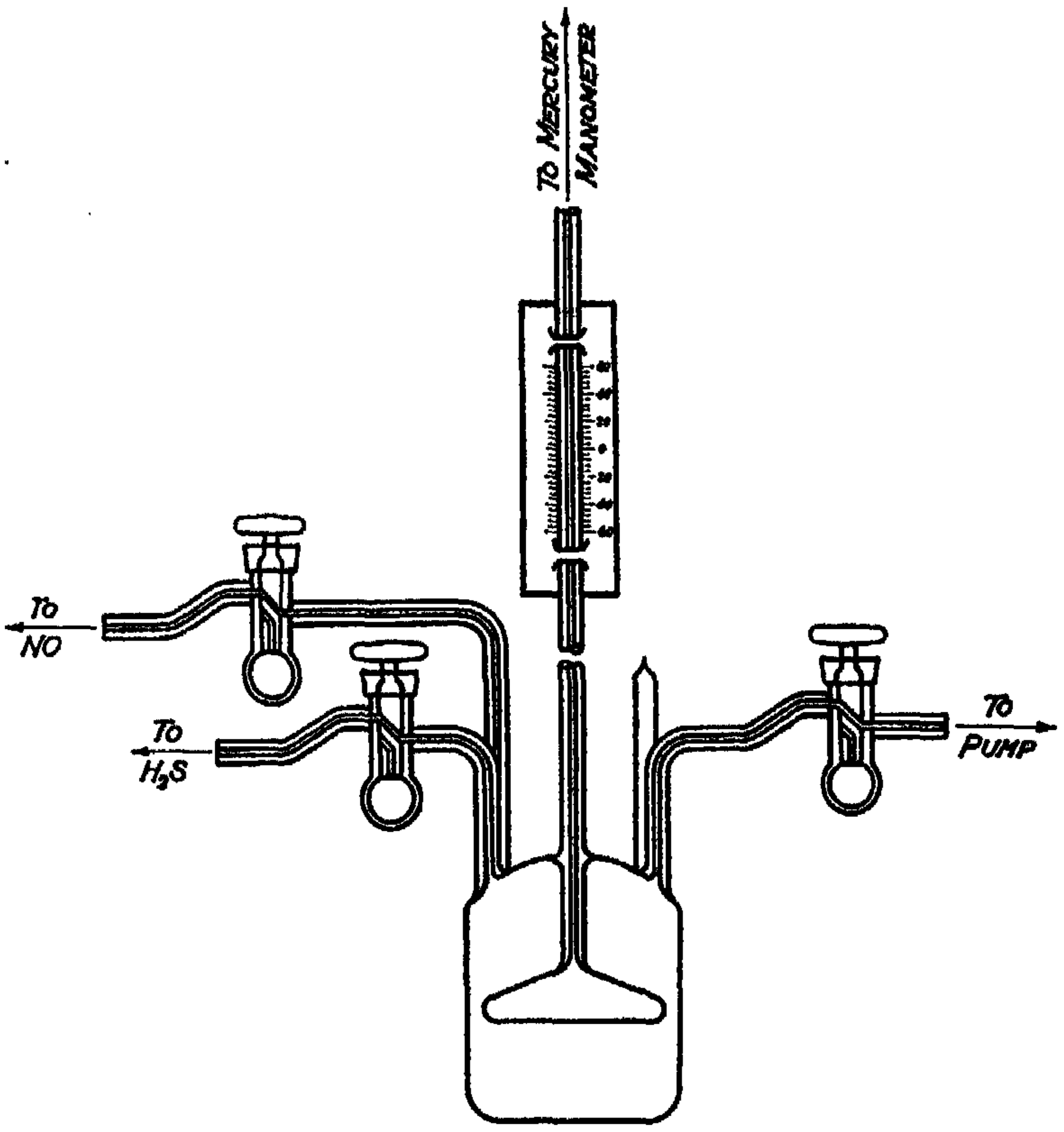

Fig. 1

Apparatus

The essential part of the apparatus used in this work consisted of a modified form of the Klemenc[1] manometer attached to a capillary mercury manometer provided with a leveling bulb. The simplicity of the apparatus eliminated many variables in the carrying on of the work.

Fig. 1 shows in detail the arrangement of the Klemenc manometer as modified by us.

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[1] J. Am. Chem. Soc., 47, 2173 (1925).

The funnel-shaped chamber in the interior of the reaction flask has walls of heavy Pyrex, while the bottom is of extremely thin Pyrex. This thin diaphragm is sufficiently thick to endure continual stress, but thin enough to respond instantly to any pressure exerted upon it. It was necessary to make several of these manometers before one was obtained which would give satisfactory results throughout a long period of use. The one finally accepted for the work is sensitive to at least 0.1 millimeter of mercury.

The funnel-shaped chamber has, as its stem, a one-millimeter capillary tube 40 centimeters in length. By evacuating the chamber with its stem under a fluid, and then releasing the pressure, the liquid was brought into the funnel and up the stem to any desired height. This capillary stem was provided with a sliding gauge, the zero point of which was set at the meniscus of the fluid when the reaction chamber was at a pressure of one atmosphere.

The fluid used in our work was alpha-bromonaphthalene fractionated to a constant boiling point and colored purple for greater ease in reading the meniscus. This compound was chosen for its high boiling point, low vapor pressure and low viscosity. Its greatest objection for work of this type is its large coefficient of expansion, which made it necessary for us to have the temperature of the thermostat constant to at least 1 500° C. However, it offers advantages not to be found in any other fluid we investigated.

Stopcocks used were of the Greiner type. When properly fitted a test extending over a week failed to show gaseous diffusion of any measurable magnitude.

The mercury manometer was of the usual type, open at one arm and provided with a leveling bulb. The bore of the glass tubing used was 2 millimeters, insuring delicacy of reading.

Projecting beyond the stopcocks were three tubes of capillary dimension: one leading to the pump, one to the source of hydrogen sulphide and the third to the source of nitric oxide. The sealed tube shown in the figure and projecting vertically was used for the admission and removal of silica gel and glass wool.

On account of the fact that it was necessary to remove the Klemenc manometer from the rest of the apparatus nearly every day for the purpose of changing the catalyst it was considered inadvisable to have glass-sealed connections between it and the other parts of the apparatus. Only three rubber connections were used, however, and these consisted of short pieces of heavy suction tubing securely wired and completely covered with Duco lacquer.

Evacuation was carried out by means of an oil pump of the most recent design. Experimental use of a mercury pump and a McLeod gauge demonstrated that, no matter how many precautions were taken, hydrogen sulphide gas would penetrate through these pieces and render their accuracy doubtful. Since complete removal of oxygen was of more importance than a high vacuum, it was found that an oil pump alone, with intermittent flushing with oxygen-free nitrogen, was the better usage.

The thermostat consisted of a ten-gallon oil bath fitted with propeller and the usual type of electrically controlled thermoregulator. It was found possible to control the temperature over a reasonable length of time to almost 0.001°C. Variation was rarely greater than 0.05°C, and in such cases the experiment was considered void.

The reaction chamber was immersed in the oil bath until all parts of it were submerged except the stopcocks and the capillary stem.

The Klemenc manometer functioned in the following manner: With atmospheric pressure in the reaction chamber the column of alpha-bromonaphthalene remained—at constant temperature—at a height which may be designated as *A*. The sliding gauge was moved so that its zero point coincided with the meniscus of *A*. Evacuation of the reaction chamber by the pump caused a downward pull on the thin glass diaphragm, and lowered the column of alpha-bromonaphthalene exactly 60 millimeters. (The exact and constant lowering of 60 millimeters throughout the work indicated that the diaphragm had lost none of its original flexibility.) When gas was allowed to enter the chamber the column of fluid ascended to a height proportionate to the amount of gas admitted. The pressure of this gas could be measured by moving the leveling bulb and forcing the alpha-bromonaphthalene column back to its original zero point. This balancing pressure, subtracted from the existing barometric pressure, gave the pressure of the gas in millimeters of mercury. This is in accord with the technique of Klemenc.

Exhaustive preliminary experiments were made to determine the direct ratio between pressure and volume as indicated by the rise and fall of the alpha-bromonaphthalene column. These results—plotted—gave a straight line which agreed, within the limits of experimental error, with calculated results. It was thus possible to measure accurately the volume of the gas in the reaction chamber at any time by the pressure exerted upon the diaphragm. To simplify the work and eliminate the necessity of using gas burettes and confining fluids, the measurement of the gases was carried out by determining their partial pressures and calculating the volume from the curve previously mentioned.

In actual experimentation the initial total pressure of the gases was found. As the reaction proceeded and the total volume of the gases diminished, this decreased volume was determined by observing the decreased pressure. A change in pressure of 0.1 millimeter of mercury was easily read.

Materials

Hydrogen sulphide came compressed in cylinders and was 99.73% pure, the chief impurities being air and moisture. Oxygen was removed by passing the gas over ferric oxide heated to 100°C, water by passing through phosphorus pentoxide. Moore's[1] recommendations as to the purity of liquid hydrogen sulphide were accepted.

Nitric oxide was made by treating sodium nitrite (C. P.) with dilute sulphuric acid (C. P.) according to the method of W. A. Noyes.[2] It was

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[1] Ind. Eng. Chem., 17, 1023 (1925).

[2] J. Am. Chem. Soc., 47, 2170 (1925).

collected over water and dried by passing it through sulphuric acid. No nitric oxide over three weeks old was ever employed.

Nitrogen, used for flushing out reaction chambers and gas containers, was of commercial grade. Oxygen was removed by passing through several columns of freshly prepared pyrogallol solution.

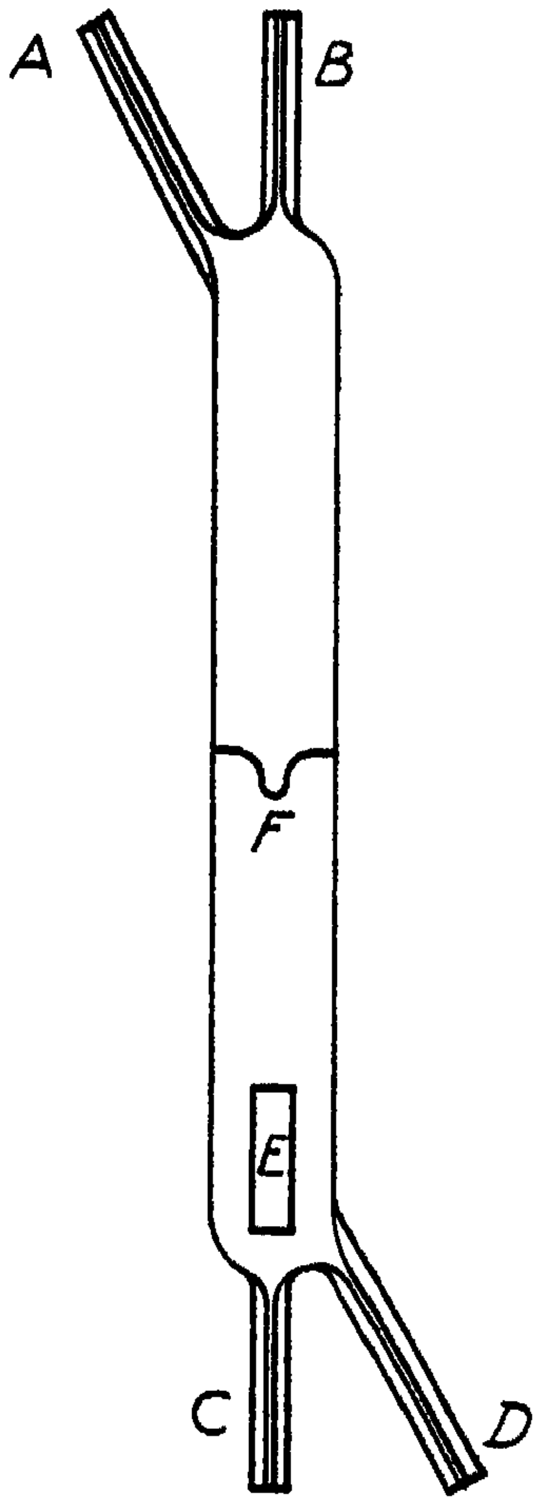

FIG. 2

Aside from treatment with phosphorus pentoxide and sulphuric acid no attempt was made to super-dry the gases.

Silica gel was employed in two forms: one was considered to be chemically pure silicon dioxide and the other to contain one percent of ferric oxide. Both were made by the Patrick process.

Glass wool was of the best grade and was strictly lead-free.

Experimental

Qualitative Part:

A few preliminary qualitative experiments were carried on before attempting quantitative work. There was placed in one section of the tube, (Fig. 2) about one gram of silica gel. The tube C was sealed: the open tube D was connected with an oil pump. The apparatus was immersed in an oil bath at 125°-150° C for three hours in an evacuated condition. Oxygen-free nitrogen was run into the chamber by slipping a rubber tube over C and breaking the glass tube at a previously scratched point within the rubber. Tube C was again sealed and the chamber once more evacuated with heating. Tube D was then sealed and oxygen-free hydrogen sulphide was run in through C as previously described until a pressure of approximately one atmosphere was obtained. Tube C was then finally sealed. Nitric oxide was run into the other section of the chamber through A and allowed to pass out through B for several minutes after all indications of a yellow color had disappeared. Tubes A and B were then sealed, the chamber inverted and the diaphragm broken by the falling of the glass rod *E*. Several of these tubes were prepared. A few were allowed to remain at room temperature for varying lengths of time while others were heated to 105° C for three hours and then put aside.

Quantitative Part:

(A) *In the case where silica gel catalyst was used.* (1) The evacuated reaction chamber of the Klemenc apparatus containing the dried and evacuated gel, and with the gas containers attached was brought to constant temperature. (2) A record was made of, (a) the thermostat temperature, (b) the room temperature, (c) the barometric pressure. (3) The sliding gauge was adjusted so that its 60-millimeter point coincided with the meniscus of the alpha-bromonaphthalene column. (4) Hydrogen sulphide was run in to elevate the alpha-bromonaphthalene column from 60 millimeters to 33.75 millimeters, which represents a volume of 75 cubic centimeters of hydrogen sulphide according to calibration experiments previously described. (5) The hydrogen sulphide was allowed to come to the temperature of the thermostat and to reach a state of adsorption equilibrium with the gel. This usually took about three minutes. (6) Nitric oxide was run in sufficiently to raise the level of the alpha-bromonaphthalene column 26.25 millimeters above the level then existing. (On account of the fact that reaction started the instant nitric oxide began to flow into the chamber it was not possible to obtain the partial pressure of this gas after it had reached the temperature of the thermostat. However, we assumed that, for practical purposes, the partial pressures of the two gases would be of equal value. It required less than three seconds to flow the gases into the chamber.) (7) An immediate reading of the pressure was made with the mercury manometer. (8) Further readings were made at the end of each minute for five minutes, then every five minutes for half an hour, and then every ten minutes until the experiment was concluded. (9) Beckmann thermometer and barometer observations were made at the end of each pressure reading at the termination of the first five minutes. Fluctuations in temperature were watched closely, and, in those cases where the thermoregulator got out of control, the experiment was discontinued and all observations discarded.

Where silica gel was used as catalyst a lowering of pressure was noted as soon as hydrogen sulphide was run in. This is ascribed to adsorption of the gas by the gel in the case of the chemically pure gel, and combined adsorption and reaction in the case of the iron-impregnated gel. A record of such depression was kept. This varied from 0.5 to 5.0 millimeters of alpha-bromonaphthalene according to the form of the gel and the temperature.

Fresh gel was used in each experiment and was previously treated by heat and evacuation to remove water and foreign gases.

(B) *In the case where no added catalyst was used.* The technique was the same as described in the preceding section except that the preliminary procedure consisted merely of heating the opened reaction chamber at about 125° C to remove accumulations of sulphur by oxidation, and to evaporate off water. The success of the treatment was probably variable, and led to some lack of uniformity of results.

(C) *In the case where glass wool was used.* The technique was exactly as in the case where no added catalyst was used. Five grams of glass wool was employed, care being taken to prevent its pressing on the diaphragm.

Results

Qualitative:

Experiments with the sealed tubes showed conclusively that a reaction took place between nitric oxide and hydrogen sulphide. This was indicated, (1) by a rise in temperature, (2) condensation of water on cooled surfaces, (3) the gradual formation of a film of sulphur on the walls of the tube and the surface of the catalyst, and (4) a decrease in pressure of the gases.

Experiments with these tubes were made with chemically pure and iron-impregnated silica gel catalysts. In the former case the pure white gel gradually assumed a lemon-yellow color due to incrustations of sulphur; in the latter case the orange-colored gel (blackened by reaction with hydrogen sulphide) slowly regained, to a limited extent, its original color.

The tube, a tip having been broken under water, showed a decrease in the original pressure of one atmosphere. No attempt was made to determine exact measurements of this decrease.

The water which entered the tube was allowed to remain until the soluble contents were believed to have dissolved. Standard tests for ammonium sulphide were negative. It is assumed, therefore, that the results of Thomson, previously cited, are in error, and, as a corollary, the statement of LeConte that the gases do not react, is without foundation.

Tubes left at room temperature for as long as six months and then opened to the air showed evidence of an equilibrium having been attained. This was indicated by the fact that the entrance of oxygen to the mixed gases formed more sulphur. That is, the reaction between nitric oxide and hydrogen sulphide having stopped, the formation of nitrogen peroxide by contact with air caused further reaction with the remaining hydrogen sulphide. Since the reaction between nitrogen peroxide and hydrogen sulphide is more rapid and more readily visible, the proof of unreacting hydrogen sulphide and nitric oxide in the unopened tube was established.

When iron-impregnated silica gel was used as catalyst the black color of the gel, due to reaction with hydrogen sulphide, was destroyed very slowly and very imperfectly in those cases where the tubes were left at room temperature. Tubes heated above the subliming temperature of sulphur, however, had their catalyst content restored almost to the original orange color. This bleaching process could be checked by again cooling the tube. From this we are led to believe that the removal of the sulphur from the surface of the catalyst eliminated the conditions effecting the equilibrium. That this continuation of the reaction at a higher temperature is not due to a positive temperature coefficient will be discussed in the Quantitative Part.

There are only two stoichiometric possibilities involved in a reaction between nitric oxide and hydrogen sulphide: (1) $H_2S + 2NO \rightarrow N_2O + H_2O + S$ and (2) $2H_2S + 2NO \rightarrow 2H_2O + 2S + N_2$. Briner and Meiner[1] state that N_2O is not a product of the thermal decomposition of nitric oxide. This is a direct rebuttal to the statement of Briner and Boubroff[2] who had

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[1] J. Chim. phys., **23**, 609 (1926).

[2] Comp. rend., **156**, 288 (1913).

reported thirteen years before that N_2O is a resultant. Thermodynamic concepts also show us, through free energy calculations, that the reaction is more likely to proceed $2H_2S + 2NO \rightarrow 2H_2O + 2S + N_2$. We have, therefore, accepted this as the basis of the quantitative work.

Quantitative:

Work with the Klemenc manometer confirmed the results obtained qualitatively.

Experimental work in this section was divided into four series as follows:

(A) In which the gases were allowed to react in the chamber containing no added catalyst.

(B) In which 1.5 grams of chemically pure silica gel served as catalyst.

(C) In which 1.5 grams of chemically pure silica gel impregnated with 1 percent of ferric oxide acted as accelerator.

(D) In which the reaction chamber was stuffed with 5 grams of lead-free glass wool.

Experiments in Series (A), (B) and (C) were made at 28°, 38°, 75° and 100° C. In Series (D) work was carried on at 28° and 100° C. A total of forty-six experiments were made—an average of 3.3 duplications. The first ten were rejected as having been made to establish a technique and to give us an opportunity to correct errors in the apparatus before attempting formal work. A few others were discarded on account of obviously faulty temperature control. The others checked well with their duplicates: this statement being subject to further comment under Discussion of Results.

In Series (A) no decrease in the partial pressure of the hydrogen sulphide due to adsorption was observed although it was very noticeable in the other series. In Series (D), where glass wool was used there was a depression within the limits of 0.5 and 0.1 millimeters of alpha-bromonaphthalene. The absence of a similar depression in Series A is thus considered to be comparative, and dependent upon the extent of the surface.

When nitric oxide was admitted to the chamber, already partially filled with hydrogen sulphide, a rise in pressure always occurred in Series (A) and (D), but never in Series (B) and (C). This increased pressure continued for four or five minutes and had variable values betwen 0.5 and 2.0 centimeters of mercury. This upward tendency of the curve is considered to be the resultant of vapor pressure, heating effect of adsorption and the downward pull of the reaction. For this reason, the first observations of pressure were discarded and the initial pressure, P_o, was taken as the first steadily decreasing point on the curve. At the termination of these initial variations curves of all series showed a rapid downward inclination for about forty minutes, and then almost abrupt flattening.

An increased rate of reaction in the presence of glass wool as compared with that where no added catalyst was used affirms our previously derived belief of hetergeneous reaction between these gases.

A direct comparison of the rate of reaction at 28° and 100°C shows a negative temperature effect.

Method of Calculation

Mathematical interpretation of the work was not entirely satisfactory. At the first attempt to find an equation to fit the rate of reaction we were confronted with positive evidence of an inhibitor. Calculations were also complicated by inadequate knowledge of the amount of water vapor each catalyst was capable of adsorbing under the existing conditions, and by a doubt as to the exact interpretation of the initial rise in pressure in experiments of Series (A) and (D). We were also badly handicapped by absence of precedents; the literature on inhibition being very vague as to exact methods of calculation.

We investigated at great length the Freundlich equation, the differential form of which is: $dc/dt = kc^{1/n}$. It failed utterly in our case, no matter what value we gave to n. It was evident that inhibition increased as the reaction proceeded.

Working from the equation: $dx/dt = k(a - x)^n - x$, a purely empirical expression was derived which finally gave fair interpretive results. Due to the unwieldy form of the equation in its integrated form when n was greater than unity, we adopted the mirror method of Latshaw[1] of this Laboratory, whereby dx/dt was determined from the tangent to the curve at each point. The integer, x, does not represent the decrease in the pressure of the volume of gas which has reacted at any particular time, but is a derived value. In the reaction $2NO + 2H_2S \rightarrow 2H_2O + N_2 + 2S$, we have started with four volumes of gas. If the reaction goes to completion we have one volume of nitrogen and two volumes of water vapor—a total of three volumes. If a is given a value of unity, a decrease of three-fourths in the pressure would mean that the reaction is complete, and $(a - x) = 0$. The value of x would be unity: a fractional change being expressed as $4/3\ \Delta P/P_0$.

A new set of curves was drawn, plotting this value of x against time in minutes, and determining dx/dt by Latshaw's method. It was then found that the modified expression, in which a represented unity and $x = 4/3\ \Delta P/P_0$ had the same defect as the Freudlich equation, and the original on which ours was based; i. e., there was a steady drop in the velocity constant. After considerable experimentation we found that if, in this equation, we substituted p for a and gave to p the observed pressure at the time t, and then divided the final x by some whole number N, fairly good constants were possible. N was found to be a large numeral, usually 25 or 50. Our equation then became: $dx/dt = k(p - x)^n - x/N$. The magnitude of the divisor N is probably a measure of the extent of the inhibition plus a measure of the condition of the reaction chamber at the beginning of the experiment. That is, if sulphur is the inhibitor and its increase in the reaction chamber in one particular experiment over that in some other experiment makes it necessary to increase the divisor, then any sulphur remaining in the reaction chamber

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[1] J. Am. Chem. Soc., 47, 793 (1925).

from a previous experiment would require a further increase in the value of the divisor. We did not realize, at the beginning of the work, the negative character of colloidal sulphur. We used reasonable care in oxidizing residual sulphur at the end of each run in preparation for a new experiment, but it is evident from the mathematical results we have obtained that our reaction chamber was not always in a standardized condition. We believe, however, that, in those cases where the divisor of one final x is equal to the divisor of the final x in another experiment, conditions may be considered as being identical, and on those cases we have determined the character of the temperature coefficient. We obtained particularly good results in Series (D); the experiments of Series (B) and (C) being the most unsatisfactory.

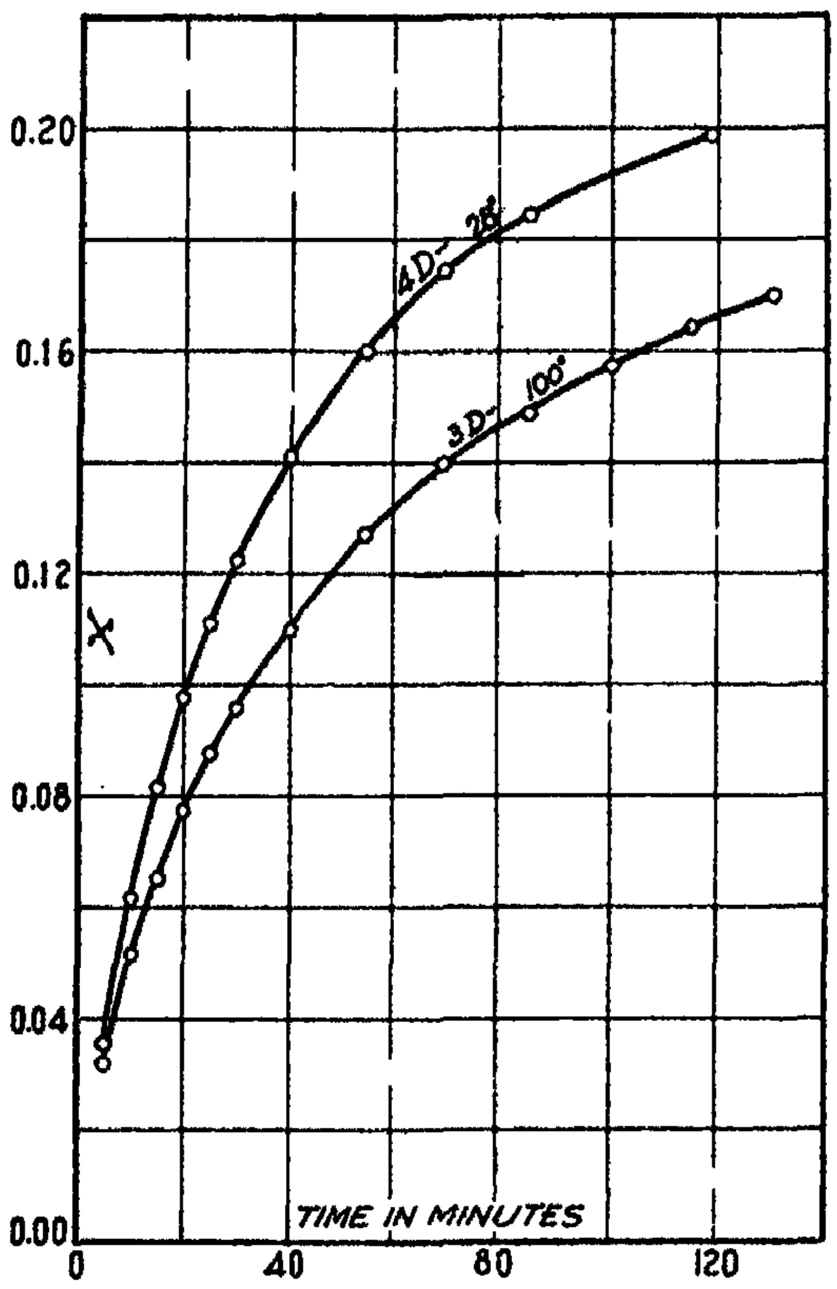

Fig. 3

The results of the measurements of two experiments in Series (D) (at 28° and 100° C) are given in Tables I and II, and are shown graphically in Fig. 3.

Temperature Coefficient

$K_{100}/K_{28} = 0.847$

TABLE I

Experiment 4-D 28° C; $P_0 = 67.89$ cm Hg; $dx/dt = k(p - x)^3 - x/50$

(T min.)	P	x	$(p - x)^3$	dx/dt	$K \times 10^{-9}$
15	4.15	0.0815	311776	0.00333	159
20	4.90	0.0979	311556	0.00281	153
25	5.97	0.1110	311377	0.00229	145
30	6.24	0.1225	311210	0.00195	141
40	7.19	0.1412	310963	0.00150	139
55	8.17	0.1604	310701	0.00105	137
70	8.89	0.1745	310495	0.00079	138
85	9.39	0.1844	310371	0.00060	138
				Mean:	144

TABLE II

Experiment 3-D 100° C; $P_0 = 67.0$ cm Hg; $dx/dt = (p - x)^3 - x/50$

(T min)	P	x	$(p - x)^3$	dx/dt	$K \times 10^{-9}$
10	2.00	0.0517	300003	0.003090	137
15	3.30	0.0653	299888	0.002570	129
20	3.90	0.0770	299714	0.002080	121
25	4.40	0.0875	299579	0.001800	118
30	4.82	0.0959	299472	0.001574	116
40	5.52	0.1099	299284	0.001234	114
55	6.50	0.1270	299050	0.001000	118
70	7.00	0.1393	298805	0.000768	119
85	7.50	0.1488	298761	0.000613	121
100	7.92	0.1570	298640	0.000498	127
				Mean:	122

Discussion of Results

The assumption of Thomson that nitric oxide and hydrogen sulphide react to form ammonium sulphide and nitrous oxide is obviously incorrect—absence of the former by qualitative tests being sufficient indication of this. The counter-claim of LeConte that the gases do not react at all is, likewise, refuted. That they do react with formation of water, sulphur and nitrogen is confirmed by our work.

(A) *Mechanism of the Reaction.*

However, the simple stoichiometric equation: $2NO + 2H_2S \rightarrow 2H_2O + 2S + N_2$ does not represent the actual mechanism of the reaction. It is this which we propose to discuss in this section.

Those known reactions in which nitric oxide is a constituent possess peculiarities which have been the subject of much investigation during the past few years. Work on reactions in which nitric oxide is involved is subject to many difficulties, the chief of which is the necessity of absolute exclusion of air. However, the investigations of recent years have been so uniform in their essential results that there are certain principles which we may accept with confidence. One is the theory of Hinshelwood and Green[1] that in reactions of nitric oxide two molecules of this gas are always involved. Another is that in such reactions as $2NO + O_2 \rightarrow 2NO_2$,[2] $2NO + Cl_2 \rightarrow 2NOCl$,[3] $2NO + Br_2 \rightarrow 2NOBr$[4] and $2NO + H_2 \rightarrow N_2 + 2H_2O$[5] there is found either a negative temperature coefficient or a very slight positive one. The extreme rareness and doubtful authenticity of termolecular reactions points to the possibility of intermediate compound formation in all of these. Hasche and Patrick (loc. cit.) have demonstrated in their work on the nitric oxide-oxygen reaction the formation of an intermediate of the composition N_2O_3 to account for the apparent third order of their reaction.

We could, with some assurance, postulate in our reaction the formation of an intermediate compound of the composition NOS. In doing so we would be conforming with the results of other investigators in reactions of nitric oxide who have proposed other additive nitrosyl compounds to explain the peculiarities of their results. However, it is quite unnecessary to do this. We prefer to present the theory of selective adsorption.

We have evidence that the reaction takes place on the wall of the chamber and on the surfaces of the catalysts. The condition of the reactants in these adsorbed zones is similar to that found where intermediate compound formation is indicated. That is, forces are brought into play which are similar in their general effect to those present when intermediates are formed. The objection which might be raised against this theory is that we could not, ordinarily, expect nitric oxide to be strongly adsorbed. However, the nitric oxide molecule is strongly reactive and we meet this difficulty by assuming the association of two nitric oxide molecules with the resultant formation of one molecule of N_2O_2, a supposition supported by Langmuir.[6]

This association of two nitric oxide molecules could reasonably be expected to occur in greater amounts at lower temperatures, and to be incomplete enough at any temperature to escape detection by ordinary density measurements. It would be more easily condensible on the surfaces than the nitric oxide and would, therefore, be adsorbed by the wall in preference to the nitric oxide. The hydrogen sulphide may thus be imagined as impinging on the adsorbed N_2O_2 molecule, and our original stoichiometric equation would become $N_2O_2 + 2H_2S \rightarrow N_2 + 2H_2O + 2S$.

Investigation of the critical temperature of the resultants of this reaction indicate that water and sulphur should, in their turn, be more strongly adsorbed than N_2O_2. Therefore, the surface is denuded of its N_2O_2 and re-

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[1] J. Chem. Soc., **1926**, 730.
[2] J. Am. Chem. Soc., **47**, 1207 (1925).
[3] Z. anorg. Chem., **88**, 283 (1914).
[4] Z. anorg. Chem., **102**, 149 (1918).
[5] J. Chem. Soc., **1926**, 730.
[6] Taylor, "Treatise on Physical Chemistry", (Dushman) II, 1072.

placed by sulphur in a colloidal form. The extremely high critical temperature of sulphur is the foundation of our belief.

It is axiomatic in colloidal chemistry that like substances are adsorbed most strongly by like substances. We may, accordingly, assert the strong possibility of active adsorption between sulphur and hydrogen sulphide, and expect the surface of the sulphur to be coated with an adsorbed film of hydrogen sulphide in preference to one of any other constituents of the reaction.

We have still to consider why we believe that an adsorbed layer of N_2O_2 will react with hydrogen sulphide in the first stage of the reaction when, apparently, the same gas will not react with N_2O_2 in the latter stage. It is undoubtedly a question of orientation. We have, as we have previously explained, a reaction between N_2O_2 and H_2S with the result that a film of sulphur has been deposited on the surfaces. We now assume a selective preference for hydrogen sulphide and consider a film of this gas to be adsorbed by the sulphur with the sulphur ion of the gas in proximity to the elemental sulphur already deposited on the wall. The hydrogen ion of the gas would, then, be turned toward the interior of the chamber. This would demand reaction of gaseous nitric oxide, or N_2O_2, not with the hydrogen sulphide molecule as a whole, but with the protruding hydrogen ion. That this cannot possibly take place at the temperature we have employed finds confirmation in the previously cited work of Hinshelwood and Green.

We may, therefore, briefly summarize our proposed mechanism of this reaction as follows:

(1) Incomplete but progressive association of two molecules of NO to form one molecule of N_2O_2.

(2) Adsorption of N_2O_2 on the surfaces.

(3) Reaction between H_2S and adsorbed N_2O_2.

(4) Adsorption of sulphur on the surfaces.

(5) Adsorption of H_2S on S with orientation of the hydrogen ion toward the interior of the chamber.

(B) *Inhibitory Effect of Colloidal Sulphur.*

The early indications of an inhibitor in this reaction led us to believe that colloidal sulphur was the responsible agency. Its critical temperature indicated that, of all the constituents of the reaction, it should be most strongly adsorbed. Our work was carried on through a range of temperature from 28° to 100° C. and even at the higher temperature there was no indication of a decided transformation of the colloidal form to the crystalline. For this reason we believe that in all of our experiments we were confronted with identical conditions. That is, as the reaction proceeded, the walls of the chamber, the capillaries of the gel and the filaments of glass wool became coated with an increasingly thick accumulation of colloidal sulphur. We had, simply, a strong protective colloid completely covering our catalyst, which eventually prevented contact of the gases with the accelerator. This is very strong confirmation of the heterogeneous nature of the reaction for, when this deposit of sulphur has reached the critical depth, the reaction stops. The plane surface of the colloidal sulphur is evidently non-catalytic.

Our explanation for the rapidity of the reaction in the experiments of Series A (plain glass walls), and the subsequent retarding of the velocity when sulphur had accumulated is that we were not dealing with plane glass surfaces even when we added no auxiliary catalyst. The corrosive effect of hydrogen sulphide on the water-soluble glass of the walls resulted in neutralization of the soluble alkalies of the glass, and left behind an efficient amount of amorphous silicon dioxide. We were, then, in all four series of our experiments, employing a silicon dioxide catalyst which became impotent when covered with the non-catalytic and impervious colloidal sulphur.

The formation of colloidal sulphur was not of a flocculent type. Thick accumulations could be pulled from glass surfaces in strips. Their elasticity and evident lack of porosity are proof of the great protection the material afforded the catalytic surfaces imbedded within the material.

Data in regard to the inhibitory effect of colloidal sulphur are not found in the literature. Its effect on the mathematical measurement of the velocity of the reaction between nitric oxide and hydrogen sulphide is disastrous. In view of the theoretical importance of both the reaction and the inhibitor, it is hoped that the writer may be in a position to continue the investigation of both.

Summary

(1) The conditions of the reaction between nitric oxide and hydrogen sulphide have been studied at temperatures between 28° and 100° C. Circumstances were varied by carrying on series of experiments in, (a) a plain glass chamber, (b) with added silica gel, and (c) with added glass wool.

(2) It was found that the reaction proceeded under all of the above conditions; the slowest velocity being where no added catalyst was used. Increased surface through the addition of glass wool accelerated the reaction to a rate comparable with that when silica gel was used. It is therefore assumed that the reaction is heterogeneous. This is confirmed by the slowing of the reaction in the presence of inhibiting colloidal sulphur.

(3) The stoichiometric expression for the reaction is: $2NO + 2H_2S \rightarrow 2H_2O + 2S + N_2$, but the mechanism is more complex. Two molecules of NO associate to form one molecule of N_2O_2. Hydrogen sulphide impinges on the adsorbed N_2O_2 with the formation of sulphur, nitrogen and water. Hydrogen sulphide is adsorbed by the colloidal sulphur on the surface and oriented in such a way that its hydrogen ion extends outward from the surface.

(4) A negative temperature coefficient was found. This is ascribed to decreased association of NO to N_2O_2 at the higher temperatures.

(5) The accumulation of colloidal sulphur as a resultant of the reaction is the cause of the inhibitory effect observed. It appears to be merely a mechanical coating of the catalyst, and to have the effect of a non-catalytic plane surface.

(6) It is believed that the glass wall of the reaction chamber and the filaments of glass wool were acted upon by water and hydrogen sulphide with formation of amorphous silicon dioxide, i. e., that the catalytic effect of the added silica gel was duplicated by the formation of this amorphous silica, and that results were merely dependent upon quantity.

Acknowledgment

The writer is deeply grateful to Doctors W. A. Patrick and J. C. W. Frazer, of the Johns Hopkins University, for having suggested this problem and for their ever-friendly readiness to cooperate. Their advice and encouragement were vitally important in carrying on the work.

The Johns Hopkins University.
Baltimore, Maryland.
June 11, 1928.

CALORIMETRIC RESEARCHES. II

The Heat of Combustion of a Proposed Secondary Calorimetric Standard: Salicylic Acid[1]

BY L. J. P. KEFFLER

Already at the end of last century, Stohmann and his collaborators made a systematic use of several independent and well-purified standard substances for the calibration of their calorimetric system. Shortly after the German firm of Merck investigated and put on the market as many as seven different preparations of known heats of combustion. Amongst these, benzoic acid, naphthalene and cane-sugar were given for many years a prominent place in scientific investigations through the pioneer work of Fisher and Wrede, Roth, Dickinson, Swarts, Richards, Swientoslawski and others.

Benzoic acid was finally selected by international agreement as the substance fulfilling best the requirements of a calorimetric standard; its heat of combustion at constant volume was fixed at 6324 cal._{15} per gram (weight in air) by the "Union Internationale de Chimie pure et appliquée", held at Lyons in 1922.

Amongst the four other substances proposed by Merck, salicylic acid has gradually come into prominence owing to its exceptional qualities from all points of view. Verkade and his collaborators, who did a great deal of careful and painstaking research[2] on this acid, with the special aim of getting it accepted as a secondary standard, have proposed for its heat of combustion the value 5242 cal._{15}. On the other hand, Berner[3] obtained from numerous and exceptionally consistent determinations of that physical constant the value 5237, 4 cal._{15}. Roth finally obtained values intermediate between these two.[4]

The first and last investigators mentioned carried out their temperature measurements with a fine Beckmann thermometer, while the second used a platinum resistance thermometer. As all three worked with a non-adiabatic calorimeter, the author considered it to be of interest to check their results with the improved type of adiabatic calorimeter he had recently devised. The value obtained last year (in collaboration with Mr. F. C. Guthrie: loc. cit.) for the heat of combustion of salicylic acid, namely 5238 cal._{11} per gram weighed in air (at the mean temperature of 16.9°C) was also intermediate between the values of Verkade and Berner, although much nearer to that of the latter investigator.

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[1] Cf. J. Phys. Chem., 31, 58 (1927).

[2] Verkade and Coops: Rec. Trav. chim., 42, 205 (1923); 43, 561 (1924); J. Chem. Soc., 1926, 1437; Kon. Akad. Wet. Amsterdam, 39, 667 (1926).

[3] J. Chem. Soc., 1925, 2747; 1927, 338; Archiv Math. Naturw. Oslo, 39, No. 6 (1926).

[4] Roth and Lasse: Z. Elektrochemie, 30, 606 (1924); Landolt-Börnstein Tabellen, 874 (1927).

In view of the great importance to thermochemists of being able to check by means of a second standard, of perfectly well known heat of combustion, the reliability of the data obtained during the calibration of their calorimeters by combustion of the primary standard (which may have become contaminated accidentally), a new series of determinations was made with the object of contributing towards the settlement of this already much debated question. And so as to give the greatest possible trustworthiness to the result obtained, many variations in the prevailing conditions, as well as various improvements, both in apparatus and in procedure, were introduced. Some of these changes are described in the following pages, others will simply be indicated, the details being left for another paper, dealing with new devices in calorimetry (cf. Communication 3, to appear shortly).

With regard to the calorimetric system, the amount of water was decreased from 3424 to 3000 grams, so as to compensate more or less for the somewhat lower relative precision resulting from a smaller rise of temperature (2°C instead of 3°C as before).

The Mahler-Berthelot bomb was replaced by a Moureu bomb, having a capacity of 310 cc (as against 283 cc before), and characterized by the three following advantages over the former:

(1) the lining is of gold instead of enamel

(2) it is designed to resist larger pressures

(3) it is provided with a capillary collar around its neck so as to separate the chamber of combustion from the lead washer and so prevent the latter being attacked by the nitric acid formed. The bomb was fixed in a permanent position inside the calorimeter by means of a brass ring allowing free circulation of water underneath; the calorimeter, in turn, was fixed inside its jacket by means of two low brass chimneys soldered to the bottom of the latter and enclosing the ivory legs by means of which the calorimeter is supported in the jacket.

The oxygen, obtained from the British Oxygen Company, was admitted into the bomb at a pressure of 35 atmospheres (instead of 25 previously), except in one or two cases, where a corrective term was introduced. Since that oxygen was from electrolytic sources, and thus liable to contamination by combustible impurities, especially hydrogen, it was passed, at least in some of the experiments, through a thick-walled nickel tube, packed with palladium asbestos, and heated to about 800°C. No perceptible change was found in the results, whether the oxygen was preheated or not. To decrease further the responsibility of any error arising from that source, as many as three different cylinders of oxygen were tested, both in the calibration experiments and in the determination of the heat of combustion of salicylic acid.

The very ordinary Beckmann thermometer used in the previous work and which could only be made reliable by the application of the "Constant Range" method, proposed by the author at the same time, was replaced by a much finer instrument, calibrated from .1 to .1°C to the nearest thousandth of a degree by the Physikalisch-Technische Reichsanstalt. The "Constant

Range" method was used all through, the constant interval being, as already stated, 2 instead of 3°C; the limits of the interval were selected at two points of the Beckmann scale where the bore corrections were nil, as well as in their immediate neighborhood.

The mean temperature of combustion was altered from 16.9 to 18.2°C.

The stirring of the calorimeter, which previously was slightly erratic at times, owing to the unsatisfactory behaviour of the water-motor used, became much more constant throughout any combustion by substitution of an electric motor; the rate of stirring, instead of being kept constant, all through the whole series of experiments, was changed purposely from one combustion to another through a rather wide range, the extreme values for the heat of stirring being approximately in the ratio 1:4.

For the ignition of the substance, an approximately constant weight of cotton wool (of heat of combustion equal to 3930 cal. per gram) was used, i. e. about half as much as previously. The length and diameter of the platinum ignition wire were kept the same as before so that the heat developed by the ignition current was still of the order of 0.2 calories and its variation therefore negligible in the calculations.

The titrations of the nitric acid formed were carried out with approximately tenth-normal sodium hydroxide solution, using methyl orange as indicator. There was never the slightest appearance of unburnt carbon; qualitative tests carried out in almost all cases with palladium chloride solution failed to reveal any sign of carbon monoxide formation.

In no case could the smell of unburnt vapors of the substance be detected.

The water equivalent of the calorimetric system was determined by burning two samples of benzoic acid (named A and B in Table I), received at two years interval from the Bureau of Standards (Washington). For some of the combustions, the substance was dried over phosphoric anhydride before use; in most cases however it was weighed straight away.

The calorimetric water was measured in three portions of approximately one liter, in a standard flask which was weighed each time, before and after delivery, to the nearest centigram. The weight of the water (including that of 1 cc in the bomb) was normally adjusted to 3000, 6 grams (in air, against brass weights), except in experiments 1 to 5 of Tables I, where a small corrective term had to be added.

In the same five experiments, a constant corrective term x = .6 calories was introduced in order to take into account the fact that 7.2 grams of material were removed from the copper hook supporting the bomb in a vertical position, after completion of experiment 5, in order to increase the effectiveness of stirring of that layer of water lying between the bomb and the stirrer partition; y = .7 cal. is a corrective term accounting for the use of a double washer in the first five combustions.

The means obtained for the water equivalent determined (1) with benzoic acid A and oxygen a (cf. Table 1, experiments 1 to 5); (2) with benzoic acid A (or B) and oxygen b (cf. experiments 6 and 7); (3) with benzoic acid A

TABLE I

Exp. No.	Corr. weight in air	Corrected Beckmann temp.		Corrections in thousandths for			Corr. rise in degree	Other corrections in cal. for			Water Equivalent	Sample and Oxygen
		init.	final	Range	Stem	Stir		HNO_3	Wool	x y		
1	1.10075	1.9003	3.9832	10	.7	4.7	1.9980	0.8	13.8	0 6		A
										.7	3497.0	a
2	1.09835	2.0162	3.9995	10	.8	2.5	1.9910	4.2	11.8	.6		A
										.7	3497.0	a
3	1.10095	1.8848	3.8700	10	.4	8.2	1.9904	5.0	11.0	.0		A
										.7	3496.7	a
4	1.09965	1.8921	3.8830	10	.1	0.7	1.9913	4.3	12.6	.0		A
										.7	3497.0	a
5	1.10035	1.9020	3.8960	10	.5	7.2	1.9973	4.8	13.6	.6		A
										.7	3495.7	a
												32atm.
6	1.10159	1.8572	3.8485	10	.5	4.4	1.9974	5.7	10.0	0	3498.4	A
												b
7	1.10216	1.8830	3.8700	10	.2	4.0	1.9992	5.9	11.4	0	3497.7	B
												b
8	1.10295	1.8953	3.8865	10	.8	1.9	2.0001	5.2	7.8	0	3497.0	B
												c
												29atm.
9	1.10005	1.8855	3.8728	10	1.0	1.5	1.9968	7.3	13.4	0	3497.1	B
												c′
10	1.08695	1.9138	3.8789	9.8	.5	1.6	1.9738	6.6	12.2	0	3495.0	A
												c′

TABLE II

Exp. No.	Corr. Weight in air	Corrected Beckmann temp. init.	Corrected Beckmann temp. final	Corrections in thousandths for Stem	Corrections in thousandths for Stirr.	Correc. rise in degrees	Corrections in calories for HNO_3	Corrections in calories for Wool	Heat of Combust. in air	Sample and oxygen
1	1.3239	1.9214	3.9026	.5	1.9	1.9898	5.1	11.4	5243.4	1 b
2	1.3236_5	1.9145	3.8958	.8	1.9	1.9902	5.8	12.8	5243.9	2 b
3	1.3237	1.8851	3.8662	.4	1.85	1.9897	5.6	12.6	5242.7	2A b
4	1.3254_5	1.9068	3.8909	.3	2.35	1.9921	6.8	11.4	5242.1	2A c′
5	1.3244	1.9006	3.8824	.1	1.62	1.9903	5.2	9.8	5243.8	(1+2)A b
6	1.3223	1.8792	3.8581	.7	2.5	1.9871	4.7	12.6	5243.6	(1+2)A c
7	1.3238	1.9302	3.9107	.5	2.4	1.9886	5.0	10.6	5241.3	(1+2)A c′
8	1.3228_5	1.8782	3.8568	.9	1.75	1.9878	7.9	11.2	5240.4	(1+2)A c′

(or B) and oxygen c (i.e. used without preheating) or c (i.e. preheated), were respectively 3497.0; 3498.0; and 3496.4 cal.

The water equivalent was thus found equal to 3497.0 cal.$_{20}$, at the mean temperature of 18.2°C, with an average error for the mean of 0.6 parts in 10000.

The results of the individual combustions are summarized in Table I.

Purification of Salicylic Acid

(1) A first preparation—obtained from Poulenc Frères—the same as that used in communication 1 and also by Verkade (loc. cit.), was recrystallised twice from freshly refractionated chloroform (see Table II, sample 1, combustion 1).

(2) A second preparation, obtained from the British Drug Houses, was recrystallised twice from freshly distilled water (see sample 2, combustion 2), then twice from chloroform (see sample 2A, combustions 3 and 4).

The four values obtained for the heats of combustion of the three samples being the same within the limits of the small experimental error, these samples were united and recrystallized as a whole from dry ether which had been refractionated twice by means of a long Crismer column, first over phosphoric pentoxide, afterwards over clean sodium wire. Only those fractions of solvent which distilled within a tenth of a degree from the true boiling-point, were used in the recrystallisation. A fourth sample, called sample (1 + 2)A, was obtained in that way (see combustions 5 to 8). After each crystallisation, the acid was carefully freed from any trace of solvent by heating over steam under a pressure of a few centimeters of mercury, for several hours; then grinding the sample up into a very fine powder, so as to prevent the occlusion of any solvent (especially water) inside the crystals; it was finally kept for several days, eventually weeks, over phosphoric pentoxide, in a vacuum exsiccator.

The mean found for the heat of combustion of salicylic acid at a mean temperature of 18.2°C, was 5242.8 cal.$_{20}$ per gram weighed in air against brass weights or 5239.2 cal.$_{20}$ per gram weighed in vacuo. (These figures include a small correction of − .1 cal. for the difference in heat capacity between the factors and the products of the combustion).

The average error for the mean is equal to 0.4 parts in 10000.

The values obtained in the individual combustions are summarised in Table II.

To the variable correction given in column 5 for the emergent stem of the Beckmann thermometer, should be added a constant corrective term equal to 10 thousandths of degree centigrade.

General Corrections—(1) for the buoyancy of air,

a) in the weighing of the calorimetric water.—

Since the same quantity of water was used in the calibration of the calorimetric system and for the measurements of the heat of combustion of salicylic acid, the reduction of the water weighings to vacuo was not necessary.

b) in the weighing of the substance burned.

No correction for buoyancy is required for the calculation of the water-value of the calorimeter since the figure used for the heat of combustion of benzoic acid refers to one gram weighed in air.

The buoyancy correction to be added to the practically constant weight 1.323 gram of salicylic acid (density = 1.48) amounts to 1.323 × 0.67 mgr so that the heat of combustion of salicylic acid per gram weighed in vacuo is equal to 5242.7/1.00067 or 5239.2 cal._{20}.

2) for the difference between the heat capacity of the products of the combustion and that of the oxygen used up.

This difference depends upon the amount and nature of the substance burnt and requires therefore a special correction for each substance.

In the case of benzoic acid, the equation of combustion is

$$C_6H_5COOH + (15/2)O_2 = 7\ CO_2 + 3\ H_2O$$

The molecular heats (at constant volume) of carbon dioxide, liquid water and oxygen are respectively 6.92, 18, and 5.84* so that this difference, when referred to 1.1 gram of benzoic acid (molecular weight = 122) is equal to $(7 \times 6.92 + 3 \times 18 - 15 \times 5.84/2) \times 1.1/122 = 0.53$ calories. This corrective term should be subtracted from the heat capacity (3497 cal.), which thereby becomes smaller by approximately 1.5 parts in 10000.

There remains to be found the difference in heat capacities between the products and the factors of the combustion of salicylic acid. The equation of combustion for the latter is

$$C_6H_4(OH).COOH + 7\ O_2 = 7\ CO_2 + 3\ H_2O$$

The difference between the heat capacities of carbon dioxide and liquid water formed and the oxygen used up, when referred to 1.323 grams of salicylic acid (molecular weight = 138) is thus equal to

$$(7 \times 6.92 + 3 \times 18 - 7 \times 5.84) \times 1.323/138 = 0.58 \text{ cal.}$$

This corrective term, which represents the increase in the heat capacity of the calorimetric system when 1.323 gram of salicylic acid is burnt in the bomb, makes the water equivalent larger by 1.69 parts in 10000. Hence the value to be used for the water equivalent in the calculation of the heat of combustion of salicylic acid must be made larger by 1.69 − 1.5 = 0.2 parts in 10000 (approximately). The heat of combustion of salicylic acid itself is thus increased in the same proportion and becomes 5242.8 cal._{20} (in air) or 5239.3 cal._{20} (in vacuo). This heat of combustion depending on a water value in which the heat capacity of the products of the combustion has been introduced, would hold for an isothermal reaction at the initial temperature of the combustion,[1] i. e. 17.2°C if the value accepted for the heat of combustion of benzoic acid did refer to an isothermal reaction at the same temperature. This is however not the case. It can indeed be inferred, with practical certainty, as was pointed out by Verkade[2], that this accepted value resting

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* Cf. Landolt-Börnstein Tabellen—5th Edition (1923).

[1] Richards: J. Am. Chem. Soc., 25, 209 (1923).

[2] Rec. Trav. chim., 44, 803 (1925).

mainly, as it does, on the excellent work of Dickinson[1], who worked purposely[2] at the nearly constant temperature of 20°C, should hold for the latter temperature. Such a reference-temperature was not fixed by the Lyons conference. It is true that the heat of combustion of a substance varies only slightly with the temperature of the calorimeter. It is true also that the temperature coefficient of a heat of combustion, depending as it does on the specific heat of the substance investigated can, as a rule, be calculated only with a rough approximation, since the specific heat of most organic substances is still unknown. The specific heat of benzoic acid having, however, just recently been determined[3], it will be possible to calculate exactly the temperature coefficient of the heat of combustion of the standard substance and to show thereby that it is not entirely negligible in work of the highest precision, especially so when substances are investigated, the heats of combustion of which have a temperature coefficient widely different from that of benzoic acid, or when different temperatures are used in the calibration combustions as compared with the experiments on the substance investigated.

The temperature coefficient of a heat of reaction is given by Kirchhoff's law:

$$dQ_v/dt = h_i - h_f$$

where h_i and h_f stand for the initial and final heat capacities, referred to one mole of substance, of the system undergoing the reaction, and Q_v, in the present case, represents the isothermal molecular heat of combustion at constant volume of benzoic acid. From the equation of combustion and the molecular heat of benzoic acid (37.1cal.), it is found that

$$h_i = 37.1 + 15 \times 5.84/2 = 81.0 \text{ cal.}$$

and that

$$h_f = 7 \times 6.92 + 3 \times 18 = 102. \text{ cal.}$$

Hence the temperature coefficient of the molecular heat of combustion of benzoic acid is expressed by

$$do_v/dt = 81.0 - 102.4 = -21.4 \text{ cal.}$$

If this equation be integrated between two temperatures differing by 1°C, it is found that the isothermal heat of combustion, at constant volume, per gram of benzoic acid, decreases by $21.4 \times 10000/122 \times 6329 = .28$ parts per 10000, per degree rise in temperature. Hence by determining the water equivalent at 17°C, with standard benzoic acid, the author should have used for the heat of combustion of the standard sample a value higher than that indicated by 3 × .28 parts in 10000. His water equivalent and consequently also his result for the heat of combustion of salicylic acid at the temperature 17°C would have been higher in the same proportion. In order to render this corrected value for the heat of combustion (now referred to the initial tem-

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[1] Bull. Bureau of Standards, 11, 241 (1915).

[2] Especially in view of the important advantage that there is a much smaller rate of change in the heat capacity of water at 20 as compared with that at 15°C, where it is about three times as large.

[3] Cf. Landolt-Börnstein Tabellen (1927 Supplement).

perature 17°C) directly comparable with that of Verkade (holding for a temperature of 19.5°C) the temperature coefficient of the heat of combustion of salicylic acid should now be calculated. Since the specific heat of the latter substance is still unknown, only an approximate value can be obtained by means of Kopp's law. If the values derived by this author[1] for the atomic heats of carbon, hydrogen and oxygen, viz. −1.8, 2.3 and 4.0 be accepted, the calculation gives $1.8 \times 7 + 2.3 \times 6 + 4.0 \times 3 = 38.4$ cal. for the molecular heat of salicylic acid. Hence from the equation of combustion of this substance, the following results

$$h_i = 38.4 + 7 \times 5.84 = 79.3$$
$$h_f = 7 \times 6.92 + 3 \times 18 = 102.4$$

are obtained for the initial and final molecular heats of the reacting system, so that the temperature coefficient is equal to

$$dQ_v/dt = 79.3 - 102.4 = -23.1$$

This corresponds to a decrease in the heat of combustion of salicylic acid of $23.1 \times 10000/138 \times 5240 = .32$ parts in 10000, per degree rise in temperature.

In order therefore to get for the heat of combustion of salicylic acid a value holding for the temperature 19.5°C, a total correction of $3 \times 0.28 - 2.52 \times 0.32 = +.05$ parts per 10000 should be introduced in the value previously recorded by the author. As such a correction is entirely negligible, at least in the present case, it follows that the isothermal heat of combustion of salicylic acid found by the author (and therefore also by Berner), holds for a temperature approximately equal to 20°C.

Calculation of the Maximum Error entailed in the Various Measurements

A general survey of the various errors prevailing in bomb calorimetry will be given shortly in another paper (cf. Communication 4); for the present, the discussion will be restricted to the most important errors only (i.e. those affecting the main measurements, apart from those entailed in the various corrections).

The water equivalent (W) upon the value of which the heat of combustion primarily depends, will thus be simply represented in the present discussion by

$$W = w_1 \times 6329/R \qquad (a)$$

leaving out therefore the corrective term $\frac{A + B - C}{R}$ (to be added to the second member in respect of the heat of combustion (A) of the cotton wool used as igniter, of the heat of formation (B) of the nitric acid formed, and eventually a correction (c) taking into account a lack of completeness in the combustion process) whose influence is relatively small in comparison with that of the main error just under consideration.

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[1] Ann., 1, 289 (1864). Suppl. 3.

In equation (a), w_1 stands for the weight in grams (in air) of standard benzoic acid burnt; R for the rise in temperature of the calorimetric system, and 6329 is the number of cal._{20} given out by the combustion of one gram of benzoic acid (weighed in air).

To evaluate the error (dW) on the water equivalent, let the logarithmic differentials of equation (a) be taken:

$$dW/W = dw_1/w_1 - dR/R$$

1) The error (dw_1) on the weight depends mainly on the real sensitivity of the balance used. In the present case, a Sartorius balance, sensitive to .05 mgr, was available. The relative error on the weight (w_1 = 1.1 gr) of benzoic acid, determined by the double-tare method, by means of flat platinum weights standardised by the National Physical Laboratories (Teddington) was thus at the most: dw_1/w_1 = .0001/1.1, i.e. approximately .9 parts in 10000.

2) The error (dR) on the thermometric rise (R) corresponding to a constant heat capacity depends:

a) on the sensitivity of the balance by means of which the calorimetric water is weighed out, and

b) on the sensitivity of the thermometer used.

As far as the temperature measurements are concerned, readings were taken to the nearest one ten-thousandth of a degree by means of a special device to be described in Communication 3, (in the course of preparation). The relative error from the two readings of the initial and final temperatures was thus at the most .0002°C in 2°C, or 1 part in 10000. (As the same Beckmann thermometer was used throughout the measurements, no correction for thermometric lag was required.[1])

The second factor on which the relative error dR/R on the rise depends, namely the weight of the calorimetric water, may now be considered. As the water was weighed in three portions of approximately one liter each on a balance of one kilogram capacity (and of sensitivity one mgr), each of the six necessary weighings (three before and three after delivery) being made within a centigram, the relative error on the total weight, under the worst possible conditions where all the partial errors would add up, was at the most .06 gram (in 3000) or .2 part in 10000.

The total relative error in the rise is thus equal to

$$dR/R = 1 + 0.2 = 1.2 \text{ parts in } 10000$$

and the maximum relative error on the water equivalent in any individual combustion, to $dW/W = 0.9 + 1.2 = 2.1$ parts in 10000.

In the same way, the maximum error on the heat of combustion (h) per gram of salicylic acid may be calculated from the expression

$$h = W \times R/w_2$$

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[1] White: Phys. Rev., 31, 562 (1910); Karper: Bull. Bureau of Standards, 8, 659 (1912)

where the corrective term in respect of the heat of combustion of the cotton wool and of the heat of formation of a little nitric acid has been left out for the same reasons as given already about the expression for the water equivalent: w_2(= 1.323 gram) represents the weight in grams (in air) of salicylic acid burned, and R stands for the corresponding rise in temperature.

The maximum error for the latter factor will be the same as before, since exactly the same temperature interval was used.

Logarithmic differentiation of equation (b) gives:

$$dh/h = dW/W + dR/R - dw_2/w_2$$

where $dw_2/w_2 = .0001/1.323 = 0.75$ so that the relative error (dh/h) on the heat of combustion per gram of salicylic acid, in the most unfavorable case, *and for a single experiment*, is only equal to: $dh/h = 2.1 + 1.2 + 0.75$, i.e. equal to 4 parts in 10000 (in round numbers). The uncertainty about the true value for the heat of combustion of salicylic acid is thus, without any doubt, extremely small.[1]

Comparison of the Author's Results with Data from the Literature

In calorimetric researches where the precision aimed at is of the order of 1 or 2 parts in 10000, it would serve no purpose to consider any values obtained before the decision taken at Lyons in respect of the standardisation of combustion results was brought into force.

The discussion of the available data will therefore be restricted to the comparison of the values published by Verkade, Berner, Roth and the author, together with a consideration of the degree of precision attained by Dickinson in his standard measurements of the heat of combustion of benzoic acid. To that end, the results obtained by the latter investigator for the means derived from several series of combustions have been summarized in Table III.

TABLE III

Year	Number of combustions	Number of samples	Heat of combustions per gram in air	Mean deviation from mean	Maximum deviation from mean
1910	14	4	6328	4.5	10
1912	5	1	6331	3.0	5.1
1912	11	1	6330	1.8	—
1913	9	1	6329	1.4	—

The weighted mean is equal to 6329 ± 2 cal._{20} per gram weighed in air.

Since the purification of those samples was carried out by specialists *from* the Bureau of Standards on unusually large quantities of substance and therefore under conditions at least as good as they could be expected to

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[1] The error due to thermal leakage by conduction, convection, radiation and evaporation, which is always small in adiabatic calorimetry, at least when a submarine calorimeter is employed, was made negligible by the use of a special device (cf. Communication 3, already referred to) which allowed of keeping constantly the temperature of the jacket within .01°C of that of the calorimeter proper, except during the first two minutes of the combustion, when the maximum deviation was 0.01°C.

be anywhere else. Table III, indicates that the value obtained for the water equivalent of a calorimetric system by burning samples of benzoic acid other than the standard sample issued by the Bureau while making the computations with the value adopted by International agreement, is very likely to be affected by an error of several parts in 10000.

The latter procedure has unfortunately been adopted by Verkade, wholly for his first series (1924) and partly for his second series (1926) of combustions. It may now be observed that an absolute error of 1 calorie in the determination of the water equivalent gives rise to an error about double in the expression for the heat of combustion of salicylic acid (at least in the experiments of Verkade, who uses about 0.8 gram of acid and gets a rise approximately equal to 1.0°C) and that this is quite independent of the partial experimental error involved in the actual combustion of the latter acid (besides that resulting from the slight but hardly unavoidable variation with the sample, of the degree of purity of the salicylic acid and eventually of the oxygen used). The latter possibilities may easily account for another one or two calories in the value of the heat of combustion. This assumption is amply justified by the consideration of Dickinson's work (already referred to) on the heats of combustion of benzoic acid, naphthalene and sucrose, partly confirmed a few weeks ago by Roth[1] in his absolute determination of the heat of combustion of benzoic acid[2]: the extreme difficulty of getting results from various investigators to agree to better than 3 or even 4 parts per 10000 needs therefore no further emphasis.

Under such difficult circumstances, it is felt that the only way of impartially judging the relative degree of precision which characterises these (after all only slightly divergent) results, is to group them together in a table

TABLE IV

Observer	Year	n	n_h	h	e_h	n_w	W	e_w
Verkade	1924	6	48	5237.7	0.3	12	2800	1.2
"	1926	6	26	5237.7	0.3	15	3051	0.6
Roth*	1924	1	4	5237.1	1.9	4	597	4.0
"	—	—	—	5236.9	—	7	2844	1.3
Author**	1927	4	11	5235.0	0.5	6	3751	0.8
" ***	1928	4	8	5234.7	0.4	10	3497	0.6
Berner	1925	3	20	5233.8	0.2	10	4066	0.4
"	1927	4	11	5234.4	0.3	11	4066	0.3

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[1] Roth, Doepke and Banse: Z. physik. Chem., 133, 431 (1928).

[2] Roth found for two different preparations of benzoic acid the values 6321.9 ± 1 cal.$_{15}$ (as a mean of 7 combustions) and 6323.3 ± 1 cal.$_{15}$ (as a mean of 5 combustions). This expression has been selected in preference to the probable or to the mean error on account of the questionable utility of applying the theory of probabilities either to a series which is likely to be affected by an (unknown) constant error or to a series constituted by four terms only, such as the first of Roth, carried out with his micro-bomb.

* The figures given in column 5 have been referred to the international value (6324) instead of that (6324.5) calculated by Kenning and used by Roth.

** In collaboration with F. C. Guthrie: loc. cit.

*** More combustions of salicylic acid were intended but the bomb was unfortunately put out of order for the best part of the year.

containing the following data: h = heat of combustion at constant volume of salicylic acid, in cal._{15} per gram weighed in vacuo; W = water equivalent in cal._{15}; n_h and n_w = numbers of combustion experiments with benzoic and salicylic acids respectively; n = number of samples of salicylic acid; e_h and e_w = the average errors in parts per 10000 of the general means found for the heat of combustion of salicylic acid and the water equivalent respectively.

While Table IV indicates that Verkade's results for the heat of combustion of salicylic acid are quite honorably consistent amongst themselves, it shows at the same time that the more important calibration experiments of his first series (quite notably the more extensive) are beset with an appreciably larger uncertainty than those of the author and still more so than those of Berner. Further, if the following values 3050.0, 3049.6, 3051.4, 3051.6, 3051.3, 3050.2, 3051.2, (sample 39a, mean = 3050.8) 3050.0, 3051.4, 3051.8, 3052.4, (sample 39b, mean = 3051.4) and 3050.9, 3052.3, 3051.8, 3051.5 (sample from Rotterdam, mean = 3051.9) obtained by Verkade for the water equivalent of his second group of combustions[1] are examined, it is noticed that those obtained with Rotterdam's benzoic acid are all larger than the mean obtained with the sample 39a, while three out of four of the former are also larger than the mean of those corresponding to the sample 39b (supplied with sample 39a by the Bureau). There is thus at least some indication that the Rotterdam sample of benzoic acid, with which part of the 1924 calibration experiments were carried out, yielded for the corresponding water equivalent a value too high by approximately the difference (0.9 cal.) between the means 3051.9 and 3051.0 obtained respectively with benzoic acid from Rotterdam and from the Bureau; this slightly too high value for the water equivalent would make the heat of combustion of salicylic acid too large by 0.9 × 0.6/0.84 = 1.7 cal., and thus bring it down to 5236.0 cal._{15} per gram in vacuo).

As far as Roth's results are concerned, those obtained with the microbomb are unfortunately very scarce and their precision appreciably less, as may be expected from the greater difficulties which had to be overcome. Amongst those carried out in the calorimeter of normal size, published details are completely lacking. The figure (5236.9) given in the table for the heat of combustion of salicylic acid is the general mean (referred to the constant 6324 instead of 6324.5 of several series of combustions. The author understands from private communications, which he is authorized to reproduce by kind permission of Prof. Roth, that the extreme means of these series were 5234.4 and 5238.4 cal_{15} (in vacuo). In the absence of details about the calibration, and so as to form however an approximate idea of the maximum precision to be expected for the unknown water equivalent, the average error of a more recent series[2] of calibration experiments has been entered in Table IV. It follows from the comparison of the values found by the various investigators mentioned that the heat of combustion of salicylic acid may be considered

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[1] Verkade and Coops: Rec. Trav. chim., **42**, 211 (1923); **43**, 566 (1924); J. Chem. Soc., 1926, 1437.

[2] Roth, Doepke and Banse: Z. physik. Chem., **133**, 431 (1928).

with practical certainty to lie between the extreme values of Verkade and Berner; the foregoing discussion indicates further that Verkade's value is probably too high by a quantity of the order of 2 calories in respect of his value found for the water equivalent. If the mean of Verkade's reduced value (5236) and of Berner's mean value (5234) be taken, the final value (5235) will be exactly the same as the rounded off value obtained by the author in both his series of combustions and be within 2 calories of those obtained by Roth. It is proposed therefore to adopt it as the true value until new improvements in the calorimetric technique makes it possible to reduce further the present very small margin of uncertainty.

In conclusion, considering that it is essential in very accurate calorimetric work on heats of combustion of organic substances, to get the purity of the calorimetric standard checked immediately before use by way of a method offering the same degree of reliability; considering further that bomb calorimetry alone supplies such a highly sensitive method and that salicylic acid fulfills perfectly all the requirements expected from a standard, the author seconds Verkade's proposal to adopt the latter substance as a secondary standard; he proposes further, for the reasons given above, to adopt the value 5235 ± 1 cal._{15} for its isothermal heat of combustion at constant volume, at the temperature 20°C, per gram weighed in vacuo.

In view however of the unavoidably provisional character of the values accepted for a heat of combustion, as in general for any physical constant; in view also of the appreciable discrepancies which would be likely to arise amongst data from various investigators who might select indifferently the one or the other standard if both were considered as interchangeable, and also of the considerable extra expenditure of energy involved in the future recomputation of data resting on two slightly different bases, it is finally suggested that benzoic acid should be the only standard the heat of combustion of which should be used in the computation of the water equivalent, that of an equally reliable preparation of salicylic acid, (supplied by one and the same agency for the whole world) being used merely as an independent criterion of purity for the primary standard.

In any case, it is recommended that the heat of combustion of this secondary standard be fixed as soon as possible by International agreement, and that a reference-temperature be decided upon for both standards.

In final conclusion, the author has great pleasure in thanking most heartily Prof. E. C. C. Baly, for his sympathetic support during the prosecution of the present research.

Summary

1. A short historical account has been given in reference to the proposal of salicylic acid as a secondary standard substance for calorimetry.

2. The heat of combustion of salicylic acid was found to be equal to 5234.8 cal._{15} per gram weighed in vacuo, as a mean obtained from 19 combustions carried out adiabatically under most varied conditions, with as many as eight different samples obtained by numerous crystallisations from three different preparations of the acid.

This value is supposed to hold for an isothermal reaction at a temperature of about 20°C, assuming that the value 6319 cal.$_{15}$ accepted by International agreement for the heat of combustion of standard benzoic acid, holds for the same temperature.

3. A short survey of the most important errors entailed in the various measurements has been presented.

4. A comparison has been made with the view of getting a quantitative expression for the degree of reliability to be attributed to the data of several investigators who have recently carried out series of experiments on the subject. As a conclusion to the discussion, the rounded off value 5235 ± 1 cal.$_{15}$ was finally suggested for the heat of combustion of salicylic acid (per gram weighed in vacuo).

Inorganic Department,
The University,
Liverpool.

THE VISCOSITY OF SUPERSATURATED SOLUTIONS. PART II

BY I. K. TAIMNI

In the paper[1] submitted by the author on the "Viscosity of Supersaturated Solutions", it was shown how the apparatus devised by Scarpa for viscosity determinations could be modified for the special case of Supersaturated Solutions. With the help of this modified apparatus, the viscosity of some solutions was measured, and it was shown that the viscosity curves, as far as they could be traced, did not undergo any abnormal change in the supersaturated region.

Having established the fact that the viscosity of such solutions changes in a continuous manner as they are cooled through and below the saturation temperature, the problem as to the quantitative relations connecting the viscosity of such solutions with changes of concentration and temperature naturally suggested itself to the mind.

Most workers who have investigated the viscosity of solutions of solids in liquids have confined their attention to dilute solutions. We know very little about the behaviour of solutions in the neighborhood of the solubility limit. Yet for a complete theory of viscosity a knowledge of the behaviour of concentrated solutions is as necessary as a knowledge of the behaviour of dilute solutions. It was with the object of extending our knowledge in this direction that the present investigation was undertaken. Till an exact and comprehensive kinetic theory of liquids is established, no theoretical advances of fundamental importance are likely to be made in this field, and our route to progress will, necessarily, consist in extending the experimental data, and correlating the results obtained in different fields of investigation.

The apparatus used and the method adopted for determining the viscosity of the solutions were the same as given in the previous paper. In view of the necessity of knowing the absolute viscosity of the solutions with greater accuracy correction for kinetic energy was applied wherever necessary. The corrected viscosity η_c is calculated by the formula[2]

$$\eta_c = K \cdot \frac{t_1.t_2}{t_1 + t_2} - X\rho \frac{t_1^2 + t_2^2}{t_1.t_2(t_1+t_2)}$$

where K and X are *constants* depending upon the dimensions of the instrument. It will be seen that the density of the liquid (P) enters into the correction term. As the correction for kinetic energy is at most five or six per cent of the value of the viscosity, and generally much less, it is not necessary to determine the density of the solution with very great precision. The variation of density with change of temperature was found to be negligible for the purpose, and an average value of the density was taken in calculating the correction.

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[1] J. Phys. Chem., 32, 604 (1928).

[2] Scarpa: Gazz., 40, 271.

The viscometers used were the same as in the previous investigation. They were, however, recalibrated, and more accurate values of the 'Viscosity Factors' were obtained by applying the correction for kinetic energy.

It is well known that the formula for determining viscosity does not apply to liquids when the flow instead of being viscous is turbulent. The conditions under which transition from linear to turbulent flow takes place have been very thoroughly investigated by Osborne Reynolds[1] and a sharp criterion is available which enables *one to distinguish* between the two régimes. According to Reynolds the maximum mean velocity of flow for which we may expect viscous flow is given by the expression $\frac{1000 \times \eta}{\rho.R}$ cms per second where η is the viscosity and P the density of the liquid and R is the radius of the capillary. The maximum mean velocity is given by the expression $\frac{V}{\eta.R^2.t}$ cms. per second where V is the volume of the liquid transpiring in the time t. In the present investigation, the actual velocities corresponding to some of the smallest values of t_1 and t_2 were in all cases well within the critical limit at which the transition from linear to turbulent flow takes place. Thus in two cases where the critical velocities were 270 and 343, the actual velocities of flow were 33 and 24.6 cms per second respectively.

The substances used in the present investigation were chosen arbitrarily from among those which are fairly soluble and thus enable one to prepare rather concentrated solutions. Both aqueous and non-aqueous solutions were investigated so as to obtain a general view of the phenomenon. The substances examined in aqueous solution were sucrose, urea, acetamide, citric acid and sodium thiosulphate. All these substances form supersaturated solutions easily and the tendency towards spontaneous crystallization which interferes with the determination of viscosity in the supersaturated region is very weak if not altogether absent. The non-aqueous solutions investigated were those of resorcinol, acetamide, urethane in ethyl alcohol, phenanthrene and urethane in toluene. The degree to which non-aqueous solutions as a whole can be supersaturated is much smaller than that which is possible in the case of aqueous solutions. Solutions in ethyl alcohol could in some cases be cooled even 20° below the saturation point but it was not found possible to cool solutions in toluene more than a few degrees below the saturation point. The parallelism between the capacity to form supersaturated solutions and the association of the solvent molecules is interesting, the solvent with the highest association factor—water—showing the phenomenon of supersaturation in the most pronounced manner. The data however, are not sufficient to deal with this question adequately.

Tables VII-XVI give the viscosities of solutions at different temperatures and concentrations. From these tables four sets of curves—(1) viscosity-temperature (2) viscosity-concentration (3) log viscosity-temperature and

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[1] Phil. Trans., 174A, 935 (1883); 177A, 157 (1886).

(4) log viscosity-concentration—were drawn. Before discussing the results, it may be explained why it was considered necessary to plot the logarithm of viscosity against concentration and temperature.

The work of numerous investigators on the viscosity of liquids has shown that in the study of this property the logarithm of viscosity plays an important rôle. Arrhenius[1] was the first to recognize the value of this function of viscosity and the formula that he proposed

$$\log \frac{\eta}{\eta_0} = \Theta.C$$

holds in the case of dilute solutions of non-electrolytes with considerable accuracy.

His logarithmic formula

$$\log \eta = \Theta_1 \log \eta_1 + \Theta_2 \log \eta_2$$

also holds satisfactorily for liquid mixtures when one component is present to the extent of less than 10 per cent. Again Dunstan and Thole[2] have shown that a fairly exact linear relationship exists between molecular weights and logarithms of viscosity in several homologous series. The same linear relationship is found to obtain in the homologous series investigated by Thorpe and Rodger,[3] and it is thus possible to calculate the additive values of log viscosities for the more important elements and radicles. Seeing that log viscosity has played an important part in the development of the theory of viscosity, it was expected that the study of this function may bring out some interesting relation between the viscosity of the solutions and their concentration and temperature. The result of the study justified this expectation to a certain extent as the following paragraphs will show.

Viscosity and Concentration

The relation between the viscosity of the solutions and their concentrations may first be discussed. When the viscosity-concentration curves are drawn, the following points of interest about them are observed.

1. Out of the ten systems examined, four—sucrose, citric acid and sodium thiosulphate in water and resorcinol in ethyl alcohol—give viscosity-concentration curves with a positive curvature, i.e. the curves are convex to the concentration axis. Fig. 1 shows the results for solutions of sucrose in water and is typical of this class of curves. The curves in the case of the other six systems are straight lines as shown in Fig. 2 for solutions of acetamide in ethyl alcohol.

2) The curvature in the case of the first four systems decreases as the temperature increases. It may be assumed, therefore, that at sufficiently high temperatures, the relation between viscosity and concentration for these systems will become linear and in a line with the behaviour of the other six systems. In the case of the solutions of resorcinol in ethyl alcohol (Fig. 3) this transition from positive curvature to linearity can actually be seen.

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[1] Z. physik. Chem., 1, 285 (1887).

[2] J. chim. phys., 7, 210 (1909); Dunstan and Wilson: J. Chem. Soc., 91, 90 (1907).

[3] Phil. Trans., 185A, 397 (1894).

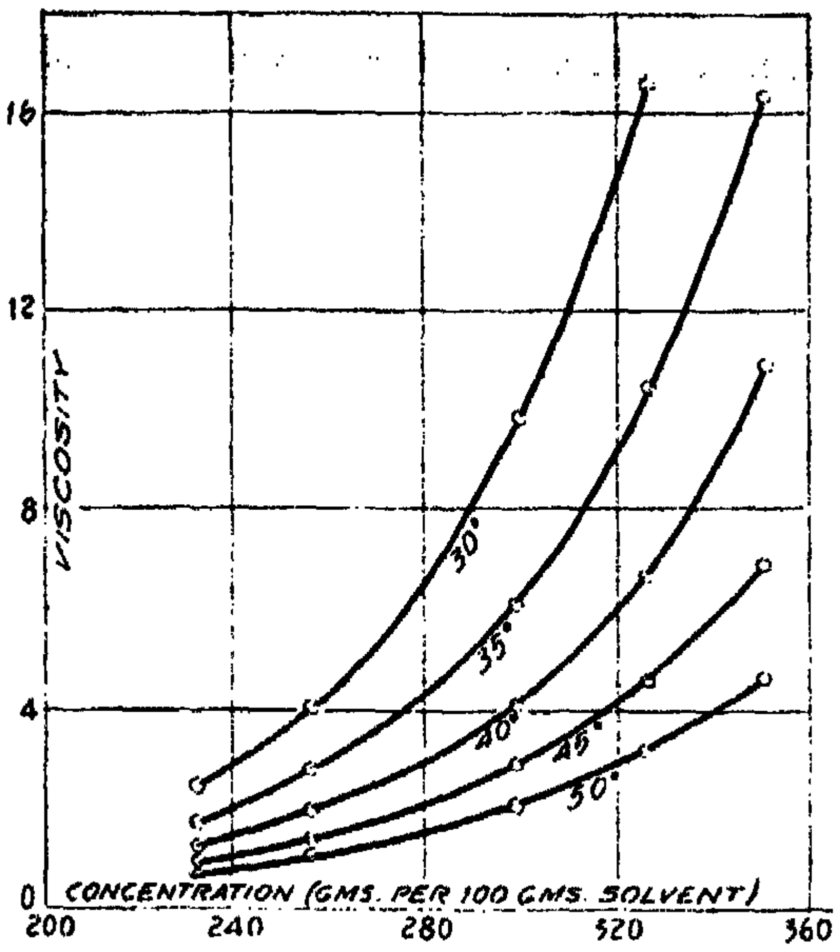

FIG. 1
Sucrose in Water

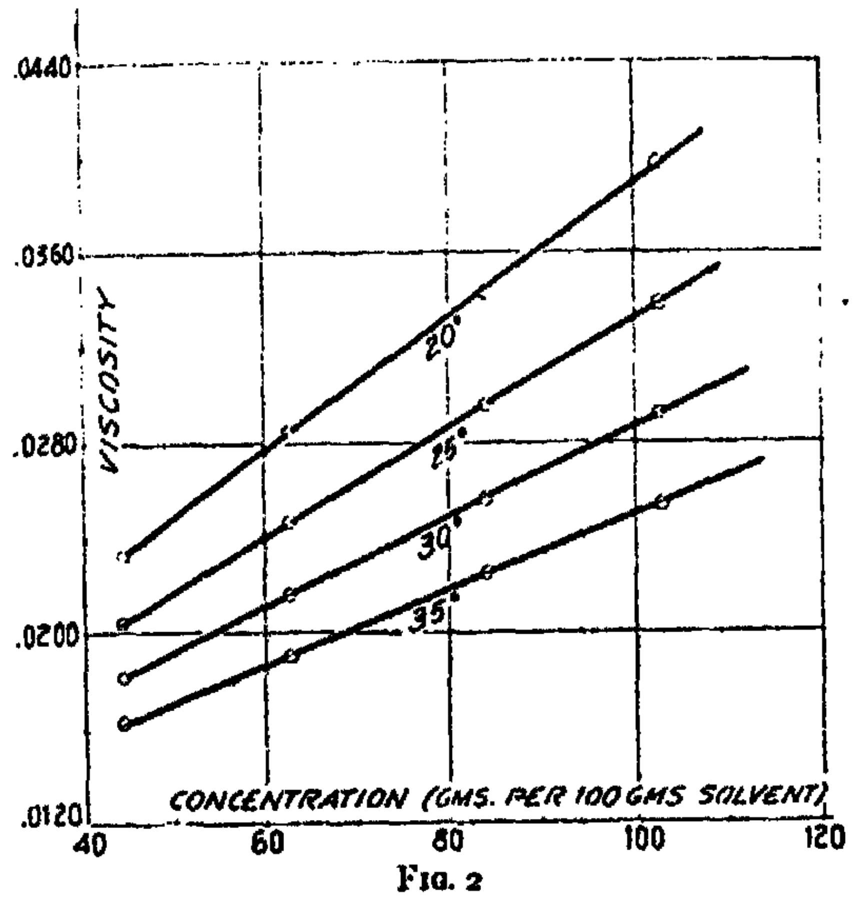

FIG. 2
Acetamide in Ethyl Alcohol

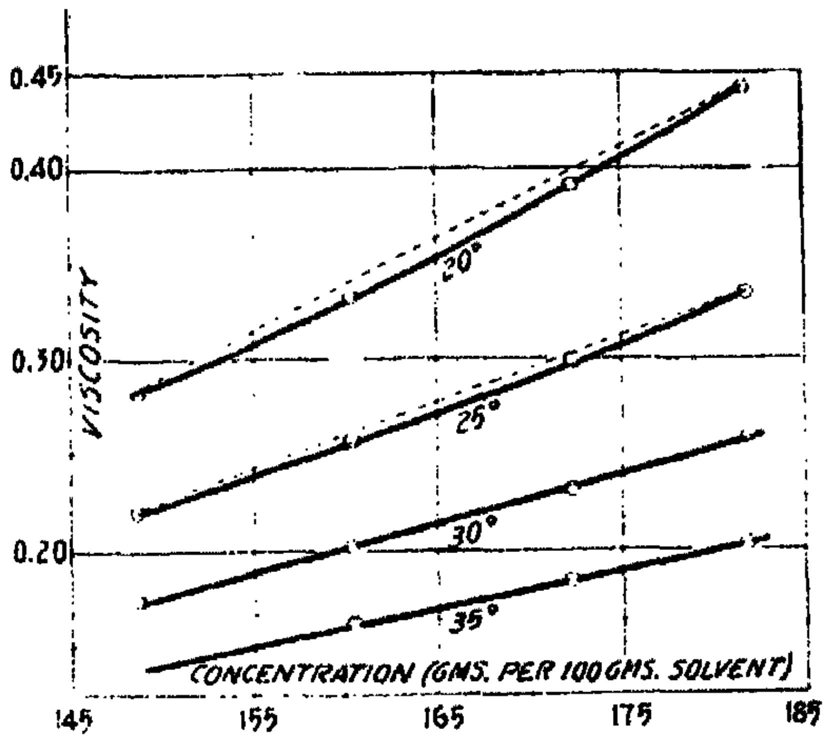

Fig. 3
Resorcinol in Ethyl Alcohol

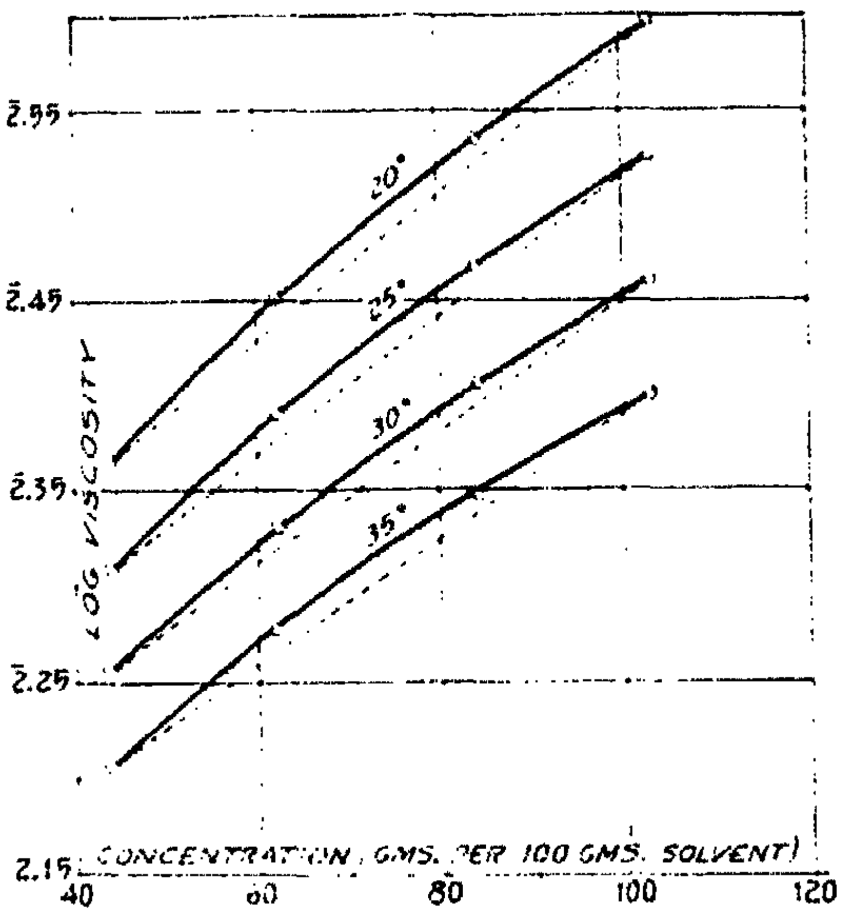

Fig. 4
Acetamide in Ethyl Alcohol

(3) The solutions for which the viscosity is not a linear function of concentration are solutions of comparatively high viscosity.

On plotting the logarithm of viscosity against concentration, the curves obtained show the following points of interest.

(1) The curves for four systems—urethane and phenanthrene in toluene, acetamide in ethyl alcohol and water—show a negative curvature i.e. the curves are concave to the concentration axis. Fig. 4 which shows the results for solutions of acetamide in ethyl alcohol is typical of this class of curves. The curves for the remaining six systems are straight lines approximately parallel to each other as shown in Fig. 5 for solutions of sucrose in water.

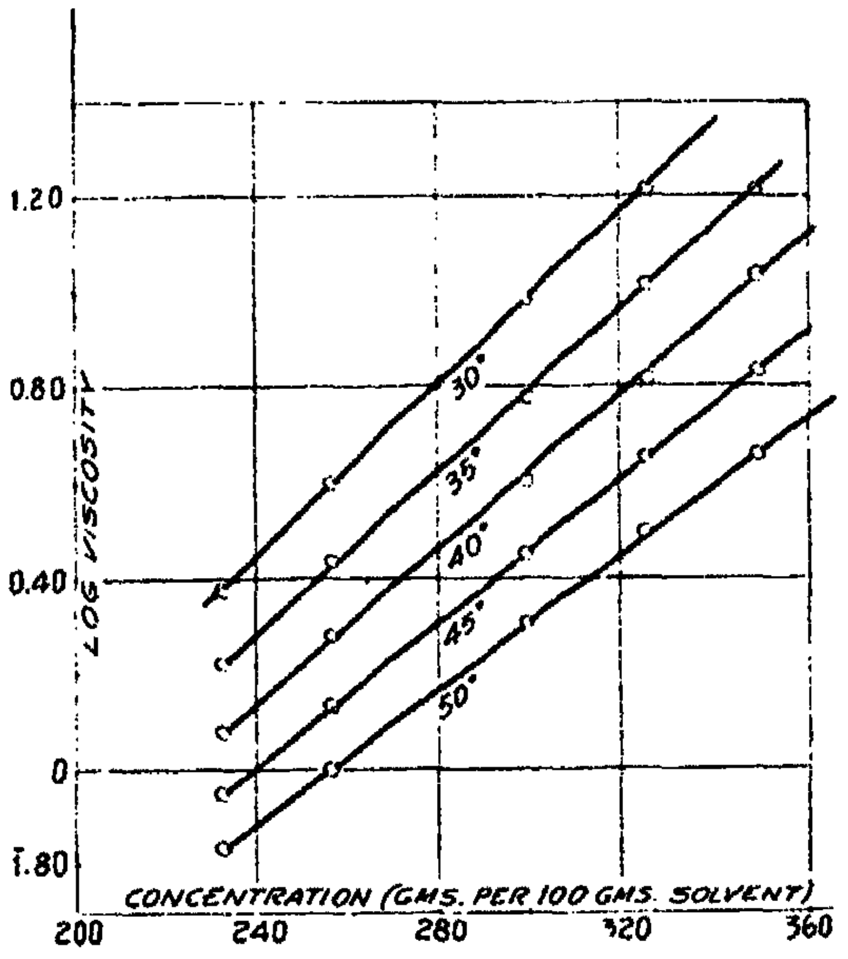

Fig. 5
Sucrose in Water

(2) Those systems whose viscosity-concentration curves are not linear give linear log viscosity-concentration curves and vice versa.

As either η or $\log \eta$ is a linear function of concentration, the variation of viscosity with change of concentration may be represented by either of the equations.

$$\log \eta = \Theta C + \phi$$
$$\eta = mc + n$$

where Θ, ϕ or m, n are constants depending on the temperature of the solution. In those cases where the viscosity or log viscosity is a linear function of concentration the linearity of the curves is marked. The equations given above should, therefore, hold with a fair degree of accuracy within the limited range of concentration examined. This range, as shown, in Table I, is sufficiently wide to make the equations of real use in calculating the viscosity of concentrated solutions.

TABLE I

System	Sucrose-water	Urea-water	Acetamide-water	Citric Acid-water	Sodium Thiosulphate-water
Range of concentration*	233–350	120–151	100–200	208–280	73–119
System	**Resorcinol-Ethyl Alcohol**	**Acetamide-Ethyl Alcohol**	**Urethane-Ethyl Alcohol**	**Phenanthrene-Toluene**	**Urethane-Toluene**
Range of concentration	149–182	44–103	149–220	40–70	61–121

*Concentrations are given as grams per 100 grams solvent.

How far the values of viscosity calculated from either of the two equations $\log \eta = \Theta C + \phi$ $\eta = mc + n$ agree with the experimental values within the ranges of concentration shown above may be illustrated by the following two examples in which the value of η or $\log \eta$ is calculated with the help of the corresponding equation and compared with the observed value.

(1) For aqueous solutions of sucrose at 45° we get by substituting known values of $\log \eta$ and C in the equation $\log \eta = \Theta C + \phi$

$$\bar{1}.0445 = \Theta \times 233 + \phi$$

$$0.8357 = \Theta \times 350 + \phi$$

Solving these two equations for Θ and ϕ we get

$$\Theta = 0.007617 \text{ and } \phi = 1.8313$$

The equation representing log viscosity of sucrose solutions at 45° thus becomes

$$\log \eta = 0.007617C - 1.8313$$

Substituting $C = 300$ in this equation we get

$$\log \eta = 300 \times .007617 - 1.8313 = 0.4538$$

$\therefore \eta = 2.84$, the observed value being 2.83.

(2) For solutions of urea in water at 40° we get by substituting known values of η and C in the equation $\eta = mc + n$

$$0.01438 = 120\,m + n$$

$$0.01065 = 151\,m + n$$

Solving these two equations for m and n we get $m = 0.0000732$ and $n = 0.00559$.

The equation representing the viscosity of urea solutions at 40° thus becomes

$$\eta = 0.0000732\,C + 0.00559$$

Substituting $C = 141$ in this equation we get

$$\eta = 141 \times 0.0000732 + 0.00559$$

$\therefore \eta = 0.01591$, the observed value being .01587.

It will be seen from the two examples given above that the equations $\log \eta = \theta C + \phi$ and $\eta = mc + n$ represent the variation of viscosity of concentrated solutions in a satisfactory manner.

Whether or not the equations are valid for concentrations lower than those used in this investigation is a question that may well be asked, but is not easy to answer. The behaviour of solutions with regard to changes in viscosity is so complicated that no definite conclusions can be drawn with regard to solutions of lower concentrations from the phenomena observed with concentrated solutions. Thus Bingham has pointed out that the fluidity-concentration curves of many solutions have a point of inflection in them, the negative curvature at lower concentrations giving place to positive curvature as the concentration is increased. Under these circumstances it is extremely hazardous to predict the behaviour of solutions of lower concentration. It is probable that the equations $\log \eta = \Theta C + \phi$ and $\eta = mc + n$ do hold for some distance beyond the limits of concentration investigated. It is also possible to determine whether they hold right up to the limit of o concentration in the following way. If we put $C = o$ in the equation $\eta = mc + n$ we get $\eta = n$. It follows from this that if the equation is applicable right up to the limit of o concentration, the constant n should be equal to the viscosity of the pure solvent at the temperature in Question. The same may be said about the equation $\log \eta = \Theta c + \phi$.

Two examples may be given to illustrate the point in question

(1) Substituting values of η and C in the equation η mC + n for solutions of phenanthrene in toluene at 35° we get

$$0.00863 = 50\,m + n$$
$$0.01014 = 70\,m + n$$

Solving these two equations we get $m = .000755$ and $n = .00485$. Now the viscosity of toluene at 35° is .00494 (Physico-Chemical Tables) which is very nearly equal to the value of n at 35°. We are, therefore, justified in concluding that the equation $\eta = mc + n$ holds throughout the whole range of concentration from 0–70 gms per 100 gms of the solvent.

(2) Substituting values of η and C in the equation $\eta = mC + n$ for solutions of urethane in ethyl alcohol at 20° we get

$$0.02701 = 149.6\,m + n$$
$$0.03321 = 220.2\,m + n$$

Solving these two equations we get $m = 0.0000878$ and $n = 0.0139$. Now the viscosity of ethyl alcohol at 20° is .0119, which is different from the value of n at 20°. It is obvious, therefore that the equation is not applicable to solutions of urethane in ethyl alcohol up to the limit of o concentration. At what point the curve begins to depart from linearity and the equation $\eta = mC + n$ ceases to be applicable can be determined only by experiment.

A number of formulae, whose applicability is rather limited, have been proposed for representing the relation between the viscosity of solutions and their concentration. In view of the success of Arrhenius' equation

$$\log\frac{\eta}{\eta_0}\,\eta = \theta C$$

in representing the viscosity of some fairly concentrated solutions with accuracy it was considered worth while to test its applicability to the concentrated solutions examined in this investigation. It has been shown that this equation gives the best results when C is taken as the number of grams of solute in a fixed weight of the solvent. Throughout in this investigation C represents the weight of solute in 100 grams of the solvent.

To determine whether the Arrhenius equation is applicable to the highly concentrated solutions under investigation the values of the expression

$$\log\frac{\eta}{\eta_0}\ C$$

for different values of C may be compared with each other. If the equation is applicable, the values of the above expression should remain constant at a fixed temperature. Table II shows the calculated values of the expression $\log\frac{\eta}{\eta_0}\ C$ at constant temperature for three of the ten systems investigated. It will be seen from this table that the expression $\log\frac{\eta}{\eta_0}/C$ does not remain constant as the concentration of the solutions varies. Similar results are obtained with the other seven systems.

As the concentration C increases, the value of the expression $\log\frac{\eta}{\eta_0}/C$ invariably decreases. Arrhenius' equation is, therefore, not applicable to the highly concentrated solutions dealt with in this investigation.

TABLE II

Sucrose in Water		Urea in Water		Acetamide in Water	
C	$\log\frac{\eta}{\eta_0}/C$ at 45°	C	$\log\frac{\eta}{\eta_0}/C$ at 40°	C	$\log\frac{\eta}{\eta_0}/C$ at 35°
233	0.00929	120	0.00282	100	0.00436
257	0.00914	128	0.00276	124	0.00396
300	0.00889	141	0.00270	160	0.00340
320	0.00880	151	0.00266	200	0.00307
350	0.00873				

Viscosity and Temperature

The relation between the viscosity of solutions and their temperature may now be discussed. When the viscosities of solutions are plotted against their temperatures curves similar to those shown in the previous paper are obtained. There is no point of special interest about them. The study of the temperature coefficients of viscosity is more interesting. The temperature coefficients for solutions of different concentrations are given in Table III.

TABLE III

Conc. of Sucrose in water	233	257	300	326	350
Temp. Coeff. 50°–40°	1.77	1.86	1.98	2.12	2.39
Temp. Coeff. 40°–30°	1.97	2.08	2.45	2.50	
Conc. of Citric Acid in water	161	178	187	207	
Temp. Coeff. 40°–30°	1.46	1.51	1.51	1.60	
Temp. Coeff. 35°–25°	1.50	1.55	1.57	1.66	
Conc. of Sodium Thiosulphate in water	73	81	92	102	119
Temp. Coeff. 45°–35°	1.29	1.34	1.35	1.37	1.41
Temp. Coeff. 35°–25°	1.40	1.39(?)	1.45	1.51	1.56
Conc. of Urea in water	120	128	141	151	
Temp. Coeff. 45°–35°	1.19	1.20	1.21	1.21	
Temp. Coeff. 35°–25°	1.23			1.24	
Conc. of Acetamide in Ethyl Alc.	44.3	62.8	84.3	102.9	
Temp. Coeff. 35°–25°	1.27	1.29	1.32	1.34	
Temp. Coeff. 25°–15°	1.31		1.36		
Conc. of Phenanthrene in Toluene	40.1	50.0	61.3	70.0	
Temp. Coeff. 50°–40°	1.13	1.13	1.14	1.14	
Temp. Coeff. 40°–30°	1.14	1.15	1.15		
Conc. of Urethane in Toluene	60.6	80.1	100.0	121.1	
Temp. Coeff. 50°–40°	1.17	1.18	1.20	1.20	
Temp. Coeff. 40°–30°	1.20	1.23			

Table III (Continued)

Conc. of Acetamide in water	100	124	160	200
Temp. Coeff. 45°–35°	1.29	1.29	1.30	1.32
Temp. Coeff. 35°–25°	1.34	1.35	1.37	1.38
Conc. of Urethane in Ethyl Alc.	149.6	170.4	200.0	220.2
Temp. Coeff. 35°–25°	1.30	1.316	1.319	1.324
Temp. Coeff. 30°–20°	1.32	1.34	1.35	1.35
Conc. of Resorcinol in Ethyl Alc.	148.7	160.4	172.2	181.7
Temp. Coeff. 40°–30°			1.57	1.63
Temp. Coeff. 30°–20°	1.63	1.63	1.70	1.71

It will be seen from Table III that the temperature coefficients of all solutions increase with increase of concentration and decrease of temperature. The effect of increasing the concentration or decreasing the temperature on the temperature coefficients of viscosity is the same as that on the viscosity itself. The parallelism between the viscosity of solutions and the temperature coefficients of viscosity may be brought out in another way. We have seen that the viscosity of solutions and the temperature coefficients of viscosity both depend upon the concentration and temperature of the solutions. But it is possible, by taking an average of these quantities (for different values of concentration and temperature) to arrange the different systems investigated in the order of decreasing values with respect to these quantities. When the different systems are arranged in this manner, they are found to fall in the same order as shown below.

Order with respect to viscosity	Order with respect to temp. coeff. of viscosity
1. Sucrose–water	1. Sucrose–water
2. Resorcinol–ethyl alcohol	2. Resorcinol–ethyl alcohol
3. Citric acid–water	3. Citric acid–water
4. Sodium thiosulphate–water	4. Sodium thiosulphate–water
5. Acetamide–water	5. Acetamide–water
6. Acetamide–ethyl alcohol	6. Acetamide–ethyl alcohol
7. Urethane–ethyl alcohol	7. Urethane–ethyl alcohol
8. Urea–water	8. Urea–water
9. Urethane–toluene	9. Urethane–toluene
10. Phenanthrene–toluene	10. Phenanthrene–toluene

From the above it is obvious that the temperature coefficient of viscosity is in some way related to the viscosity itself. The greater the viscosity of the solution the greater is its temperature coefficient. It is difficult to say in the present state of our knowledge what is the significance of this relationship.

When the logarithms of viscosity are plotted against temperature, it is found that the curves approach linearity to a greater or less extent. If the range of temperature is not too great, a straight line can be made to pass through all the points. Fig. 6 gives log viscosity-temperature curves for solutions of urethane in ethyl alcohol. All other systems give similar curves. It will be seen that the curves are a series of almost parallel straight lines. A very slight positive curvature is noticeable, however, the points in the middle invariably falling below the straight lines. The effect of change of temperature on log η unlike the effect of change of concentration is the same in all the systems investigated, the log η-temperature curves invariably showing a slight positive curvature. Log η-concentration curves, on the other hand are linear in the case of some systems and show a negative curvature in the case of others.

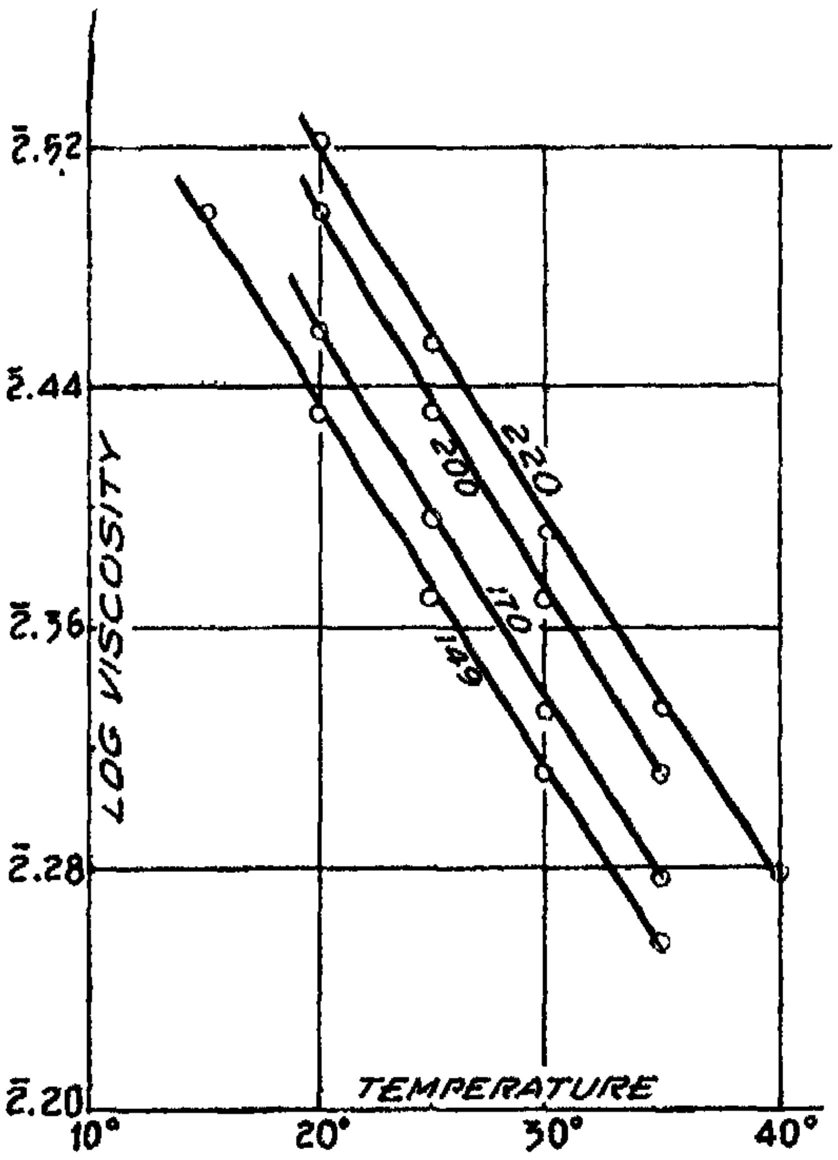

Fig. 6
Urethane in Ethyl Alcohol

Inasmuch as the logarithm of viscosity is only approximately a linear function of temperature the applicability of the equation of the type log η =

kt + k' is very limited. The values of η calculated with the help of this equation do not agree very well with the observed values unless the range of temperature chosen is small.

Viscosity, Concentration and Temperature

A number of equations have been put forward connecting viscosity and concentration on the one hand, and viscosity and temperature on the other, but no effort has been made, as far as the author is aware, to connect all the three quantities in a single equation. It is shown below that an equation of this kind can be made to represent the viscosity of solutions when the following two conditions are satisfied.

(1) Arrhenius equation $\log \eta/\eta_0 = \Theta C$ should be applicable to the variation of viscosity of the solution with change of concentration.

(2) Θ should be a known function of temperature.

From Powell's[1] observations it can be shown that the viscosity of sucrose solutions is given by the equation $\log \eta' = \Theta C$ where η' is the relative viscosity of the solution (absolute viscosity of the solution divided by the viscosity of water at the same temperature), C is the concentration of the sugar in grams of solute per 100 grams of water and Θ is a constant for a fixed temperature.

The constancy of Θ is shown by Table IV prepared by the author from Powell's observations.

TABLE IV

Temp. = 25°

Concentration C	Relative Viscosity η'	Log η'	Log η'/C = Θ
96.7	12.701	1.1038	.0114
73.0	6.825	0.8341	.0114
53.6	4.073	0.6099	.0114
45.0	3.267	0.5141	.0114

The value of Θ depends on the temperature and in order to discover what function of temperature Θ is, the values of Θ for different temperatures were calculated and are given in Table V.

TABLE V

Temperature	Relative Viscosity η'	Log η'	Log η'/C = Θ
25°	12.701	1.1038	.0114
30°	11.677	1.0675	.01104
35°	10.724	1.0302	.01065
40°	9.911	0.9961	.01030
45°	9.159	0.9618	.00995
50°	8.560	0.9325	

On plotting these values of Θ against temperature a straight line is obtained, so that the relation between Θ and temperature t is given by the equation

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[1] J. Chem. Soc., 105, 1 (1914).

$$\Theta = kt + k'$$

where k and k′ are constants independent of C. Substituting kt + k′ for Θ in the equation

$$\log \eta' = \Theta C$$

we get the equation

$$\log \eta' = (kt + k')\,C$$

This is a relation between the relative viscosity of sucrose solutions, their concentration and temperature, and with its help we should be able to calculate the relative viscosity of any sucrose solution provided the concentration and temperature of the solution are given.

In order to determine the values of the constants k and k′ we substitute known values of Θ and t in the equation Θ = kt + k′ and get

$$0.01065 = 35\,k + k'$$
$$0.00995 = 45\,k + k'$$

from which k = 0.000070 and k′ = 0.01314.

So that the general equation between the relative viscosity, concentration and temperature of sucrose solution becomes

$$\log \eta' = (0.01314 - 0.000070\,t)\,C$$

The validity of this equation may be tested by substituting known values of C and t in it and comparing the values of relative viscosity thus calculated with those found experimentally by Powell. Table VI gives the calculated and observed values of relative viscosity of sucrose solutions.

TABLE VI

C	t	Calc. η'	Observed η'
53.6	25°	4.08	4.07
96.7	30°	11.68	11.68
45.0	40°	2.91	2.95
73.0	50°	5.06	5.11

The agreement between the calculated and observed values of relative viscosity is fairly satisfactory.

The equation log η′ = ΘC is not applicable to the solutions of dextrose and laevulose investigated by Powell. The values of the expression log η′/C for dextrose and laevulose solutions calculated from Powell's observations do not remain constant but gradually decrease as the concentration increases. The equation log η′ = (kt + k′)C cannot, therefore, be expected to give correctly values of η′ from known values of C and t. In the case of the concentrated solutions examined in the present investigation log η′/C likewise, diminishes gradually, as the concentration increases. The equation log η′ = (kt + k′)C cannot, therefore, be applicable to these solutions either. The equation should, however, be applicable to all solutions in whose case Arrhenius' equation has been shown to hold, provided Θ is a linear or some other definite function of temperature.

TABLE VII

Sucrose in Water

Conc.	50°	45°	40°	35°	30°
233.0	0.68	0.88	1.20	1.67	2.37
257.0	1.02	1.35	1.90	2.70	3.96
300.0	2.02	2.83	4.00	6.05	9.80
326.0	3.11	4.50	6.60	10.42	16.50
350.0	4.55	6.85	10.88	16.25	

TABLE VIII

Urea in Water

Conc.	50°	45°	40°	35°	30°	25°
120.0	0.01240	0.01327	0.01438	0.01574	0.01740	0.01938
128.0		0.01370	0.01490	0.01638	0.01810	0.02016
141.0	0.01328	0.01452	0.01587	0.01752	0.01940	0.02164
151.0	0.01389	0.01520	0.01665	0.01830	0.02026	0.02268

TABLE IX

Sodium Thiosulphate in Water

Conc.*	45°	40°	35°	30°	25°	20°
73.0	0.031	0.035	0.040	0.047	0.056	0.068
81.0	0.038	0.044	0.051	0.060	0.071	0.087
92.0	0.049	0.056	0.066	0.079	0.096	0.119
102.0	0.059	0.068	0.081	0.098	0.122	0.152
110.0	0.088	0.103	0.124	0.152	0.193	0.252

* Conc in case of sodium thiosulphate is given in terms of anhydrous salt.

TABLE X

Acetamide in Water

Conc.	45°	40°	35°	30°	25°
100.0	0.0153	0.0173	0.0198	0.0230	0.0265
124.0	0.0174	0.0196	0.0225	0.0258	0.0303
160.0	0.0200	0.0228	0.0260	0.0303	0.0355
200.0	0.0228	0.0260	0.0300	0.0350	0.0415

TABLE XI

Citric Acid in Water

Conc.*	45°	40°	35°	30°	25°	20°
161.0	0.091	0.108	0.129	0.158	0.194	0.246
178.0	0.114	0.136	0.166	0.206	0.258	0.331
187.0		0.159	0.195	0.240	0.306	0.399
207.0	0.165	0.208	0.260	0.332	0.432	0.568

TABLE XII
Acetamide in Ethyl Alcohol

Conc.	40°	35°	30°	25°	20°	15°	10°
44.26		0.01608	0.01805	0.02040	0.02322	0.02666	
62.81		0.01899	0.02145	0.02458	0.02832		0.03829
84.33		0.02240	0.02557	0.02951	0.03434	0.04023	
102.9	0.02218	0.02530	0.02911	0.03382	0.03970		

* Conc. in case of citric acid is given in terms of anhydrous acid.

TABLE XIII
Phenanthrene in Toluene

Conc.	50°	45°	40°	35°	30°	25°
40.1	0.006581	0.006988	0.007417	0.007882	0.008466	
50.0	0.007132	0.007549	0.008036	0.008626	0.009227	0.009988
61.3	0.007776	0.008282	0.008869	0.009478	0.01023	
70.0	0.008250	0.008803	0.009422	0.01014		

TABLE XIV
Urethane in Toluene

Conc.	50°	45°	40°	35°	30°
60.57	0.007605	0.008240	0.008927	0.009761	0.01069
80.05	0.008772	0.009530	0.01033	0.01148	0.01270
100.0	0.009823	0.01075	0.01183	0.01313	
121.1	0.01096	0.01194	0.01315	0.01477	

TABLE XV
Urethane in Ethyl Alcohol

Conc.	40°	35°	30°	25°	20°	15°
149.6		0.01800	0.02044	0.02342	0.02701	0.03150
170.4		0.01889	0.02144	0.02486	0.02880	
200.0		0.02047	0.02340	0.02701	0.03148	
220.2	0.01896	0.02152	0.02460	0.02849	0.03321	

TABLE XVI
Resorcinol in Methyl Alcohol

Conc.	35°	30°	25°	20°	15°	10°
148.7		0.1726	0.2187	0.2818	0.3682	0.4854
160.4	0.1601	0.2006	0.2550	0.3280		0.5883
172.2	0.1823	0.2293	0.2975	0.3896	0.5216	
181.7	0.2022	0.2575	0.3332	0.4404		

Summary

(1) The effect of change of temperature and concentration on the viscosity of concentrated solutions of several substances in the neighborhood of their respective solubility temperatures has been studied.

(2) It has been shown that Arrhenius' equation $\log \eta/\eta_0 = \Theta C$ is not applicable to the solutions but the relation between viscosity and concentration may be represented by either of the two equations.

$$\log \eta = \Theta C + \phi$$

$$\eta = mC + n$$

(3) It has been shown that log viscosity is approximately a linear function of temperature.

(4) A relation between the temperature coefficient of viscosity and the viscosity itself has been pointed out.

(5) It has been shown that under certain conditions the viscosity of solutions of a substance under varying conditions of concentration and temperature may be obtained from a single equation

$$\log \eta' = (kt + k')C$$

I desire to express my thanks to Professor Donnan for his helpful criticism and advice during the course of this investigation.

The Sir William Ramsay Laboratories of Physical
and Inorganic Chemistry,
University College,
London.
July 12, 1928.

THE EFFECT OF GASES ON THE RESISTANCE OF GRANULAR CARBON CONTACTS

BY P. S. OLMSTEAD

When the surface of carbonized anthracite coal or other charcoal is examined microscopically, the surface resembles that of a sponge. As the magnification is increased, more and more surface irregularities may be seen. This, together with other evidence, has led investigators to believe that the submicroscopic surface is of the same type. Opening into the surface are pores or canals of submicroscopic cross-sectional areas which may approach molecular dimensions. Studies of adsorption of gases by carbon indicate not only that gas condenses on the surface of carbon, the phenomena of adsorption, but also that there are capillary forces sufficient to hold additional gas within the submicroscopic pores or canals, the phenomena of adsorption. In addition, in some experiments in which two granules of carbon were brought close enough together to conduct electricity, Holm[1] found that the areas of contact for the individual conducting portions of the granules were less than 3×10^{-5} cm. in diameter and that the current path was from carbon to carbon.

The present paper corroborates these ideas and shows that:

(1) Gas adsorbed on the surfaces of a carbon contact, increases its resistance and since conduction is from carbon to carbon this is interpreted to be an indication of a decrease in the effective area of contact.

(2) In accordance with studies on the structure of the carbons the existence of pores opening into the contact areas and therefore having diameters less than 3×10^{-5} cm. has been demonstrated. When the contact area is partly outgassed, the pores act as reservoirs for additional gas which may have an effect on the resistance of the contacts.

(3) A resistance measured under particular conditions has been related to the hydrogen content of the granules as determined by combustion.

Apparatus and Method

Due to the surface irregularities and the dependence of the resistance on the nature of the gas atmosphere surrounding the carbon granules, special precautions must be taken to insure reproducibility of results. In order to control the nature of the gas held by the carbon it is necessary that the contacts can be outgassed at temperatures up to 200°C to pressures of the order of 1×10^{-5} mm.Hg and that pure gases can be obtained and admitted to the contacts.

In addition, since no two successive single contacts between granules could be expected to be identical on account of the nature of the carbon sur-

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[1] Z. tech. Physik, 6, 166 (1925).

face, an important step toward securing reproducible conditions was the use of a cell containing a large number (approximately 50,000) of grains of granular carbon so that each measurement was the result of an average effect. One of the cells used is illustrated in Fig. 1. It is essentially a short circular cylinder of brass with a non-conducting constriction of lavite in the center.

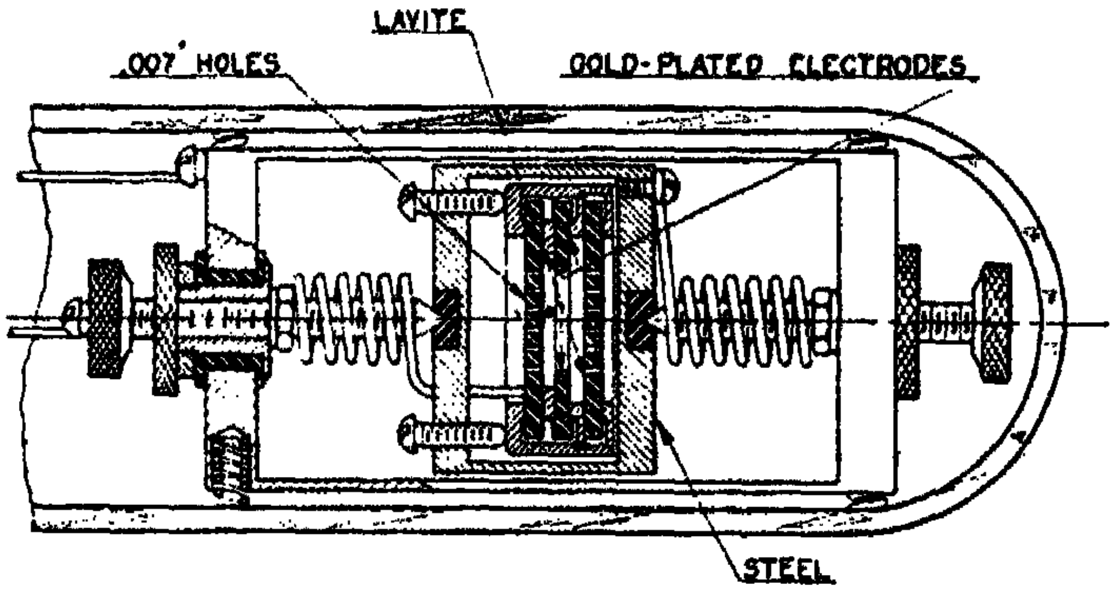

Fig. 1

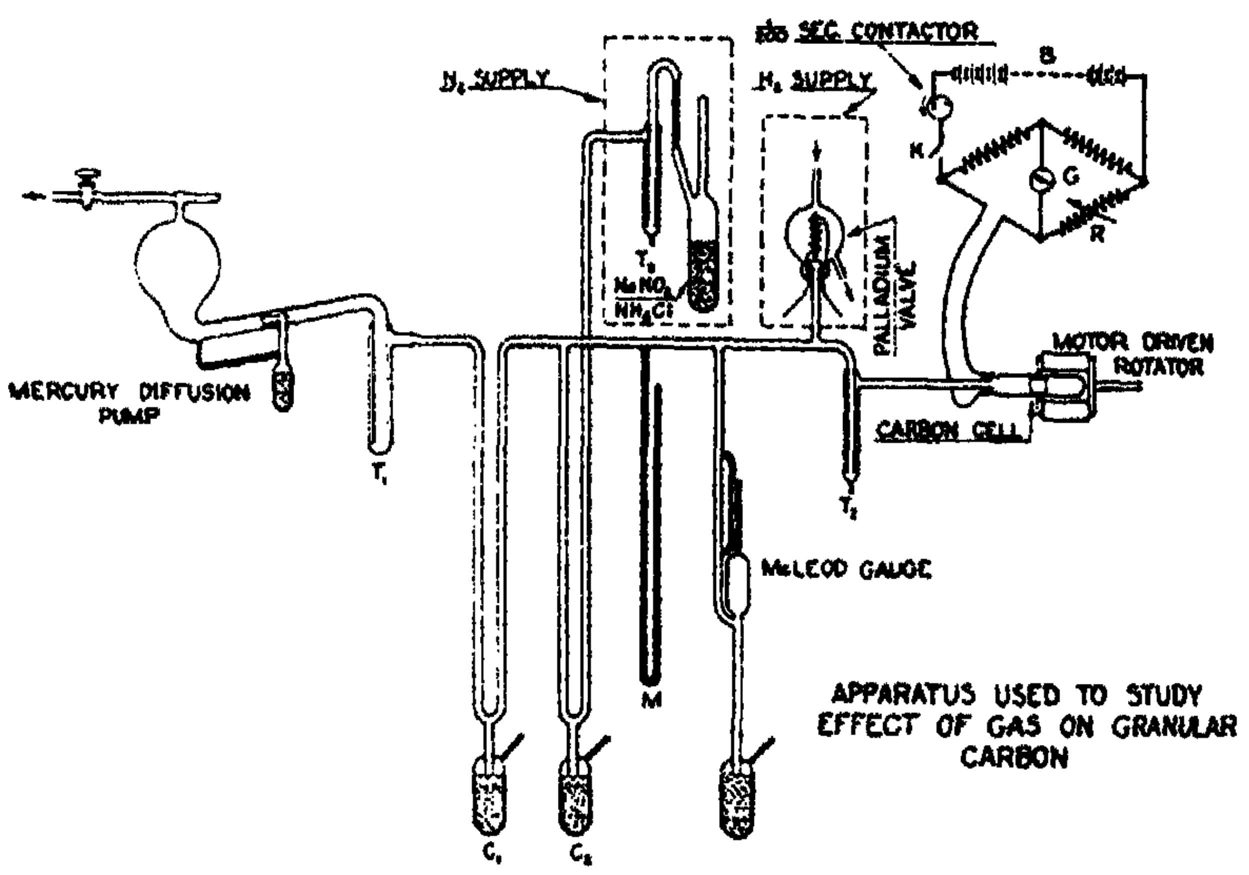

Fig. 2

The portions of the cylinder on either side of this constriction are gold-plated and serve as electrodes. Discs of lavite with holes as indicated close the ends of the cell. This is held in a steel frame supported on steel points in lavite bushings, permitting rotation about its axis by means of a motor-driven magnetic field. The amount of rotation is limited only by the spiral conductors of flexible copper wire.

To shield the cell from building vibrations, it and the associated apparatus (except the measuring circuit), shown schematically in Fig. 2 were mounted on a heavy suspension unit which was supported from the ceiling by steel springs wrapped with friction tape to produce damping of building vibrations.[1] To secure the most probable force per contact configuration the carbon chamber was rotated and stopped in a definite position. After each rotation, the resistance was measured at a predetermined voltage by the Wheatstone bridge arrangement indicated in the figure. This included a contacting device which allowed current to flow for only 0.005 second. The object of limiting the time of flow to such a short interval was to confine the heating to the contact surfaces only.

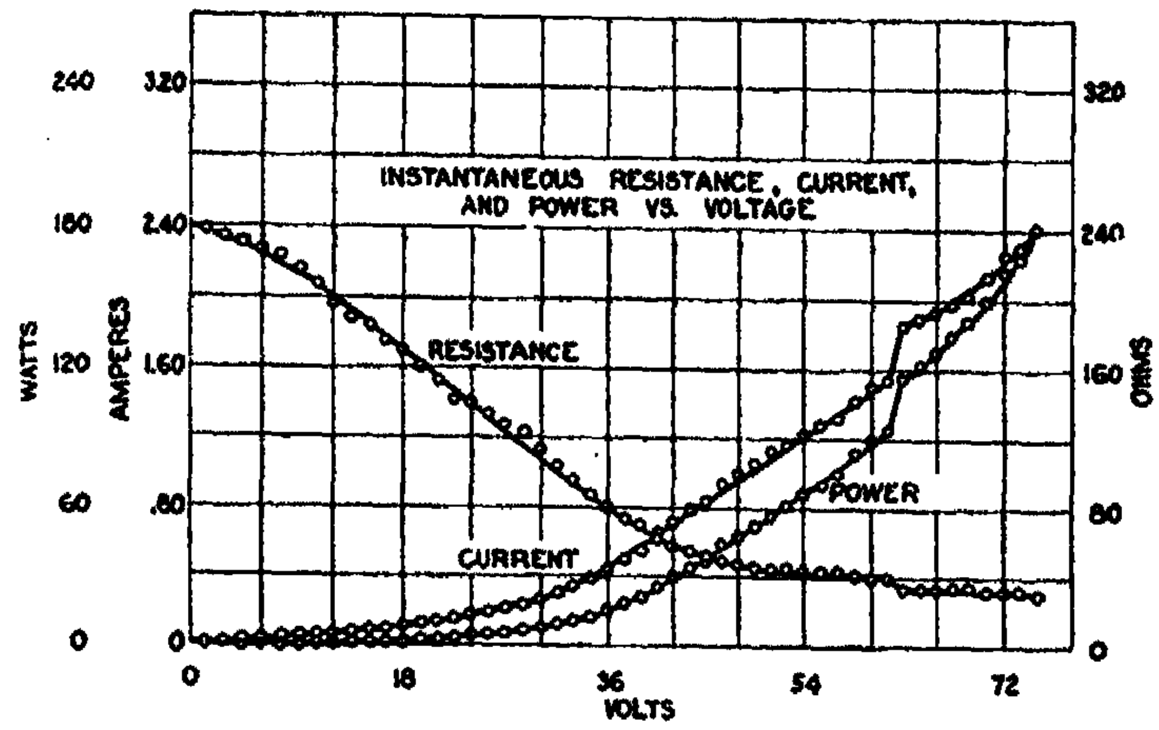

FIG. 3

To control the kind and pressure of the gas surrounding the carbon, the cell was mounted in a glass tube, which was supported in a horizontal position and connected by glass tubing through liquid air traps to a mercury diffusion pump. Numerous holes were drilled in the endplates of the cell to permit rapid changes in pressure of the enclosed gas. Hydrogen was admitted from a tank of commercial hydrogen through the walls of a heated palladium tube. Nitrogen was generated by the reaction of a mixture of chemically pure sodium nitrate and ammonium chloride. The reaction was self-sustained after being started by the application of a small amount of heat. The gas was admitted through liquid air traps and a mercury cut-out. By these means it was possible to obtain hydrogen and nitrogen of a high degree of purity.

In preparing the cell for use, all parts except the carbon were baked to red heat in an electric oven to remove impurities, such as oil, etc.

After assembly, the entire cell including the carbon was outgassed for approximately 50 hours at a temperature of 200°C to a pressure of 1×10^{-5}

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[1] Johnsrud: J. Opt. Soc. America, 10, 609-611 (1925).

mm. Hg. This was sufficient to remove all gases except those which combine definitely with the carbon. These are not driven off until the carbon granules are treated in a destructive manner. Hence, they may be considered as part of the adsorbent.

The main tool in these experiments has been the measurement of resistance at various voltages. A typical resistance versus voltage curve obtained at atmospheric pressure is shown in Fig. 3. It was obtained by making resistance balances at successively higher voltages. The contacts were not disturbed between measurements. The significant characteristics of such a curve are: a decrease in resistance with increase in voltage; and a discontinuity at a relatively high voltage. The latter is more prominent in the corresponding current and power curves given in the same figure. A resistance-voltage curve of the type shown will be called a packing curve and the contacts used, packed or sealed contacts.

Effect of Adsorbed Gas

In experiments dealing with the sorption of gases by carbon, it has usually been found that the amount of nitrogen taken up varies with pressure and that at room temperatures the final equilibrium is reached practically instantaneously as is characteristic of adsorption. For this reason we may assume that the major effect of nitrogen on the resistance of carbon contacts will be due to the interposition of gas condensed on the contacting carbon surfaces.

In order to insure the complete removal of all residual adsorbed gases from the carbon before testing for the effect of nitrogen on the contact resistance of carbon granules, nitrogen was alternately admitted to a sample of carbon outgassed as indicated previously and pumped out to a pressure of 1×10^{-3} mm. Hg several times. Then, starting with the nitrogen at approximately atmospheric pressure, the resistance at 1.5 volts was measured at room temperature in the manner mentioned. Resistances were obtained at various pressures down to 1×10^{-3} mm. Hg. In these measurements the voltage was applied for a short interval of time in order to limit the heating effects to the contact areas. Two sets of measurements were made while the pressure was being increased and two while it was being decreased. The results are shown in Fig. 4. These represent approximately 1000 observations of resistance at the various pressures indicated. It is found that the resistance increases approximately logarithmically with the gas pressure. The resistance at 50 mm. represents a change from the resistance at the lowest pressure used of about 25%. This difference is quite significant, since the measurement had a standard deviation of only 0.4%. Whenever the pressure was changed, the resistance changed within the time necessary to make the measurement. This indicates that the effect being measured depends on a very rapid equilibrium between the atmosphere and the carbon surface.

The data shown in Fig. 3 demonstrated the fact that the resistance of a carbon contact decreases as the voltage increases. From the additonal fact

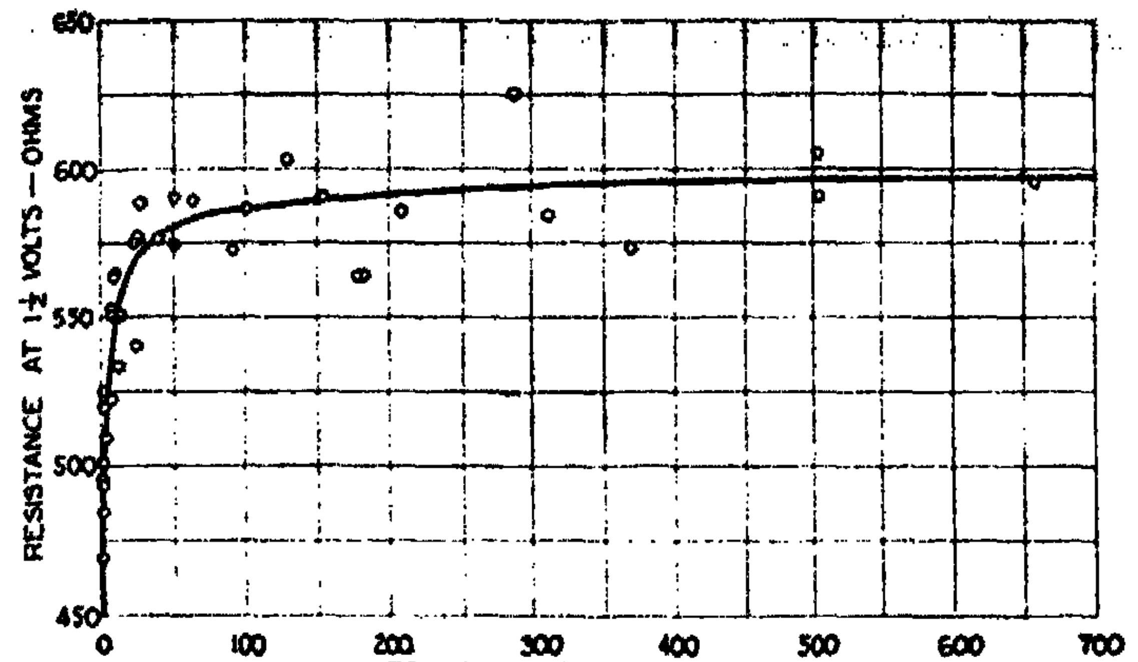

Fig. 4

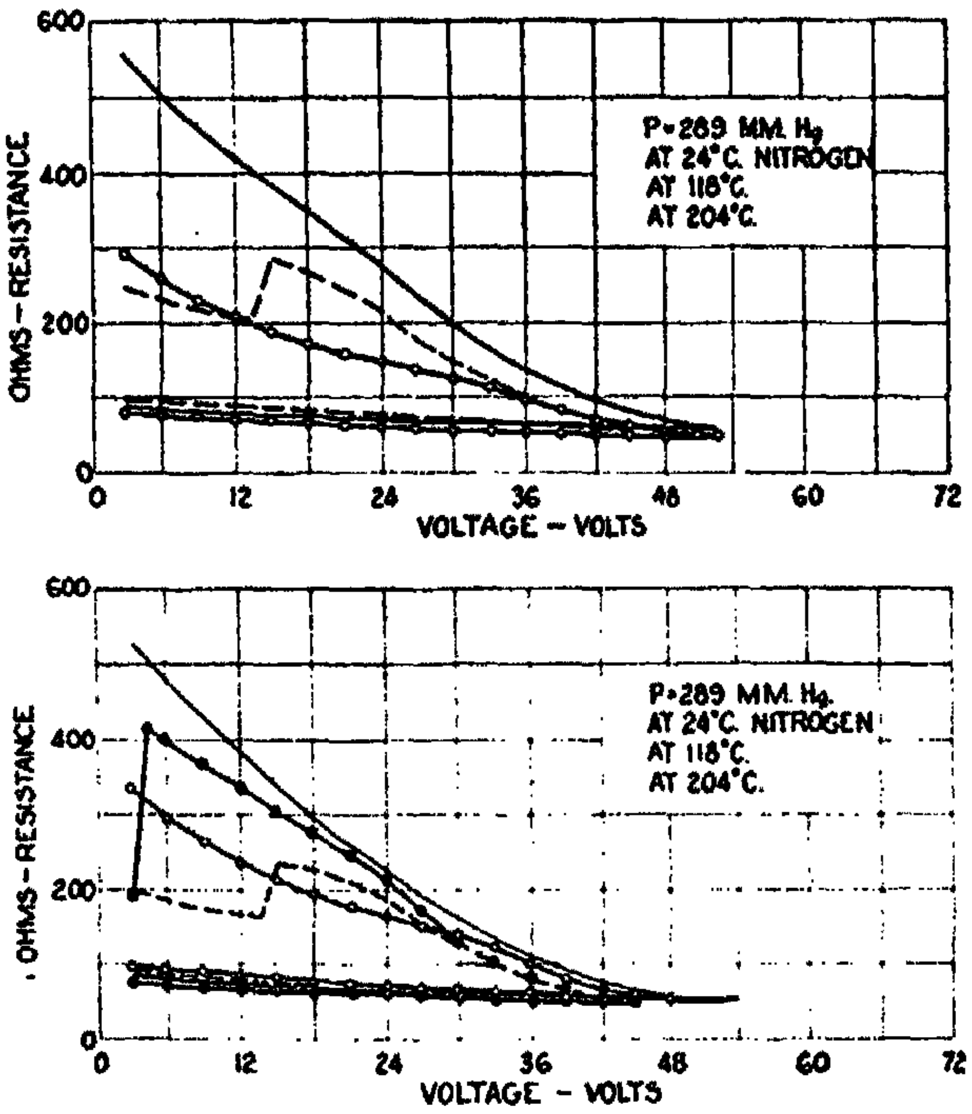

Fig. 5
Instantaneous resistance vs. voltage curves to show the effect of temperature

that the resistance also decreases as the adsorbed gas is removed from the carbon surface, i.e., as the pressure is decreased, we may conclude that the effect of the applied voltage is to remove gas from the contacting carbon surfaces. Whether the removal of the gas by an applied voltage is due to an electrostatic effect or is due to heating[1] of the contacts or to a combination of both effects has not been indicated.

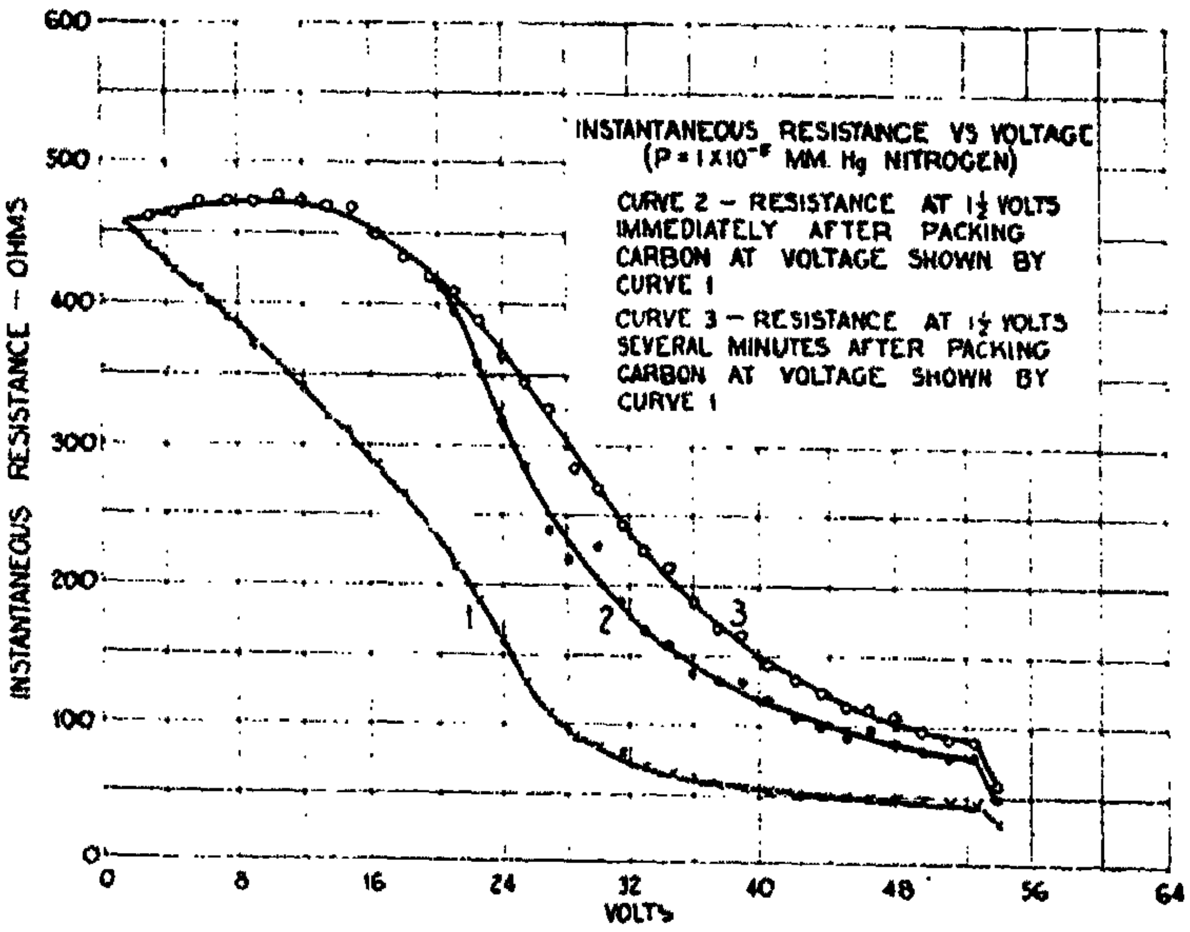

FIG. 6

Adsorption measurements have shown that the amount of gas adsorbed by carbon decreases as the temperature increases. Therefore, whether or not the voltage effect is to be attributed to heating of contacts, the external application of heat at constant voltage should produce a decrease in resistance. This is shown to be the case at all voltages by the data presented in Fig. 5. In this figure measurements are shown as the applied voltage was increased to 52 volts and then decreased to 1.5 volts. Although the return curves are practically identical, the packing curves show a decrease in resistance of approximately 50% at low voltages due to heating the carbon to a little over 100°C. The irregularities in the 204°C curves will be referred to in a later paragraph.

Effect of Gas held in Pores

It has been observed in the last paragraph that the resistance-voltage curve is not reversible for packed contacts, especially when the applied voltage has been very high. To test the question of reversibility at all voltages, meas-

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[1] Holm has shown that the temperature at the contacts is proportional to the square of the voltage, cf. Z. tech. Physik, 3, 290-294, 320-326, 349-357 (1922).

urements of resistances at 1.5 volts were made between readings at the high voltages. A set of curves of this type are shown in Fig. 6. It will be observed that up to about 15 volts the curve must be reversible since the 1.5 volt points are approximately the same as the original. Above this voltage, the resistance at 1.5 volts is never as high as it was originally. This may be interpreted to be the effect of driving some of the gas from the surface and producing a larger area of contact. As the voltage is increased further, the resistance at 1.5 volts seems to increase with time. This has been attributed to the redistribution within the contacts of the gas which is being supplied from the pores to take the place of some of that driven from the contact surfaces. These must be quite effectively sealed, because the resistance at 1.5 volts does not at any time resume its original value. (If the contacts are broken and a measurement made at 1.5 volts, the value has always been that of the original within the error of the test.) If sufficiently high voltages are used, the resistance at 1.5 volts becomes practically constant at a low value which is slightly above that at the high voltage. This difference may be attributed to the cooling of the sealed contacts, the effects of which will be shown later.

It is now possible to explain the behavior of the 204°C curves in Fig. 5. Obviously, the pores were not outgassed at this temperature and when sufficient power was dissipated at the pore opening to upset the equilibrium, the gas expanded blowing the contacts apart, and caused new contacts higher in resistance to be formed. The same type of effect has been observed when the voltage was increased by too large intervals. In some cases it becomes impossible to balance the bridge at a high voltage unless the voltage has been increased in small steps.

The curves shown in Fig. 6 were obtained at a relatively low gas pressure. At atmospheric pressure the time effect may entirely disappear or be in the opposite direction. Curves of this type have been obtained, but, since the next set of measurements show the same type of effect, they will not be illustrated.

The data considered cover the life history of a set of sealed contacts. These were sealed at a pressure of 1×10^{-5} mm. Hg, and, for a period of two weeks, the carbon chamber was carefully shielded from extraneous sound and building vibrations. First, several observations of the resistance vs. voltage curve at a low gas pressure were taken. Then, the pressure of nitrogen was increased to 63.5 mm. Hg. The resistance remained practically the same since the contacts were sealed and gas from the surrounding atmosphere could not reach the contacting surfaces. The pressure was reduced to 26.4 mm. Hg with no apparent change. Other measurements were taken until the carbon chamber was rotated and the return curve at a pressure of 70 mm. Hg taken. This checked very closely that taken at a pressure of 289 mm. Hg two months earlier, as would be expected from the data given in Fig. 4. It was also noticed that the packing curve taken after these data was very nearly identical with that taken before. In addition, a comparison of measurements of resistance at 1.5 volts indicated that no change had taken place. Hence, if the contacts had not been sealed during these observations, the resistances at 63.5 mm. Hg would have been approximately the same as those on the return curve taken later.

It was observed that the resistance at 1.5 volts for the packed contacts showed a tendency to decrease with continued applications of the packing voltage. It is believed that during this period of time, the contact was continually losing gas as a result of the successive application of high voltages.

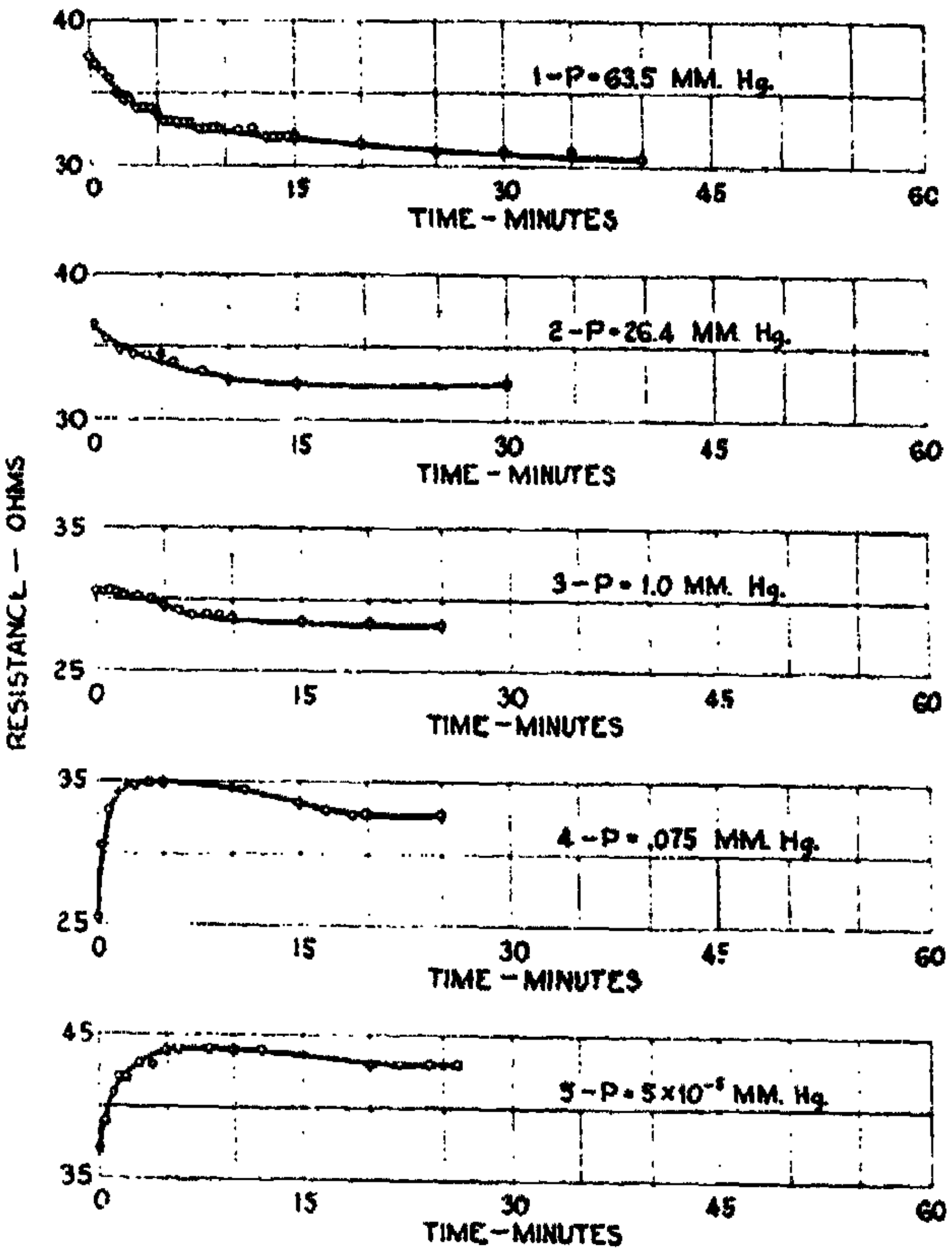

Fig. 7
Instantaneous resistance at 1-1/2 volts vs. time at different pressures of nitrogen carbon previously packed at 54 volts.

While this set of data was being taken, measurements were also made to determine the time drift, at 1.5 volts, after the contacts had reached equilibrium at 54 volts. The types of curve obtained are shown in Fig. 7. They illustrate two kinds of time drift: one, an increase in resistance which took a relatively short time; the other, a decrease which took a longer period of time, but of which the larger part took place in the first three minutes. When the external gas pressure was approximately 1 mm. Hg, the resistance remained practically constant as indicated in the fourth curve. If, however, the external pressure was less than 1 mm. Hg, the resistance increased with time, and, if greater, it decreased.

A simple explanation is that the pressure inside and outside of the contacts must be in equilibrium. When heat in the form of power dissipated at the contacts is applied, the amount of free gas within the contacts is increased. Then, if the gas pressure outside is low, the contacts tend to increase in resistance due to decreasing area of contact caused by expansion of the gas within the contacts. The resistance may show a final tendency to decrease due to cooling, that is, the pressure inside becomes lower. If the gas pressure outside is high, it, combines with the cooling of the contacts, causes a decrease in resistance due to increased area of contact.

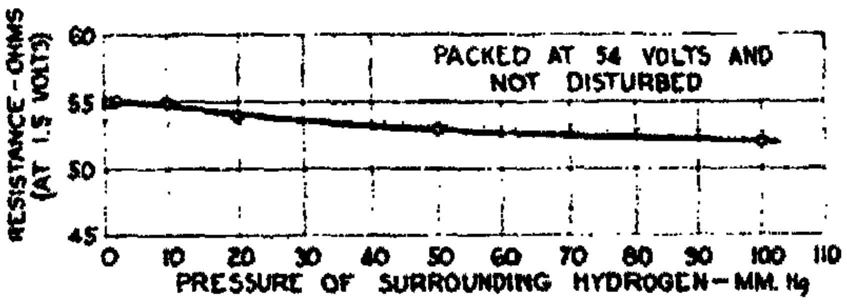

FIG. 8

If this explanation is correct, it should also be possible to change the equilibrium resistance of packed contacts by changing the gas pressure surrounding them. Fig. 8 shows that this condition has been experimentally verified.

Another check of the above explanation is presented in Table I. The third row of data gives the averages of resistances determined at 54 volts corresponding to the four pressures of hydrogen indicated in the table. In determining these resistances, the packing voltage was intermittently applied until the resistance remained constant. Under these conditions, the pressure in the contacts should have been higher than when the contacts were at room temperature. Hence, the resistance immediately after packing should be and was higher than that at the same voltage after cooling. It should also be noted that the difference between the hot and cold resistance was greater at the higher external gas pressures. This was to be expected since upon cooling the

TABLE I

Number of Observations	3	3	2	2
Pressure of Hydrogen in mm. Hg	310	150	10	1
Resistance after Packing (Hot Contacts)	48.7	47.0	46.0	37.0
Resistance after Cooling (Cold Contacts)	46.7	45.7	44.5	36.0

contacts would be forced closer together at the higher than at the lower external pressures.

A similar increase in resistance with temperature was observed by applying small temperature changes to a sealed contact and its surrounding atmosphere. In this case, illustrated in Fig. 9, the increase in temperature caused some of the gas within the contacts to be driven from the surface, increasing the pressure. This in turn, caused the area of contact to be decreased, and, hence, the resistance to increase. The results are in accord with those shown in Table I.

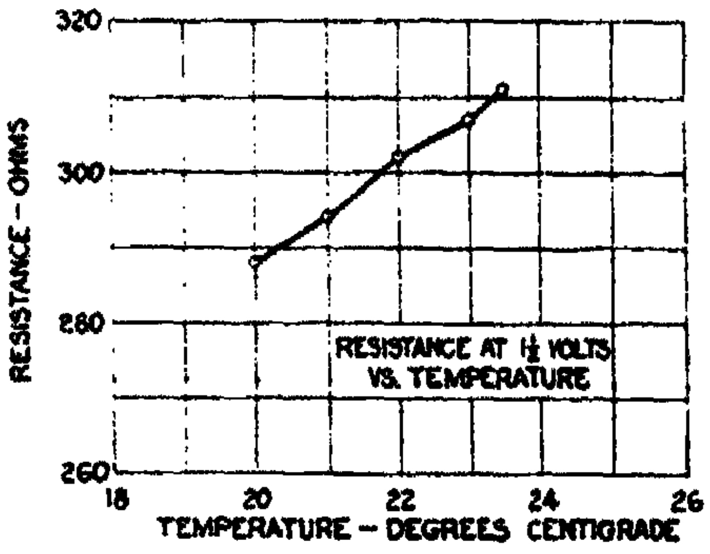

Fig. 9

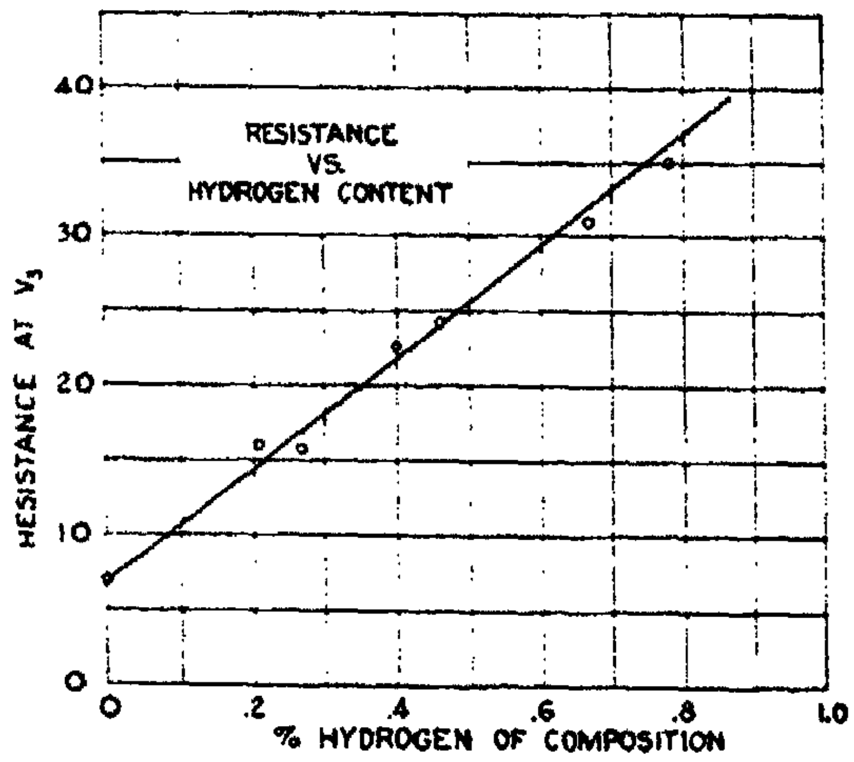

Fig. 10

Effect of Combined Hydrogen

For measurements of this type, the resistance of several carbons which contained amounts of combined hydrogen up to 1.0% were compared. In other experiments it has been found that the presence of larger amounts of hydrogen are due to the fact that the thermal decomposition of the raw materials has not been carried as far as in the case of samples containing less hydrogen. In Fig. 3 it is shown that when the voltage exceeds a certain value a break appears in the instantaneous resistance versus voltage curve. This voltage corresponds approximately to a temperature of the contacts just exceeding the maximum temperature reached during the preparation of the samples. It seems reasonable that the magnitude of this break would depend on the amount of combined hydrogen. In some cases, the resistance decreased from as high as 35 ohms to 7 ohms. The low value of resistance was the same for all carbons and is therefore interpreted to be the resistance of the contacts after the chemically combined gas in the neighborhood of the contacts is removed. Fig. 10 shows that the resistance at this critical voltage V_3 is directly related to the percent of combined hydrogen contained in the carbon and therefore probably to the specific resistance of the carbon. There was no relation whatever between the instantaneous resistance at any other voltage and the percent of hydrogen.

Summary and Conclusions

A method has been described whereby reproducible measurements of the resistance of granular carbon contacts can be made. The experimental arrangement was such that the resistance could be measured as a function of gas pressure, applied voltage or time.

Experiments have been described which show that when their surfaces are in equilibrium with the surrounding atmosphere, the contact resistance between carbon granules increases with the gas pressure over the range 1×10^{-3} mm. Hg to about 760 mm. Hg. This increase in resistance was shown to be reversible and was related approximately logarithmically to the pressure of the surrounding gas over this pressure range. At constant pressure the increase in resistance diminished as the temperature was raised. Since these experiments were performed with nitrogen, which has been shown by other investigators to be adsorbed reversibly by carbon, the amount adsorbed increasing logarithmically with the pressure and decreasing with the temperature, we are led directly to the conclusion that the resistance of a granular carbon contact is determined in part by the amount of gas adsorbed on the carbon surfaces at the contact.

At constant pressure it was shown that the contact resistance decreased as the voltage was increased. Experiments were also described which showed that at both constant pressure and constant voltage the resistance decreased as the temperature was increased as would be expected from adsorption measurements since the amount of gas adsorbed by carbon decreases as the temperature increases. These facts, together with the fact that the temperature at a contact is proportional to the square of the voltage, indicate that at least part of the effect of the applied-voltage in reducing the resistance of a granular carbon contact may be due to the increased temperature of the contact. The experiments do not preclude, however, the possibility of there being also a purely electrostatic effect.

The effect of gas held in the pores of the carbon on the contact resistance was described. Depending on the gas pressure surrounding the granules, the resistance increased or decreased with time after the equilibrium was disturbed by applying heat at the contact only. This phenomenon was due to evolution of gas entrapped in pores opening into the areas of contact.

It was shown that after the voltage increases above a certain value, dependent on the kind of carbon used, there occurred a sudden decrease in the resistance. It is suggested that this critical voltage is related approximately to the temperature at which further thermal decomposition of the granules begins. If it is assumed that the amount of combined hydrogen, as determined by ultimate analysis, is an approximate measure of the specific resistance of the carbon, then the instantaneous resistance at this critical voltage is also a measure of the resistivity of the carbon. The results indicate that there is a linear relationship between the resistance in ohms at this voltage and the percent hydrogen of composition.

In conclusion, it may be stated that it has been demonstrated by a study of the resistance of granular carbon contacts that experiment can readily distinguish the effects of gas held by carbon (1) on surfaces in contact, (2) within pores, and (3) interatomically or chemically combined.

The success of these experiments has been enhanced by helpful criticisms and suggestions by Drs. W. A. Shewhart and H. H. Lowry. The work itself was performed with the assistance of Messrs. W. E. Orvis and G. G. Muller. I am also indebted to Miss A. E. Hamilton for the preparation of the illustrations.

Bell Telephone Laboratories,
New York City.

THE ACTION OF HYDROGEN SULPHIDE ON CHROMATES. PART I

BY H. B. DUNNICLIFF AND C. L. SONI

While studying the action of hydrogen sulphide on potassium chromate, potassium dichromate, and chromic acid in aqueous solution, it was found that with potassium chromate the products of the reaction are potassium thiosulphate and pentasulphide, sulphur and chromium hydroxide. When, however, an aqueous solution of chromic acid is treated with excess of hydrogen sulphide, the filtrate is neutral and the green precipitate which is formed contains the sulphate group. This coordination compound is slowly hydrolysed by water giving chromic hydroxide and sulphuric acid. It is decomposed by alkalies giving chromium hydroxide and a soluble sulphate and by hydrochloric acid giving a chromic salt and sulphuric acid. In neither case have thionic acids been detected. Further, when potassium dichromate is treated with hydrogen sulphide, a brown precipitate first forms which contains the sulphate group and the filtrate from the incomplete action also contains sulphate. Obviously therefore sulphates can be formed by the action of chromic acid and a dichromate on hydrogen sulphide and the details of these reactions will be given in another communication. Since sulphates are not decomposed by hydrogen sulphide, it appears that the presence of hydroxyl ions presents the formation of sulphate in the action of hydrogen sulphide on potassium chromate. The interpretation of this reaction is the subject of the following report.

Experimental

Potassium chromate was recrystallised until free from carbonate and sulphate and analysed by standard methods.

Found : Cr = 26.73%. K = 40.22%, CrO_4 = 59.7%. (K_2CrO_4 requires Cr = 26.77%; K = 40.28% and CrO_4 = 59.74%).

A 2% solution of potassium chromate was used. It was found necessary to pass sulphuretted hydrogen, purified by passing successively over iodine and through water, for about 16 hours in order to complete the reaction. The following sequence of colour changes took place:—

Yellow→dirty yellow→light green→green→dirty green.

On standing, there was a green precipitate formed and the supernatant liquid was golden yellow. The reaction is accompanied by marked rise of temperature and the final solution is strongly alkaline. The precipitate was filtered off but, on evaporating the filtrate, a further quantity of precipitate separated. The filtrate from the second precipitate could be concentrated without any deposition of sulphur.

The two precipitates consisted of chromium hydroxide mixed with sulphur. No sulphur acid, possibly present as a basic salt, could be detected. When the precipitate was digested with dilute hydrochloric acid, the chromium hydroxide went into solution and the sulphur remained and was easily filtered off. The chromium was precipitated as chromium hydroxide and weighed as Cr_2O_3. Found Cr = 26.75–26.82%. K_2CrO_4 requires Cr = 26.77%.

The golden yellow, strongly alkaline, filtrate was treated with white lead to remove hydrogen sulphide, and filtered. The solution then contained a considerable amount of potassium carbonate and, on adding barium nitrate to it, a copious precipitate was obtained. When thoroughly washed this precipitate was shown to be free from sulphate and sulphite. The latter was not likely to occur in view of the large excess of sulphur present in the strongly alkaline solution. The filtrate was carefully neutralised and tested for sulphur acids in the manner discussed by Dunnicliff and Nijhawan.[1] Thiosulphate was present but none of the thionic acids was detected. The reaction was carried out under different conditions of temperature and concentration, but the end products were always the same: chromium hydroxide contaminated *with sulphur* was precipitated and, in solution, sulphide, polysulphide and thiosulphate of potassium and colloidal sulphur.

H. Böttger[2] states that if sodium pentasulphide is boiled with lead hydroxide, lead sulphide and sodium thiosulphate are formed, and gives this as evidence for stating that the alleged pentasulphide behaves like a mixture of sulphur and sodium monosulphide, lead sulphide and sodium hydroxide being first produced, and sodium hydroxide subsequently reacting with sulphur to give thiosulphate. Hence to avoid the use of white lead for the removal of sulphuretted hydrogen, the excess of hydrogen sulphide was removed by heating the clear filtrate under reduced pressure.

In order to obtain a higher concentration of filtrate, 10% solutions of potassium chromate were used and, to accelerate the completion of the otherwise very slow reaction, the reaction vessel was maintained at about 80–85°C on a water bath. The liquid was filtered and the filtrate was evaporated under reduced pressure until no further precipitate of chromium hydroxide and sulphur occurred. The liquid was filtered into a distillation flask and evaporation under reduced pressure continued until crystals appeared in the liquor on cooling. Provided these crystals were kept out of air contact they could be redissolved, re-evaporated and recrystallised without the separation of any sulphur.

The yellow crystals were dried on a porous plate and were completely soluble. A turbid liquid resulted if they were shaken with water owing to access of oxygen. With dilute acids, a copious evolution of hydrogen sulphide took place and much sulphur separated. All efforts to separate the polysulphide by means of alcohol were unsuccessful. This confirms the observations of W. P. Bloxham[3] who states that, "though potassium pentasulphide is soluble in alcohol, it cannot be separated from the thiosulphate by means

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[1] J. Chem. Soc., **128**, 1 (1926); Kurtenacker and Wollok: Z. anorg. allgem. Chem., **161**, 201; Kurtenacker and Goldbach: **166**, 177 (1927).

[2] Ann. Suppl., **223**, 352 (1884).

[3] J. Chem. Soc., **77**, 753 (1900).

of this solvent because in the presence of potassium pentasulphide some thiosulphate dissolves."

Attempts were made to find the composition of the mixture of polysulphide and thiosulphate which separates in the crystalline form though, in view of the work of Küster and Heberlein[1], its appeared probable that the nature of the product would depend upon experimental conditions such as temperature, concentration and time.

W. P. Bloxham states that "hydrogen sulphide rapidly decomposes polysulphides, if passed through a cold solution, sulphur being copiously deposited and potassium hydrosulphide formed. If, however, hydrogen sulphide is passed through a hot solution of a polysulphide, no deposition of sulphur is observed, but the depth of colour is increased. It is suggested that some potassium hydrosulphide is formed on passage of hydrogen sulphide through a hot solution of K_4S_9, and that the liberated sulphur, at the moment of its separation, is taken up by unaltered K_4S_9, forming the higher compound K_4S_{10}".

The following are the properties of the crystals obtained from filtrate, which is golden yellow when concentrated and bright yellow when dilute. If the crystals are left in contact with the mother liquor for some time the polysulphide is oxidised to thiosulphate and free sulphur appears. The crystals are hygroscopic and cannot be dried completely. They decompose if complete dehydration is attempted and also on preservation, hydrogen sulphide being evolved. This reaction finally ceases and very old crystals contain no sulphide but much free sulphur. Fresh crystals are very soluble in water giving a clear solution which decomposes potassium chromate giving chromic hydroxide and which is decomposed by salts and dilute acids giving free sulphur. When heated on a platinum loop the crystals burn. Dreschel[2] states that this indicates the presence of a pentasulphide.

In view of the impossibility of drying the product, the following method of analysis was adopted. The crystals were filtered from the mother liquid as far as possible out of air contact and then quickly pressed on a porous plate or between filter paper and the product used for analysis.

(a) *Total Sulphur* was determined by treatment with sodium peroxide and estimation of sulphate in the melt.

(b) *Total Potassium.* A solution of a weighed quantity of the substance was divided into two parts. To one, strong hydrochloric acid was added and the solution boiled in order to coagulate all the sulphur which separated out. The filtrate from this was evaporated to dryness in a platinum dish and the amount of potassium chloride in the dish determined by titration against standard silver nitrate. The corresponding amount of potassium was calculated.

(c) *Thiosulphate.* To the other half of the solution, acetic acid was added. The solution was kept just acid and gently warmed. After filtering off the

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[1] Z. anorg. allegem. Chem., 43, 53 (1905).

[2] J. prakt. Chem., (2) 4, 20 (1871).

sulphur, and removing hydrogen sulphide, the clear filtrate was titrated against standard iodine solution to determine the amount of potassium thiosulphate present. This method was shown to be valid by control experiments.

These estimations make it possible to calculate the formula of the polysulphide of potassium, K_2S_y, present in the crystals (vide Table I, column I).

Hydrogen sulphide was passed through six different samples at 85°C and the filtrate obtained from them was evaporated, crystallised, and analysed separately. The results so obtained are given in Table I. The variations in the results indicate the instability of the crystals. Each result represents the average of two or three determinations.

TABLE I

Results of Analysis of Different Samples

	Analysed immediately after crystallisation				Analysed after 24 hours	Analysed after 4 days
Concentration of K_2CrO_4 solution used	2% approx.	5% approx.	10% approx.	15% approx.	10% approx.	10% approx.
a. Total potassium present	29.40	23.30	22.31	32.02	20.68	24.50
b. Total sulphur present	39.05	27.44	30.98	44.00	27.90	29.51
c. Potassium thiosulphate $K_2S_2O_3$, $5H_2O$	61.18	56.34	45.43	67.39	42.38	70.12
d. Potassium present as thiosulphate (Calculated from c)	17.05	15.69	12.65	18.77	11.80	19.53
e. Sulphur present as thiosulphate (Calculated from c)	13.98	12.87	10.39	15.40	9.69	16.03
f. Potassium present as sulphide = (a−d)	12.35	7.61	9.66	13.25	8.88	4.97
g. Sulphur present as sulphide = (b−e)	25.07	14.57	20.59	30.60	18.21	13.43
h. Calculated formula K_2S_y	$K_2S_{4.95}$	$K_2S_{4.67}$	$K_2S_{5.20}$	$K_2S_{5.24}$	$K_2S_{5.00}$	$K_2S_{6.61}$

Discussion of Results

In sample 6, the formula $K_2S_{6.6}$ is obtained for the polysulphide. When crystals of this sample, apparently quite clear, were dissolved in water the liquid became cloudy from the separation of sulphur. From this it is conjectured that some of the sulphur was present in solid solution. It was probably developed by the action of the air on part of the polysulphide present since H. Rose[1] showed that all polysulphides take up oxygen from the atmosphere forming thiosulphate and sulphur.

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[1] Pogg. Ann., **17**, 327 (1829); **55**, 353 (1842).

$$2K_2S_5 + 3O_2 = 2K_2S_2O_3 + 6S \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

This would lead to high values for the thiosulphate and for *y* in the formula K_2S_y (Table I). Pentasulphides react with water to give thiosulphate and hydrogen sulphide[1]

$$K_2S_5 + 3H_2O = K_2S_2O_3 + 3H_2S \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

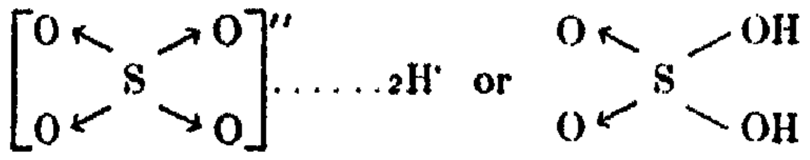
This would result in an increase in the relative amount of thiosulphate at the expense of the polysulphide present without affecting the composition of the resulting sulphide. The crystals obtained smell strongly of hydrogen sulphide and the variation in the thiosulphate content in the final moisture when the formula of the polysulphide is K_2S_5 may possibly be accounted for in this way.

Sample 5 was closed up in a small bottle and may not have suffered oxidation as shown in the above equation (1). The 6th sample was kept in a desiccator which happened to be opened several times during the four days it was kept there. It was not possible to determine the proportions in which thiosulphate and polysulphide are formed. Bloxham (loc. cit.).

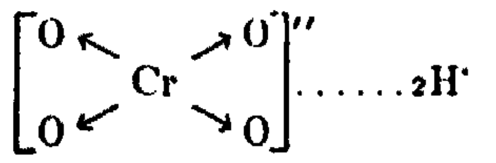
The Mechanism of the Reaction:—

It has been shown[2] that the sulphate ion consists of four oxygen atoms grouped tetrahedrally round a central sulphur atom (S^6).

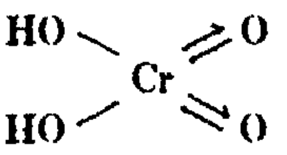
If a coordination linkage is represented by the sign, — and a covalent linkage thus, → the formula of sulphuric acid becomes:



Similarly chromic acid is:



Jaeger[3] and Freiman and Sugden[4] give the formula as:



the semipolar linkage ⇄ of Lowry having the same significance as the coordinate valency → of Sidgwick.

R. Luther and T. F. Ruther[5] suggest that in certain reactions the reduction of a chromate to a chromic salt proceeds in the stages $Cr^{vi} \rightarrow Cr^{v} \rightarrow Cr^{iv} \rightarrow Cr^{iii}$. Evidence is adduced for the existence of a quinquevalent chromium

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[1] H. C. Jones: J. Chem. Soc., 37, 461 (1888).

[2] Bradley: Phil. Mag., (6) 49, 1225 (1925); James and Wood: Proc. Roy. Soc., 109A, 598 1925); Wasastjerna: Phil. Mag., (7) 2, 292; Dickson and Binks: 114 (1926).

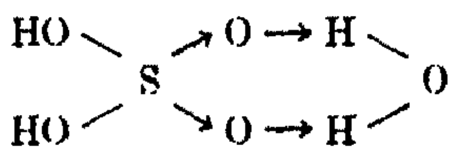
[3] J. Chem. Soc., 1141I, 33 (1918).

[4] J. Chem. Soc., 1928, 263.

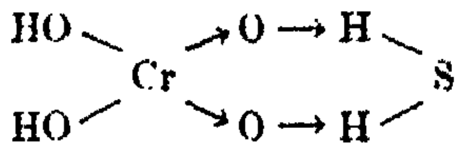
[5] Z. anorg. Chem., 54, 1 (1907).

atom,[1] which is a more rapid oxidising agent than chromic acid. This does not appear to be the course of the reaction in the reduction of chromic acid by hydrogen sulphide. Potassium chromate solution undergoes partial hydrolysis forming potassium hydroxide and chromic acid and their dissociation products. Potassium hydrosulphide is formed in solution. The decomposition of the chromic acid is attended with the separation of sulphur. The potassium compounds formed in this reaction, i.e. polysulphide and thiosulphate correspond exactly with those produced by the action of potassium hydrosulphide on sulphur in the presence of water under the conditions of the experiment. (v.s.). The quantitative formation of chromium hydroxide and the total absence of sulphate in the products of the reaction may be accounted for as follows:—

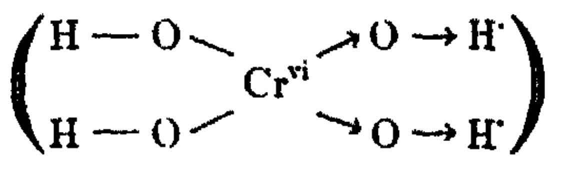
The hydrate of sulphuric acid has been shown to have the formula[2]:—



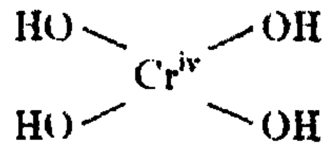
By analogy it is suggested that the first action of hydrogen sulphide on chromic acid is



Hydrogen sulphide is an endothermic compound and the disturbance caused by the linking of the atoms as shown involves an exothermic reaction resulting in a disruption of the molecule with loss of sulphur and the formation of a compound:



which immediately resolves itself into



a rearrangement involving the reversion of electrons from a valency orbit to one of the inner orbits. Tetravalent chromium or chromium compounds showing a coordination number = 4 have so far not been observed and, even if they existed they would, on decomposition in the presence of a reducing agent, probably yield chromous compounds.

If chromous chloride is dissolved in ammonia, the complex $[\mathrm{Cr^{II}(NH_3)_6}]^{\cdot\cdot}$ $2\mathrm{Cl}'$ is formed. This compound resolves itself spontaneously into the

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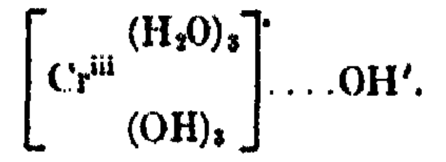
[1] Weinland and Fridrich: J. Chem. Soc. 901, 37 (1906). See also Wagner and Preiss· Z. anorg. allgem. Chem., 128, 265 (1928).

[2] Sidgwick: "Electronic Theory of Valency", p. 286 (1927).

trivalent compound $[Cr^{iii}(NH_3)_6]^{\cdots}\ldots 3Cl'$ with evolution of hydrogen. Similarly the compound $Cr^{iv}(OH)_4$ (v.s.) apparently rearranges itself into a coordination compound of the type:—

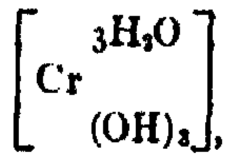


$$\left[Cr^{iii}\begin{matrix}(H_2O)_3\\ \\ (OH)_3\end{matrix}\right]^{\cdot}\ldots OH'.$$

which reacts with the ionisation products of hydrogen sulphide,

$$H_2S \rightleftarrows H^{\cdot} + HS' \rightleftarrows 2H^{\cdot} + S'',$$

the latter stage being considerable in alkaline media.[1] The hydroxy and hydrogen ions form water and the electrons associated with the S'' or SH' ions are transferred to the complex with the formation of colloidal sulphur or polysulphide and, also in the colloidal form, the compound:



$$\left[Cr\begin{matrix}3H_2O\\ \\ (OH)_3\end{matrix}\right],$$

a gray-green substance[2] also formed by the complete hydrolysis of $CrCl_3 . 6H_2O$. This loses its coordinated molecules of water and eventually coagulates giving chromium hydroxide[3] $Cr(OH)_3$.

Conventionally the reaction may be represented by the equation:

$$2H_2CrO_4 + 3H_2S = 2Cr(OH)_3 + 2H_2O + 3S.$$

A confirmation of this equation by a determination of the sulphur acids and free sulphur is not practicable on account of the complicated action between sulphur and potassium hydroxide.

Department of Chemistry,
Government College,
Punjab University,
Lahore, India.

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[1] Bassett: "Theory of Quantitative Analysis," pp. 40, 160, et seq.

[2] Bjerrum: Z. physik. Chem., 73, 724 (1910).

[3] Bjerrum: loc. cit., where evidence for the single formula is given; see also Weiser: J. Phys. Chem., 24, 277 (1920); 26, 401 (1922).

NOTES ON DUAL EMULSIONS, WITH EXAMPLES OF INTEREST IN THE SPRAYING OF TREES

BY ROWLAND MARCUS WOODMAN

Robertson[1], Clayton[2], Seifriz[3], Woodman[4] and others, have shown that in some emulsion systems inversion can be accomplished simply by alteration of the phase-volume ratio. Instances of dual emulsions existing at the *same* phase volume ratio with the *same* emulsifier present in the *same* amount, are, however, of much rarer occurrence: Clayton[2] noted a tendency of margarine emulsions to invert completely when subjected to violent agitation; Seifriz[3] has shown that standing, with subsequent reshaking, of emulsions containing certain petroleum oils causes inversion, whilst Woodman[4] demonstrated this standing effect to hold in the system cresylic acid-water-gelatine, and also that an actual prediction of the emulsion type formed by shaking together the phases may be made according to the mode of shaking employed. The present paper consists of observations on other systems giving dual emulsions at the same phase-volume ratio, special attention being paid to the significance of the results in the preparation of spraying emulsions.

The first example was a sample of B.D.H. petroleum ether A.R., b.p. 100 – 120°C., guaranteed to conform to the standard of purity given in "The B.D.H. Book of A.R. Standards (1926)." Ten c.c. of this were vigorously and intermittently shaken in a cylinder with 10 c.c. of 0.5% potassium oleate solution[5], three hand-shakes at intervals of 30 sec. being found necessary at 25°C. to form the O in W type[6], which creamed normally upwards[4]. The experiment was repeated in another cylinder, 3-5 shakes apparently producing a perfect O in W emulsion, judging by the film on the cylinder side[4]; owing however, to a lack of that permanent and abundant foam which characterises *complete* emulsification of large quantities of oil in an aqueous medium[7], the shaking was continued, 11 shakes producing no obvious difference. The emulsion was found to be W in O by the drop test, and emulsification must have been complete according to the continuously-draining film on the cylinder side[4]; the emulsion, however, *creamed upwards*, as if O in W, and not *downwards*, as would be expected of a W in O type when the oil is less dense than water[4], and, therefore, both types of emulsion were suspected as being present at the same time. On reshaking and keeping the emulsion 42 hr., drop tests showed both types of emulsion present in the cream, the lower

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[1] Robertson: Kolloid-Z., 7, 7 (1910).

[2] Clayton: J. Soc. Chem. Ind., 36, 1205 (1917); Trans. Faraday Soc., 16, Appendix, 22 (1921).

[3] Seifriz: J. Phys. Chem., 29, 834 (1925).

[4] Woodman: J. Phys. Chem., 30, 658 (1926).

[5] Potassium oleate from the sample described by Woodman: J. Agric. Sci., 17, 44 (1927).

[6] O represents the non-aqueous phase in all cases.

[7] Woodman: J. Pomol. Hort. Sci., 4, 95 (1925).

portions containing more W in O; after 50 hr., the emulsion was wholly O in W, thus showing inversion.[1]

The experiment was repeated twice; in one, vigorous intermittent shaking being employed, and, in the other, gentle partial rotation previous to vigorous shaking.[2] The first emulsion was a perfect O in W type, formed in 3-4 shakes at intervals of 30 *sec.*, and creaming upwards and normally. The second, by drop tests, was found to be an imperfect (*i.e.*, incomplete and unstable), W in O type, creaming rapidly to give excess oil continuous phase over W in O emulsion cream surmounting unemulsified aqueous phase; on reshaking once and leaving 15 min., the cream was O in W, showing inversion[1], though this emulsion was unstable and completely cracked in about an hour. It will be noted that the methods of shaking are the reverse of those in the system previously examined[2].

A third set of experiments was made with the ultimate notion of employing certain hydroxyl compounds as insecticides, ovicides and winter washes for the spraying of trees. Phenol, hexalin (*cyclo*hexanol), cresylic acid and methyl-hexalin, though good contact poisons, are impracticable when used "naked", both from the points of view of expense and of harmful effects on vegetation even when trees are in the so-called "dormant period" in winter[3]). Two methods of dilution are, however, possible in the special case of these substances, both methods, because of the presence of soap, yielding washes which will wet easily and spread over the plant surfaces, the skins of insects and eggs, and mosses and lichens on the trunks and branches[4]. The first is to make solutions in soap solutions[5]; the second is to emulsify them.

Emulsions for spraying plants are prepared in two ways[5]: the toxic oil may be incorporated with the emulsifier to form a clear solution known in practice as a "miscible oil", which should readily give perfect emulsions on stirring into water; or a concentrated "stock" or "free" emulsion may be stored and diluted down to the required concentration just previous to spraying.

The hydroxyl compounds mentioned need not be made into "miscible oils" as they are soluble in soap solutions, though they are, assisted by soaps, valuable *aids* in the formation of solutions and "miscible oils" of such toxic hydrocarbons as petroleum fractions[6], and of such compounds as tetra- and deca-hydronaphthalene[7]. The formation of stock emulsions of these phenols

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[1] The first emulsion, judged by the abnormal creaming, must have been a mixture of W in O and O in W; partial mixing in the drop test is apt to escape notice or be neglected if one gets globules denoting non-mixing, *i.e.*, the experimenter tends to judge types by the drop test by non-mixing rather than by mixing. It is only fair to record that in some of these examples of inversion on keeping and re-shaking, the removal of emulsion for drop tests might have altered the phase-volume ratio to such an extent as to cause inversion. In others, however, no drop tests were done, the type of emulsion being judged entirely by eye.

[2] Woodman: J. Phys. Chem., 30, 658 (1926).

Hexalin and methyl-hexalin, in virtue of their lack of phenolic properties, might be used in dilute solution or emulsion form as contact insecticides when foliage is on the trees, to replace the more expensive nicotine.

[4] Woodman: J. Pomol. Hort. Sci., 4, 38 (1924); *J. Soc. Leather Trades' Chemists*, 8, 517 (1924).

[5] Woodman: J. Agric. Sci., 17, 44 (1927)

[6] Woodman: J. Agric. Sci., 17, 44 (1927).

[7] Unpublished data.

and hydrogenated phenols, capable of dilution, will be a matter of some difficulty in view of their solubility in soap solutions; thus to obtain spraying emulsions containing 1-10% of these hydroxyl compounds, the ratio of emulsifiable phase to emulsifier (soap), must be comparatively high to avoid solutions[1]. In these circumstances the farmer might as well prepare his own emulsions in the dilute form at the actual place of spraying.

The method of experiment was as follows: the emulsifier solutions (from the stock potassium oleate mentioned previously, a stock solution being diluted down as required), were kept at room temperature; as occasion demanded, a given number of c.c. were pipetted into a 50 c.c. cylinder, and a given number of c.c. of the hydroxyl compound then added in such a manner as not to disturb the aqueous medium (if the soap solution were the less dense, the process was reversed). The cylinder was placed in a thermostat at 25°C. for 30 min., stoppered, rapidly withdrawn, given a vigorous and complete shake (up and down motion of the hand), and then replaced rapidly in the thermostat; the cylinder was withdrawn and shaken every 30 sec. until complete emulsification occurred. Parallel experiments were performed in every case, the method of preparation (at 25°C.), being to give partial gentle rotation or *very gentle* shaking first[2], followed by vigorous and continuous shaking. The emulsions were all examined by the drop test, though it was found possible, after some experience, to tell the type by appearance and by the character of the film on the cylinder's side.

The results are given in Table I: they show that, in the case of O in W emulsions, if the phase volume ratio be kept constant, increase in the concentration of emulsifier causes easier emulsification; if the phase volume ratio be altered, preponderance of one phase tends to make that phase, as previously-mentioned work has demonstrated for other systems, the continuous one, especially when the amount of emulsifier present is low; and, that, in some cases, where inversion occurs with phase-volume ratio change, a critical phase-volume ratio is obtained where both types of emulsions are possible according to variation in the method of shaking, as discussed in a previous paper[1], this also occurring mostly when the initial concentration of the emulsifier is small.

A spraying emulsion must necessarily be of the O in W type: otherwise the object of making the emulsion—to dilute the "naked" and, in large masses, phytocidal oil, with a commonly-occurring, inexpensive and non-phytocidal medium such as water—is defeated. In view of the fact that both types of emulsions are given, it will be unsatisfactory to use the systems experimented on here in actual practice; this is because the grower tends to make concentrated emulsions initially: diluting these down to the required concentrations. The wrong type might thus be prepared, with trouble consequent on the inversion to the desired type when diluting to the spraying

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[1] It is worthy of note in this regard that emulsions are often found, in actual spraying, to be much more toxic to insects and insect eggs, than solutions; cf., Lees: J. Pomol. Hort. Sci., 4, 104 (1925), for an example of this in the case of cresylic acid.

[2] Woodman: J. Phys. Chem., 30, 658 (1926).

TABLE I

Volume of Potassium Oleate Solution (c.c.):	Volume of Hydroxyl Compound (c.c.):	Method of Treatment:	Type of emulsion formed, as found by drop tests, and no. (given in brackets) of 30-second shakes necessary to form emulsion at 25°C., at concentrations of anhydrous pot. oleate of:—														
			2%		1%			0.5%				0.25%			0.1%		
20	5	A	CW	—	CW	—	—	CW	MW?	—	—	CW	—	—	CW	—	—
20	5	B	CW(2)	—	CW(1)	—	—	CW(1)	MW(>10)?	—	—	CW(1)	—	—	CW(2)	—	—
10	5	A	CW	MW	CW	MW*	PW‡	CW	MW?	PW	HW	CW	PW	HW	CW	PW	HW*
10	5	B	CW(1)	MW(2)	CW(1)	MW*(>10)	PW‡	CW(1)	MW?	PW(2)	HW(2)	CW(2)	PW(2)	HW(2)	CW(2)	PW(2)	HW*(>5)
10	7.5	A	—	MW*	—	MW?	—	—	—	—	—	—	—	—	—	—	—
10	7.5	B	—	MW*(>10)	—	WM?	—	—	—	—	—	—	—	—	—	—	—
10	10	A	CW	WM†	CW	WM†	PW	CW	WM?	PW	HW	CW	PW	HW	CW	PW	HW*
10	10	B	CW(1)	WM†	CW(1)	WM†	PW(2)	CW(1)	WM?	PW(2)	HW(3)	CW(2)	PW(2)	HW(3)	CW(2)	PW(2)	HW*(>10)
8	10	A	—	—	—	—	—	—	—	—	—	—	—	—	—	—	HW*
8	10	B	—	—	—	—	—	—	—	—	—	—	—	—	—	—	WH*
10	15	A	CW	—	CW	WM†	PW	CW	WM?	PW	HW	CW	PW	HW	CW	PW	WH*
10	15	B	CW(1)	—	CW(2)	WM†	PW(2)	CW(2)	WM?	PW(2)	HW(3)	CW(2)	WP*	HW(4)	CW(2)	WP*	WH*
5	10	A	CW	—	CW	—	WP?	CW	WM*	WP?	HW	CW	WP*	HW	CW	WP*	WH*
5	10	B	CW(3)	—	CW(3)	—	WP?	CW(3)	WM*	WP?	HW(3)	WC*	WP*	HW(4)	WC*	WP*	WH*

Key to, and notes on, the Table:

A = Gentle partial rotation previous to shaking (see Woodman: J. Phys. Chem., 30, 658 (1926)).

B = Vigorous intermittent shakes, one every half-minute.

C = Cresylic acid phase.

H = Hexalin (cyclohexanol) phase.

M = Methyl-hexalin phase.

P = Phenol phase.

W = Aqueous phase.

} Bracketed results denote proportions of the two phases such that both types of emulsion are possible, the type formed depending on the mode of shaking employed.

{ Denotes parallel experiments.

* Denote that vigorous shaking (treatment B) always gives the W in O type where that type is a possible one of two, and that treatment A gives the reverse, as was noted in the previous system (Woodman: J. Phys. Chem., 30, 658 (1926). The emulsions marked in this manner are imperfect and unstable, but perfectly definite; the excess disperse phase was allowed to settle out—a matter of a minute or so—before drop tests were done. In no case was a stable W in O emulsion obtained.

† Rapidly became coarse-grained and tend to separate.

? Denotes very unstable and transitory emulsions, which break practically instantaneously, and cannot be experimented on with surety. Similar behaviour to that on shaking two pure immiscible liquids, (e.g., toluene and water), together. Resultant layers are turbid.

‡ Very coarse unstable emulsions quickly creaming to give a thin layer of emulsion over a clear layer. This underlayer consists of practically the whole of the phenol, unemulsified. The non-formation of stable emulsions of phenol in 1% soap solution is probably accounted for by the comparatively great solubility of phenol in soap solutions of this concentration, (c.f., Woodman; J. Agric. Sci., 17, 44 (1927).

strength with water or soap solution. The results show, however, that by first making the emulsion so that the phase volume ratio of aqueous to oil media is at least (2 – 4): (1), the desirable type of emulsion is obtained.

It happens that the stable type of emulsion in the cases discussed is that needed for spraying. This is not so with cresylic acid (or pure cresols), and aqueous gelatine[1]; here the wrong type (W in O) is stable, and hence, as the O in W type usually cracks to give free acid quickly, *emulsions in these systems will be extremely dangerous to trees.*

Seifriz[2] is inclined to attribute this peculiarity of dual emulsion formation to the wide boiling range and consequent heterogeneity of composition of the oily phase, but this notion is not borne out by the author's results with pure cresols and the present single compounds; Seifriz, however, shows that the existing theories of the mechanism of emulsion type, and also Robertson's explanation for a particular case of phase-volume ratio alteration[3], are not feasible.

The author has previously tried wetting a finely-divided inert emulsifier—cork dust—with either liquid phase—water and toluene—before emulsification, and obtained the same O in W type in both cases; this was put down to the preferential wetting of cork by water[1]. Other experiments were now carried out to see if previous wetting of the containing vessels by one of the phases has any effect on the type subsequently formed.

The most favourable conditions for this to occur were chosen, the system investigated being known to yield dual emulsions by different mechanical treatment at the phase-volume ratio used[1]. Four 50 c.c. cylinders were dry-cleaned; into two were pipetted 10 c.c. lots of 40 hr. old 0.4% gelatine, and, into the other two, 10 cc. lots of cresylic acid; the contents of the cylinders were now swished round so that the insides of the vessels were wetted as far as possible, perfect, continuously-draining films being left on the sides. To the cylinders containing aqueous gelatine, 10 c.c. lots of cresylic acid were carefully added; to those containing cresylic acid, the same amount of the aqueous gelatine. One of each pair of similarly-treated cylinders was subjected to continuous vigorous shaking, and one to gentle partial rotation previous to vigorous shaking[1].

If this wetting theory were correct, each pair should, irrespective of mechanical treatment, tend to give the opposite type, the pair of cylinders first wetted by aqueous gelatine giving O in W types, and those first wetted by cresylic acid giving W in O types. The pairs, however, followed the rule given for this system before[1], mechanical treatment being found to determine the type formed, and not previous wetting of the cylinder by one of the phases; thus continuous vigorous shaking gave the W in O type, and previous gentle rotation the opposite type. *Moreover, the O in W emulsion formed in the cylinder previously wetted by cresylic acid was much more stable*

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[1] Woodman: J. Phys. Chem., 30, 658 (1926).

[2] Seifriz: loc. cit.

[3] Robertson: loc. cit.

and lasting than that from the cylinder treated oppositely, which, even though regarded as an accidental occurrence, is, nevertheless, contrary to what one would expect.

The emulsions so prepared were of the usual kind described previously[1]; thus the O in W types were unstable, breaking completely in 6-24 hrs., both re-shaking to the O in W type. The W *in* O type were stable and lasting, creaming upwards and fully in the normal manner in about two days, and inverting[1] to the more unstable O in W type on re-shaking[2].

One hypothesis which has been advanced to some extent previously, and which might explain the mechanism of the formation of emulsions, can be founded on the partition of the emulsifying agent between the two liquid phases[1]. Such an hypothesis would account for the fact that the liquid phase which tends to dissolve, or, in the limit, wet the emulsifier more easily, becomes the external phase of the emulsion, for then the partition coefficient will be in its favour.

The partition coefficient must be largely in favour of the continuous medium where one type of emulsion only is possible in the system. Whilst it may still be largely in favour of the more usual external phase in the case of a system where both types of emulsions are possible by alteration of the phase volume ratio (and may show this by one of the types being more stable), it cannot be so greatly in favour of this phase as is the case with a system yielding one type only in all circumstances. Alteration of the phase-volume ratio, where two types are possible, say by increasing the volume of one phase, the other volume being kept constant, might tend to make that phase the external one, for then a significantly greater amount of emulsifier—but not a greater *concentration*—would occur in this phase if the partition were anything approaching a finite quantity.

A partition theory of formation of types would also account for the apparently inexplicable case quoted by Seifriz[3], for the partition coefficient will be different for systems differing in the oil constituent, even though the emulsifier remains the same.

It is noteworthy that in many systems where dual emulsions are possible by alteration of the phase-volume ratio, the emulsifiers are appreciably soluble to give some kind of solution—true or colloidal—in both phases; thus soaps are soluble in water, and have been proved soluble to a great extent in various mineral oils[4], whilst gelatine is soluble in cresylic acid and the cresols

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[1] Woodman: J. Phys. Chem., 30, 658 (1926).

[2] *One O in W emulsion* got by *re-shaking* an old, creamed W in O emulsion seemed perfectly stable; it creamed normally downwards, the supernatant layer being clear aqueous gelatine; no trace of cracking was perceived for 5 days, when a little acid was noted underneath the cream; by the 6th. day there were 8 c.c. of cresylic acid.

[3] Seifriz: loc. cit., p. 839. Experience of emulsions teaches that there is a kind of specificity of oils in emulsification, as there is for emulsifiers, *i.e.*, that two oils with water and the same emulsifier might give opposite types, just as two emulsifiers with water and an oil can give opposite types; *this*, then, is the primary explanation *of Seifriz's* case, though the argument as regards the existence of different partition coefficients still holds good.

[4] Pickering: J. Chem. Soc., 111, 86 (1917).

as well as in water[1]. But, as has been stated, great solubility of emulsifier in both of the phases is not probably necessary for the formation of dual emulsions: in the limit, wetting of the emulsifier by one phase and solubility to some kind of solution in the other might dispose to dual types on alteration of the phase volume ratio, especially when it is remembered that in some simple one-type systems, wetting of solid particles by one liquid is all that is necessary for emulsification (*e.g.*, use of finely-divided solids as emulsifiers[2]), and that liquid is invariably the external phase.

An explanation of the formation of the two types when the constituents of the system are present in the same proportion, simply by altering the mechanical treatment given during preparation, or by subsequent re-shaking of one type, is much more difficult. It cannot be assumed that there are two partition coefficients under the same conditions of age, *etc.*, for the same emulsifier, for the probability is that only one partition coefficient exists for a substance between two liquid media; but it may be assumed that mechanical conditions interfere with the establishment of this definite partition coefficient, causing a temporary and unstable partition coefficient, or even allowing the definite partition coefficient to obtain only for a portion of the emulsifier. Thus adsorption due to a certain method of shaking has been assumed to have some such effect in preventing establishment of a final and definite partition coefficient in the system gelatine—water—cresylic acid, and to account for the instability of the O in W type[3]; in this case also, ageing of the system has had to be taken as a cause of prevention of the establishment of this definite partition coefficient, for old emulsions of both types give the unstable O in W type on reshaking in any manner.

Attempts at determining a partition coefficient in this system are now being made by the author and a colleague.

Horticultural Research Station,
Cambridge, England.
June 1, 1928.

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[1] Stocks: "Brit. Ass. Colloid Rpts.," 1, 74 (1917); Woodman: J. Phys. Chem., 30, 658 (1926); Cooper: Biochem. J., 6, 362 (1912).

[2] Pickering: J. Chem. Soc., 91, 2001 (1907).

[3] Woodman: J. Phys. Chem., 30, 658 (1926).

DISTRIBUTION OF AMMONIA BETWEEN WATER AND CHLOROFORM AT 25°*

BY HAROLD G. DIETRICH

This work was undertaken with a view to determining, by a distribution method, the effect of dissolved zinc hydroxide upon the activity of ammonia in water. It was planned as an extension of an investigation of the solubility of crystalline zinc hydroxide in solutions of ammonium hydroxide,[1] in order to secure further information as to the nature of the zinc-ammonia complexes; the existence of at least two, $Zn(NH_3)_2^{++}$ and $Zn(NH_3)_4^{++}$, has been deduced by de Wijs[2] from measurements of the partial pressure of ammonia in equilibrium with zinc-ammonia salt solutions. When, however, a study at 25° of the system, ammonia-water-chloroform, was extended to include zinc hydroxide, the length of time required to establish equilibrium between all phases was so great as to result in the formation, by hydrolysis of the chloroform, of acidic products; and no successful means of inhibiting this hydrolysis was found. Under such circumstances the solubility of zinc hydroxide in the aqueous layer in contact with chloroform is clearly of no significance, and consequently work along these lines was discontinued. As a necessary preliminary to this work, the distribution of ammonia between water and chloroform, in terms of concentrations by weight, had been determined; in this simpler system no difficulty caused by hydrolysis was encountered, the period required for the attainment of equilibrium being much shorter. It seemed worth while to present the results, particularly as the values hitherto available are in terms of concentration by volume, which is, for many purposes, less advantageous than weight-concentration as used here; moreover, chloroform is apparently still the only favorable non-aqueous competitor with water for ammonia.

Experimental

Ammonium hydroxide solutions were prepared by dilution of a strong solution made by distilling commercial C. P. ammonium hydroxide into a Pyrex flask containing laboratory-distilled water. Since there was some doubt as to whether all stock samples of chloroform would give the same results, owing to the presence of traces of stabilizers[3] not removable by distillation only, three stock samples (Mallinckrodt's C. P. Quality, Merck's U.S.P. X, and Baker's C. P.) were each redistilled.

A sample of distilled chloroform, about 350 cc., was washed a half-dozen times with ammonium hydroxide of the lowest desired concentration, then

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* Contribution from the Department of Chemistry, Yale University.

[1] Dietrich and Johnston: J. Am. Chem. Soc., 49, 1419 (1927).

[2] de Wijs: Rec. Trav. chim., 44, 663 (1925).

[3] Ethyl alcohol, a small amount of which is usually added to minimize decomposition, would be largely removed during the preliminary washing of the sample of chloroform with ammonium hydroxide. Underwood (Proc. Nat. Acad. Sci., 11, 78 (1925)) has, however, indicated a number of additional substances which may serve as stabilizers; and Newcomb (Analyst, 51, 19 (1926)), has pointed out the presence of ethyl chloride in, and the difficulty of its removal from, anaesthetic chloroform.

placed with approximately 100 cc. of the solution in a bottle of 500 cc. capacity, and rotated at five to six revolutions per minute in a water thermostat at 25° (±0.02) for four hours, preliminary experiments having indicated that equilibrium is established in less than this time.[1] After determination of its ammonia content, this chloroform was washed a half-dozen times with the ammonium hydroxide of the next higher concentration to remove hydrolysis products, and the procedure repeated.

Although Abbott and Bray report that the emulsion of water in the chloroform may be broken merely by rotation over a period of from one to three hours, the chloroform layer was still cloudy at the end of four hours; consequently a filtration method was used. A tube of 7 mm. bore and 24 cm. long, the lower 10 cm. of which was filled with cotton loosely packed, was passed rapidly through the water layer into the chloroform layer; then the chloroform was forced through the cotton filter by air pressure into a pipette the lower end of which was fitted with a stopcock to control delivery of the liquid. The first 50 cc. was rejected, this amount being necessary to saturate the cotton filter. Samples weighing approximately 80 g. were then withdrawn, delivered into weighed flasks containing about 20 g. water, and the exact weight of each sample obtained by difference. The ammonia content was determined by titration against hydrochloric acid, the strength of which was somewhat less than 0.01*M*, all titrations being made by weight, with sodium alizarin sulfonate as indicator. The same procedure, but without filtration, was used for the water phase, with the titration carefully carried to the same endpoint color as that reached in the titration of the chloroform phase.

As the distribution of ammonia is between water and aqueous chloroform, and as the solubility of water in chloroform is influenced by the presence of ammonia, the value of the distribution coefficient tends to decrease with increasing concentration of ammonia in the water phase; this change, however, is pronounced only in the range of high concentrations of ammonia in the aqueous layer, and for the low concentrations employed in this investigation, in general less than 0.1*M*, comes within the experimental error involved in carrying out the analyses. Furthermore, de Wijs[2] has shown that Henry's Law is not applicable to aqueous ammoniacal solutions much above 0.2*M*.

In Table I, the experimental data have been assembled and the distribution coefficient for each solution of ammonium hydroxide calculated. In the first and third columns the total ammonia content, as determined by analysis, of the water and chloroform phases respectively, has been expressed as the number of mols present per 1000 g. solvent, each value being the mean of at least two concordant determinations. However, in the system, ammonia-water-chloroform, two equilibria must be taken into consideration:

$$(1)\quad NH_{3(water)} \rightleftarrows NH_{3(chloroform)}$$

$$(2)\quad NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

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[1] That this equilibrium is established almost instantaneously has been reported by Hantzsch and Sebaldt: Z. physik. Chem., 30, 258, (1899); and by Abbott and Bray: J. Am. Chem. Soc., 31, 729 (1909).

[2] de Wijs: Rec. Trav. chim., 44, 655 (1925).

Before the equilibrium constant (distribution coefficient) for the first of the above equilibria can be calculated, a correction must be applied to the total ammonia content of the water phase for that ammonia which is present otherwise than as NH_3. By means of the equilibrium constant at 25° for the second equilibrium,[1] this correction has been calculated, and in the second column of the table the number of mols NH_3 per 1000 g. water is given. The fourth column, the distribution coefficient, is then the ratio of the concentrations expressed in the two preceding columns.

TABLE I

Distribution of ammonia between water and chloroform at 25°C

Total NH_3 in H_2O phase Mols per kilo m'_w	Actual NH_3 in H_2O phase Mols per kilo m_w	Total NH_3 in $CHCl_3$ phase Mols per kilo m_c	Distribution Coefficient in terms of molality ratio m_w/m_c
	Mallinckrodt's C. P. Quality		
0.02183	0.02120	0.0005936	35.71
0.03203	0.03127	0.0008735	35.80
0.04610*	0.04519	0.001263	35.77
0.04983	0.04888	0.001361	35.92
0.05871	0.05768	0.001611	35.81
0.1011	0.09975	0.002772	35.99
			35.83 (Mean)
	Merck's U.S.P. X		
0.02001	0.01941	0.0005405	35.91
0.04453	0.04363	0.001216	35.88
0.05680	0.05579	0.001556	35.86
0.06951*	0.06839	0.001919	35.63
0.1294 *	0.1279	0.003573	35.80
			35.82 (Mean)
	Baker's C. P.		
0.02624	0.02555	0.0007165	35.66
0.04724	0.04632	0.001302	35.57
0.05497	0.05398	0.001525	35.40
0.07166	0.07053	0.001988	35.48
0.07276	0.07162	0.002022	35.42
0.1315	0.1300	0.003671	35.41
			35.49 (Mean)

* Data on these concentrations were obtained after the experiments performed with Baker's C. P. $CHCl_3$, for the purpose of assuring that the procedure employed in the analyses had remained the same, and that the discrepancy between the results obtained *with this sample and those obtained with the first two was due to a fundamental cause.*

Discussion

Examination of the values of the distribution coefficient shows no particular trend for a given sample of chloroform. Upon comparison of the mean

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[1] The value, 18.12×10^{-6}, calculated from conductivity measurements by Burke: J. Am. Chem. Soc., 42, 2500 (1920) is in accord with 18.1×10^{-6} derived in the same manner by Noyes: Carnegie Inst. Pub., 63, 228 (1907).

values, however, a discrepancy greater than that accounted for by experimental error manifests itself when chloroform of Baker's stock is used; this may be accounted for in part by the presence in the chloroform of traces of impurities which increase slightly the solubility of ammonia. Such a factor may also account for the differences existing between the coefficients determined, on a volumetric basis, by different investigators, and for the discrepancies in individual investigations. For the purpose of comparison a correction has been applied in the same manner as presented in this paper to the data of each investigator,[1] and the distribution coefficient recalculated; and from the distribution ratio, 35.8 ± 0.1, expressed in terms of weight-concentration as a result of the experimental work presented above, a value for the ratio in terms of volume-concentration has been computed, upon the somewhat erroneous assumptions that the specific gravities of chloroform solutions and of water solutions of ammonia at 25° are the same as those of aqueous chloroform[2] and of pure water. The mean value for each investigation at 25°[3], with the average deviation, is given in Table II, which shows that the computed value, despite the assumptions made in its calculation, is of the same order of magnitude as that determined directly in terms of volume concentration.

TABLE II

Comparison of Distribution Coefficients, in terms of concentration by volume, at 25°

Observer	Number of Determinations	Distribution Coefficient	Average Deviation
Hantzsch and Sebaldt[4]	5	24.3	±0.9
Dawson and McCrae[5]	3	24.7	±0.2
Dietrich (calculated)		24.1	±0.07

Summary

The value, 35.8 ± 0.1, has been determined for the distribution coefficient, expressed as the ratio of the number of mols ammonia per 1000 g. water to that per 1000 g. of the chloroform phase in the system, ammonia-water-chloroform, at 25°. The dependence of this ratio upon the character of the stock sample of chloroform has been demonstrated: a probable explanation of this and of the divergent results of former investigators lies in the presence of traces of foreign substances used to inhibit hydrolysis of the chloroform. For this reason the discovery of a suitable non-hydrolyzing, non-aqueous solvent for ammonia would be extremely advantageous for distribution experiments.

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[1] By an extrapolation method Bell and Feild (J. Am. Chem. Soc., 33, 940 (1911)) have derived an approximate value of 24 at 25°. Such an extrapolation, however, is of little significance, inasmuch as it is made over a range from 1 N to 0 concentration, for which no experimental data are presented, and over which the correction for ammonia other than as NH_3 increases rapidly as the concentration of ammonia in the water layer decreases.

[2] The value, 1.4785, has been calculated for the density of aqueous chloroform at 25° by the method suggested by Newcomb.

[3] A table of limiting values of the distribution ratio (for which the concentration unit is volumetric) for very dilute solutions as found at different temperatures by various investigators is given by Bell and Feild.

[4] Hantzsch and Sebaldt: Z. physik. Chem., 30, 258 (1899).

[5] Dawson and McCrae: J. Chem. Soc., 77, 1239 (1900).

THE INFLUENCE OF ADSORBED FILMS ON RATES OF EVAPORATION

BY RONALD PERCY BELL

Introduction

In a previous paper[1] it has been shown that it is possible to investigate the adsorption of solute at the interface of a solution by a study of kinetic phenomena taking place at the interface. In this case the phenomenon studied was the velocity of a reaction taking place at the interface, and the present work is an attempt to evolve a method of more general application for the investigation of adsorption from solution, by studying rates of evaporation.

As was pointed out in the previous paper,[2] the most striking general conclusion arrived at by applying the Gibbs adsorption equation to the surface tension curves of solutions of non-electrolytes is that above a certain limiting concentration, the excess surface concentration becomes constant, presumably corresponding to the formation of a "saturated" monomolecular film such as is known to exist in insoluble films on liquid surfaces and films of gases on solid adsorbents It would therefore afford valuable support of the Gibbs equation if the existence of stable soluble films over a range of concentrations could be confirmed independently, and the work described in this and the preceding paper is directed especially towards this point.

It has been shown by Rideal[3] and Langmuir[4] that the rate of evaporation from a liquid surface is influenced by the presence of an insoluble monomolecular film. The use of such methods for soluble presupposes a certain degree of stability in such films, which seems justified by the fact that both static and dynamic methods of measuring the surface tension of solutions leads to the same results. The work of Lenard[5] shows that adsorption at a newly formed surface is complete in $10^{-8} - 10^{-6}$ seconds, so that any small disturbances of the film will be very quickly repaired. It is probable that at high concentrations of solute a film is formed more than one molecule thick, which will have no further effect upon the surface tension although it may influence the kinetic relationships. It is probable, however, that the forces holding the first layer of molecules together are considerably greater than those for subsequent layers, and that this greater stability of the monomolecular film will give it a prodominant influence upon kinetic processes.

The process of evaporation takes place in two stages, the escape of molecules from the liquid phase to the gas phase, and the removal of vapour from

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[1] Bell: J. Phys. Chem., 32, 882 (1928).

[2] Bell: loc. cit., p. 889.

[3] Rideal: J. Phys. Chem., 29, 1585 (1925).

[4] Langmuir: J. Phys. Chem., 31, 1719 (1927).

[5] Lenard: Sitzungber. Akad. Heidelberg, 5A, 28 Abhand. 28, p. 16 (1914); also, "Ueber die zeitliche Aenderung reiner Flüssigkeitsoberflächen." Diss. Heidelberg (1913).

the surface of the liquid. As has been pointed out by Rideal[1] and Adam,[2] only the first of these stages will be influenced by the nature of the interface, so that in order to detect this influence experimentally, the rate of removal of vapour from the surface must be an appreciable fraction of the "ideal" rate of evaporation. The "ideal" rate is the rate of evaporation in vacuo, or the rate of interchange between the two phases when the liquid is in equilibrium with its vapour, and according to the kinetic theory is given by the Herz-Knudsen equation,

$$R = P.\ 0.0583\ \sqrt{M/T} \tag{1}$$

where

R = ideal rate in grams per sq. cm. per second.
P = vapour pressure in millimetres of mercury.
M = molecular weight.
T = absolute temperature.

This accounts for the fact that Hedestrand[3] found no reduction in the rate of evaporation of water which was covered with an insoluble monomolecular layer of oleic or palmitic acid, since (as was pointed out by Rideal and by Adam) the maximum rate he measured was 5.05×10^{-6} grams per sq. cm. per second, while the ideal rate for water at 20°C. is 0.253 grams per sq. cm. per second. Hedestrand thus only obtained 0.0023% of the ideal rate, and the fact that he obtained a concordance of 1% between the values obtained with and without a film present only shows that the rate of escape was not diminished to less than 1/500th of its normal value by the presence of the film.

Rideal studied the influence of films of lauric, stearic, and oleic acids upon the rate of evaporation of water, and by removing the vapour by condensation, he obtained rates of about 0.4% of the ideal rate. Under these conditions he found that the films of acid caused reductions of about 20-50% in the rate of evaporation. These positive results, together with the negative results of Hedestrand, show that insoluble surface films exert a large retarding effect upon the rate of escape of water molecules into the gas phase, but that this retarding effect is only apparent in the rate of evaporation when the latter is an appreciable fraction of the ideal rate. It has been suggested, however, that in dealing with the evaporation of a component from solution (as opposed to that of a pure solvent) other factors may lead to a reduction in the evaporation rate in the presence of surface films. Langmuir[4] has studied the rate of evaporation of aqueous ether solutions in presence of different insoluble films, using relatively slow air currents. Although the rates of evaporation of ether obtained were only about 10^{-6} times the ideal rate, it was found that each of these films caused a reduction of the order of 80-90%. (As would be expected from Hedestrand's results, the rate of eva-

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[1] Rideal: J. Phys. Chem., 29, 1585 (1925).
[2] Adam: J. Phys. Chem., 29, 610 (1925).
[3] Hedestrand: J. Phys. Chem., 28, 1245 (1924).
[4] Irving Langmuir and D. B. Langmuir: J. Phys. Chem., 31, 1719 (1927).

poration of the water was not affected.) Langmuir therefore supposes that the films cause retardation not directly by influencing the rate of escape, but by preventing convection currents in the neighbourhood of the surface. This may be expressed by saying that in the case of evaporation of a solute, the resistance caused by the presence of a surface film is due not only to the film itself, but also to a layer of solvent molecules adjoining it.

The present work uses the evaporation of chlorine from dilute solutions in carbon tetrachloride, thus avoiding complications due to association or ionisation. The vapour is removed from the surface by a current of air, and the rate of evaporation of the chlorine determined by passing the air current into an absorption apparatus containing potassium iodide solution, and titrating the iodine liberated.

Before studying the effect of adsorbed films in a quantitative manner, it is necessary to consider the kinetics of evaporation in a current of gas. Very little theoretical or practical work has been done on this subject, and a rigid application of the laws of gaseous diffusion to the problem leads to differential equations which appear to be insoluble. However, by making several simplifying assumptions, Jablczynski and Przemski[1] have obtained a semi-empirical equation which is in good agreement with their experimental results.

They deduce the equation

$$\sqrt{v}\,\log_{10}\frac{P_o}{P_o - P} = K \qquad (2)$$

Of a different nature is the work of C. Bohr[2] on the invasion and evasion coefficients of solutions of gases. He defines the evasion coefficient γ as the amount of gas which would escape in unit time from unit surface of a perfectly stirred solution of unit concentration into a space containing none of the gas in question,—i.e., the ideal rate of evaporation for a solution of unit concentration. Bohr measures the evasion coefficients for aqueous and alcoholic solutions of carbon dioxide by passing a current of air over the surface of the stirred liquid. It is obvious, however, that the rates which he measures are not true evasion rates. For example, using a saturated solution of carbon dioxide in water at 0°C., he finds for γ the value 0.077 ccs. per minute per sq. cm. for a solution containing 1 cc. carbon dioxide in 1 cc. solution. This equals 2.5×10^{-6} grams per second per sq. cm., while the value calculated for the ideal rate by the Herz-Knudsen equation (equation (1)) is 10.4 grams per second per sq. cm. Thus under the conditions of Bohr's experiments, evaporation takes place at only about 10^{-7} times the true rate of evasion, and must therefore be considered essentially as a diffusion phenomenon.

Bohr has also defined the invasion coefficient (β) as the amount of gas at 760 mm. pressure which would dissolve in unit time in unit area of perfectly stirred liquid containing none of the gas in question, and measures these invasion coefficients by passing carbon dioxide over stirred water. Here

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[1] Jablczynski and Przemski: J. Chim. phys., **10**, 241 (1912).

[2] C. Bohr: Ann. Physik, (3), **68** 500 (1899); (4) **1**, 244 (1900).

again it is obvious from the values obtained that the case is essentially one of diffusion within the liquid, and not of true invasion. If β and γ are respectively the true invasion and evasion coefficients, and α is the coefficient of absorption, then for equilibrium,

$$\gamma = \alpha\beta$$

Bohr finds an approximate agreement with this relation using experimentally determined values of β and γ, from which he concludes that they correspond to the quantities he defines, and that there is no undisturbed layer at the gas-liquid interface. However, all the experiments were conducted under constant conditions of stirring, air current, containing vessels, etc., and it is certain from the results of other workers that had he varied these factors, different evasion and invasion coefficients would have been obtained. The approximate agreement between γ and $\alpha\beta$ can only be attributed to a chance relation between the velocities of diffusion of carbon dioxide in air and water under the unvarying conditions of the experiments.

Practical Part

Materials.

Chlorine was prepared by the action of concentrated hydrochloric upon pure potassium permanganate, and was washed with water and dried with concentrated sulphuric acid and phosphorus pentoxide. It was found that a tenth-molar solution of chlorine in ordinary pure carbon tetrachloride speedily became cloudy and deposited globules upon the glass. This did not occur if the carbon tetrachloride was previously dried over phosphorus pentoxide and distilled, but a solution approximately M/50 prepared in this way was found to undergo a continuous diminution of apparent chlorine concentration on keeping, to the extent of about 1% per day. This instability of solutions of chlorine in carbon tetrachloride has previously been noticed by Plotnikow[1] who attributed it to reversible photochemical reactions. Grüss[2] has shown however, that Plotnikow's results were due to traces of an unknown impurity in his carbon tetrachloride, and that by a rigorous purification stable solutions could be obtained. Since the method of purification employed by Grüss is very laborious, experiments were carried out with a sample of carbon tetrachloride purified specially for medicinal purposes supplied by Messrs. Albright and Wilson. This was dried over phosphorus pentoxide, distilled, and used to prepare chlorine solutions as before. At intervals 10 ccs. of solution was pipetted out and run into an excess of potassium iodide solution, the iodine liberated being titrated with N/100 sodium thiosulphate solution. It was found that there was no steady decrease in chlorine concentration.

The method finally adopted for preparing pure carbon tetrachloride was as follows. The "medicinal" grade was dried for twenty-four hours over phosphorus pentoxide, and was then poured off and fractionated. Only the

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[1] Plotnikow: Z. wiss. Phot., 19, 22 (1919).

[2] Grüss: Z. Elektrochemie, 29, 146 (1923).

middle fraction (about 90% of the whole) boiling over a range of not more than 0.05°C. was retained.

The apparatus used to prepare the chlorine solutions is shown in Fig. 1. The ground-in top of the flask A and the ground joints B and D were lubricated with syrupy phosphoric acid, while the top of the vessel G and the joint H were not lubricated at all, H being held together by an external coating of cement. The concentrated solution thus obtained was at once transferred to a large glass-stoppered flask and diluted to the required extent. When it was required to transfer from the large flask, it was forced over by dry air under pressure, thus minimising any loss of chlorine.

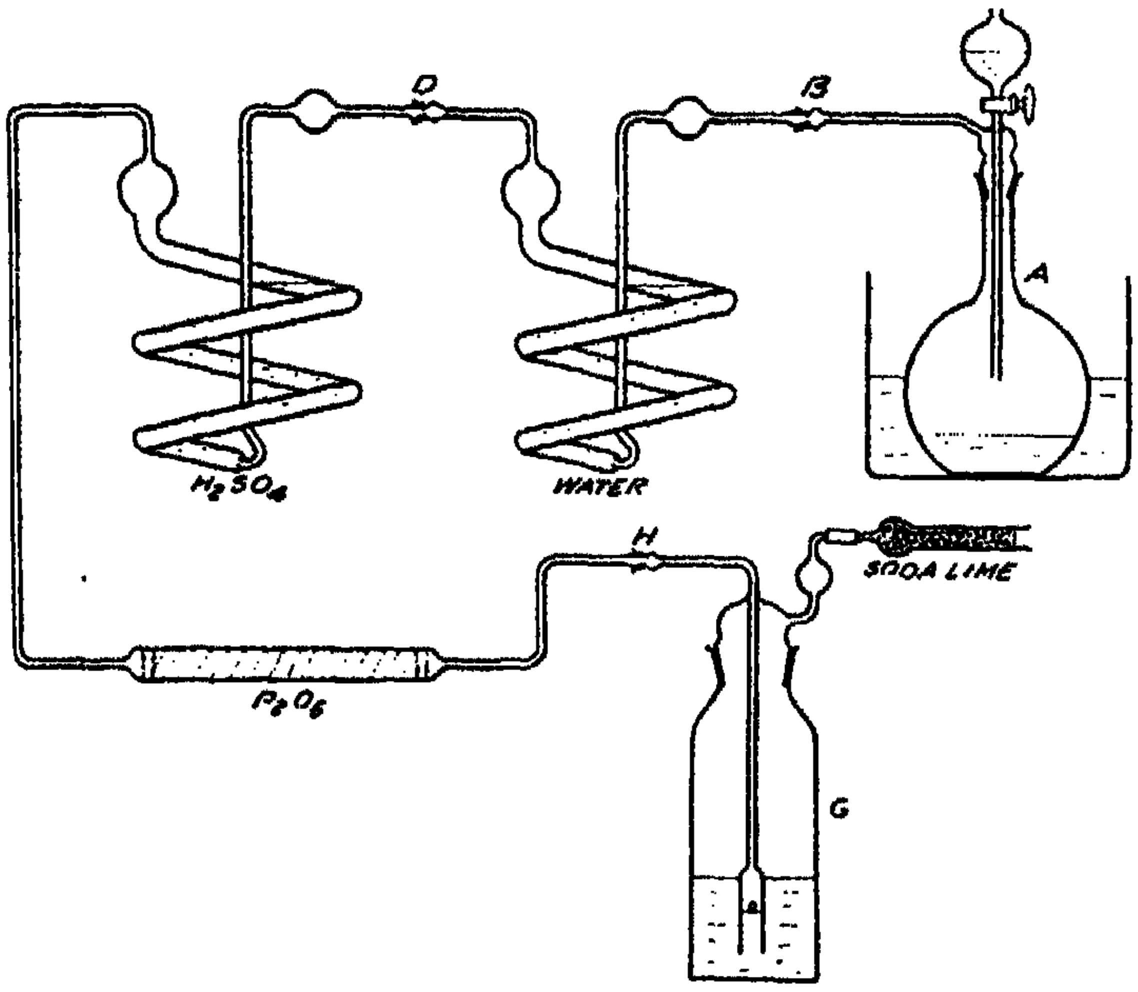

Fig. 1

Apparatus.

The apparatus used for determining the rates of evaporation is shown diagrammatically in Fig. 2. The air current used was produced by the rotary blower A, and, the volume of air passing through the apparatus was measured by the meter C. In order to indicate the pressure of the air leaving the meter, a manometer containing carbon tetrachloride was attached to the capillary tube F. The oil-trap E contained glass wool, and during the first few experiments was immersed in a freezing mixture to remove oil spray vapour derived from the blower. However, nothing was found to condense except a little water, so that in subsequent experiments the freezing mixture was omitted, although the oil-trap still formed a part of the circuit. The air was dried by passing through the calcium chloride tube G, about 1.5 metres long. The spiral H immersed in the thermostat was of thin-walled glass tubing about 3 metres long and 1 cm in diameter. It was fused on to the presaturator J, in which the air current passed over the surface of pure carbon tetrachloride. The air current was thus brought to the temperature of the thermostat and approximately saturated with carbon tetrachloride vapour, so as to avoid appreciable loss of carbon tetrachloride or cooling effect in the evaporation bulb. Preliminary tests showed that both the temperature attainment and saturation were practically complete.

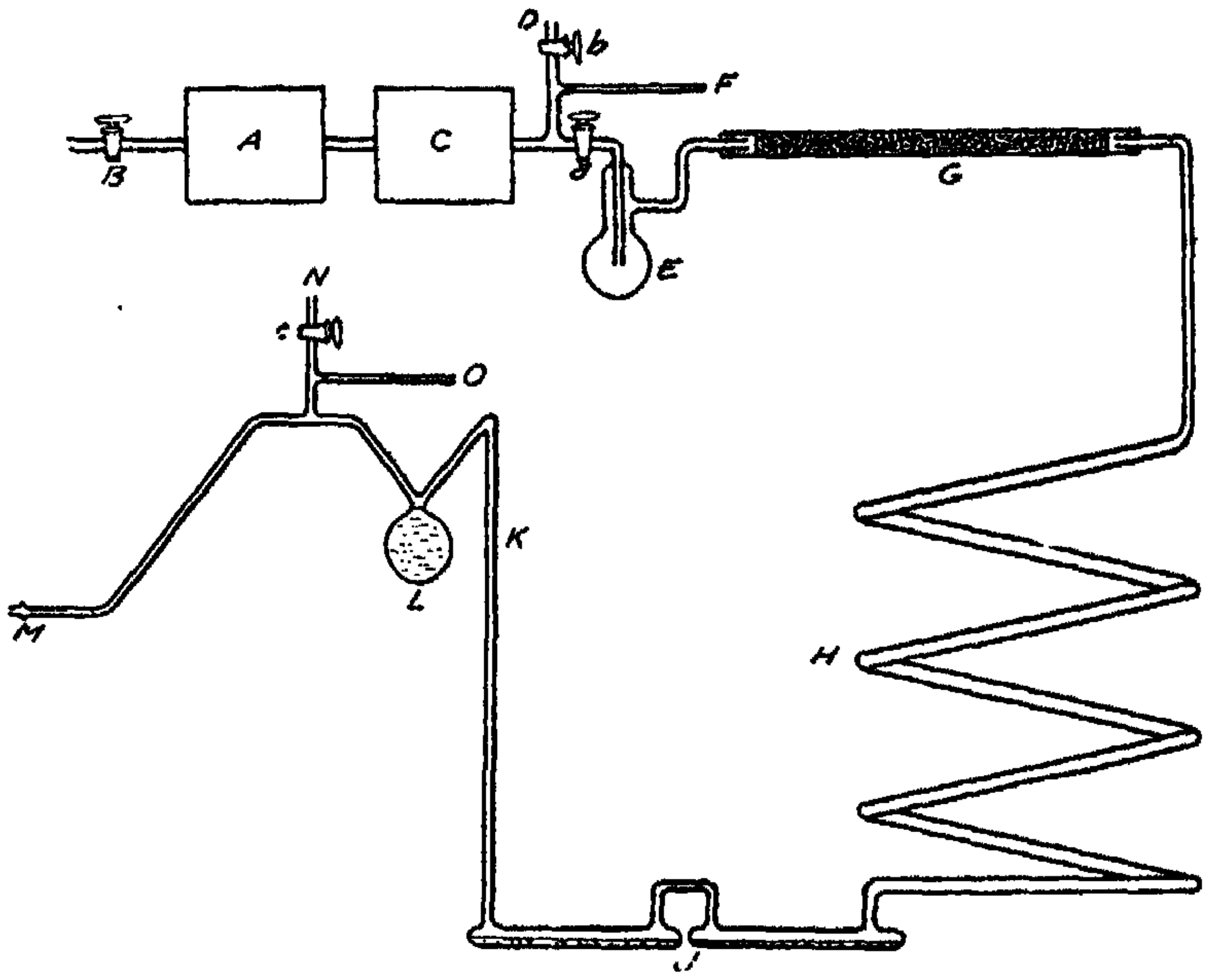

FIG. 2

The tube K was connected to the evaporation bulb L by a short piece of rubber tubing just above the thermostat level. (The air current only passed through rubber joints *before* it entered the evaporation bulb.) The bulb was designed to give a high degree of hydrodynamic stability, and had a mark etched around the neck. It was always clamped in a fixed position, so that the liquid surface was exactly reproducible. It was found that the surface remained steady with air currents up to 15 litres per minute, provided that the velocity was constant. If, however, any fluctuations took place in the speed of the motor, the surface was immediately disturbed, and no significance could be attached to the results obtained. Many experiments had to be rejected for this reason. To indicate the pressure of the air in the evaporation bulb, a manometer was attached to the capillary tube O. The tube between the evaporation bulb and the ground joint M was heated electrically.

The tap 'c' was lubricated with phosphoric acid, with a narrow layer of vaseline at the top and bottom to prevent deliquescence. The other taps were lubricated with ordinary tap-grease, as they did not come into contact with chlorine. The spiral, presaturator, and evaporation bulb were in an electrically controlled water-thermostat at 25.00 ± 0.01°C.

Preliminary Experiments.

The motor blower was tested for constancy of running and it was found that after a small gradual decrease in the first 3-5 minutes, the velocity remained constant with fluctuations of less than 1%.

The type of apparatus used for absorbing the chlorine from the air current is shown in Fig. 3. The ground joint A, lubricated with phosphoric acid, fits on to M in Fig. 2. The bulb B was packed loosely with glass wool to prevent splashing, and the flask C served to check the completeness of absorption. The absorbent used was a solution of potassium iodide containing 50 grams per litre, and the back pressure was about 2-5 millimetres of mercury with slight fluctuations. The efficiency of absorption was tested under conditions similar to those in actual experiments, and was found to be practically 100%. There was never enough iodine liberated in the small flask to give any colouration with starch solution, which also points to 100% absorption.

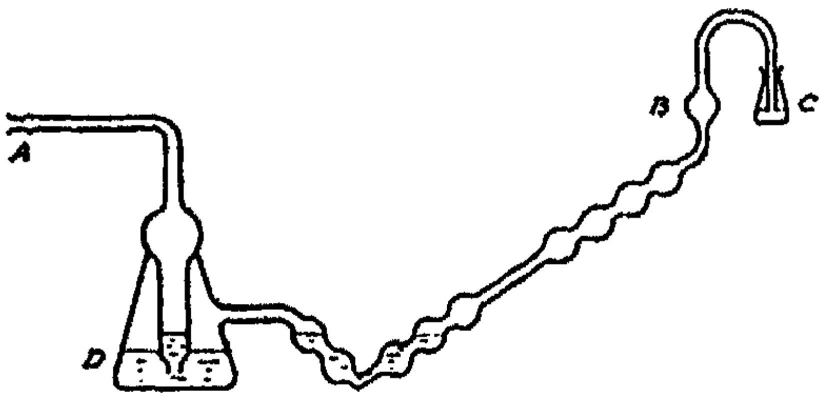

FIG. 3

First Series of Experiments.

These experiments were all carried out with the same solution of chlorine, using different velocities of air current. The solution was brought to the temperature of the thermostat in a small glass-stoppered flask, while the motor was allowed to attain constant running, by blowing air through the first by-pass D (Fig. 2). The solution was forced over into the evaporation bulb by dry air under pressure, and the air current was passed for about one minute through the bulb and out via the second by-pass N in order to evaporate the chlorine from any solution adhering to the walls of the bulb. The thermostat heating current and the thermostat stirrer were both switched off for a few minutes, so as to avoid electrical disturbances of the blower and mechanical disturbance of the liquid surface. Absorption was then carried out by closing the tap 'c' for 1-3 minutes, the exact time being taken by a stop-watch. During the absorption the two manometers were read to the nearest 0.5 millimetres. The absorption apparatus was removed and its contents washed out into a titration flask: it was then refilled again with potassium iodide solution and fitted again to the rest of the apparatus. The run was then immediately repeated, proceeding exactly as before, and the two lots of iodine titrated.

Calculation shows that the amount of chlorine evaporated during a pair of runs was always less than 1% of the total chlorine in the bulb, so that it was legitimate to consider the concentration of chlorine in the solution as constant throughout each pair of runs. Every time the flask in the thermostat was refilled, 10 ccs. of the solution was titrated, and the chlorine concentration for the first series of experiments was taken to be the mean of the values thus obtained, which shows an extreme variation of 1% and no downward trend.

The barometer was read and the temperature of the meter taken directly after each run. The pressure of the air leaving the meter (P_A) and the pressure in the evaporation bulb (P_B) were calculated, and the volume of air which passed through the meter, corrected to 25 C. and pressure P_B.

The following is a typical example of the figures obtained for one determination (first half only).

Run No. X

Meter	Manometer	Time	Barometer	Temp.
96743	*A* 18.0 − 3.0 = 15.0 mm.	1 min. 41.7 secs.	763.3 mm.	13.6 C.
96748	*B* 22.0 − 11.0 = 11.0 mm.	= 1.70 mins.		

Titrations

Bubbler	1st 0.00 ccs. 2nd 27 .10 ccs. 27 .10 ccs.
Flask	None

$$P_A = 763.3 + \{15.0 \times 1.63/13.6\} = 763.3 + 1.8 = 765.1 \text{ mm.}$$

$$P_B = 763.3 + \{11.0 \times 1.63/13.6\} = 763.3 + 1.3 = 764.6 \text{ mm.}$$

Velocity of air current (v) = $\{15/1.70\} \times \{298.0/286.6\} \times \{765.1/764.6\}$
= 9.18 litres per minute.

Mass of chlorine absorbed = $27.10 \times 0.0002371 = 0.006428$ grams.

Rate of evaporation (R′) = $0.006428/101.7 = 0.00006322$ grams per second.

When the values obtained for R′ were plotted against the corresponding values for V, it was found that the points become more and more erratic as V becomes greater, probably owing to disturbance of the surface at these high velocities. In the final results, therefore, only points corresponding to a velocity of air current less than II litres per minute were retained.

"Ceteris paribus," it is obvious that the rate of evaporation will depend upon the pressure of the gas passing over the surface, since this will affect the diffusion coefficient of the chlorine. Therefore, in order to make the above results strictly comparable, it is necessary to apply a small correction for the variations in P_B, the pressure over the surface. Since the theoretical equation connecting the rate of evaporation with the diffusion coefficient is not known, the true form of the correction is not known, but since the total correction is small, it has been assumed that the rate of evaporation is inversely proportional to the pressure. (Jablczynski and Przemski[1] state that $R \alpha P^{\frac{1}{2}}$, but since their experimental results give values varying from 0.289

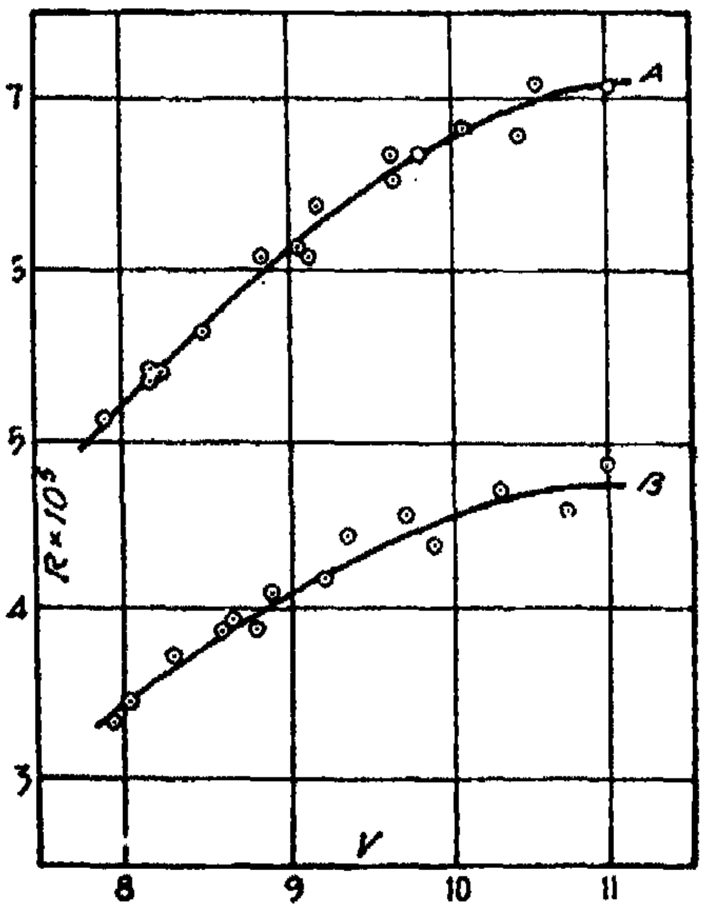

Fig. 4

TABLE I

Concentration of chlorine = 0.8658 grams per litre

V	P_B	$R' \times 10^4$	R × 10
7.90	764.2	5.097	5.125
8.16	748.7	5.488	5.406
8.17	748.7	5.428	5.347
8.24	762.9	5.376	5.398
8.49	764.1	5.608	5.640
8.85	762.8	6.042	6.065
9.07	764.7	6.082	6.119
9.13	754.2	6.028	6.061
9.18	764.6	6.322	6.359
9.65	764.2	6.617	6.655
9.66	768.2	6.438	6.507
9.81	765.4	6.612	6.659
10.09	768.3	6.744	6.823
10.55	765.3	7.036	7.087
11.02	767.0	6.993	7.058

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[1] J. Chim. phys., **10**, 241 (1912).

to 1.014 for the index, the matter seems very doubtful). Table I summarises the results, where

$$R = R' \times P_B/760$$

V = velocity of air current in litres per minute.
R′ = observed rate of evaporation in grains per second.

The corrected values are plotted in Fig. 4 (curve *A*) and give points which lie far better on a curve than do the uncorrected values.

Second Series of Experiments

These experiments were carried out in exactly the same manner as the first series, but with a chlorine concentration of 0.5801 grams per litre. The results obtained are summarised in Table II, and the corrected values of R are plotted against V in Fig. 4 (curve *B*).

TABLE II

V	P_B	$R' \times 10^4$	$R \times 10^4$
7.88	758.7	3.337	3.332
8.03	760.4	3.446	3.448
8.29	758.3	3.723	3.715
8.58	757.1	3.870	3.856
8.65	747.4	3.991	3.924
8.79	747.9	3.940	3.877
8.88	757.6	4.103	4.090
9.21	758.4	4.170	4.161
9.35	749.5	4.472	4.411
9.71	750.2	4.597	4.538
9.88	750.2	4.410	4.353
10.31	759.2	4.689	4.684
10.73	759.1	4.558	4.553
10.98	758.8	4.857	4.840

In order to determine whether any simple relation exists between the rate of evaporation and the chlorine concentration in the solution, the values of R for round values of V were read off from the two curves in Fig. 4 and are tabulated in Table III.

TABLE III

V	$R^{I} \times 10^4$	$R^{II} \times 10^4$	R^{I}/R^{II}
8.00	5.19	3.45	1.50
8.50	5.68	3.80	1.49
9.00	6.11	4.10	1.49
9.50	6.48	4.34	1.49
10.00	6.76	4.52	1.50
10.50	6.96	4.65	1.50
11.00	7.08	4.71	1.50
		Mean	= 1.496

Ratio of concentrations = 0.8658/0.5801 = 1.492

It is thus established that for values of V between 8.0 and 11.0 litres per minute, and solutions of chlorine having concentrations between 0.5801 and 0.8658 grams per litre,

$$R \propto C$$

where C = concentration of chlorine in solution.

Experiments with trichloracetic acid solutions.

The solute used for the study of adsorption was trichloracetic acid, which has a strongly polar carboxyl group and does not react with chlorine. It was found by analysis to be at least 99.98% pure.

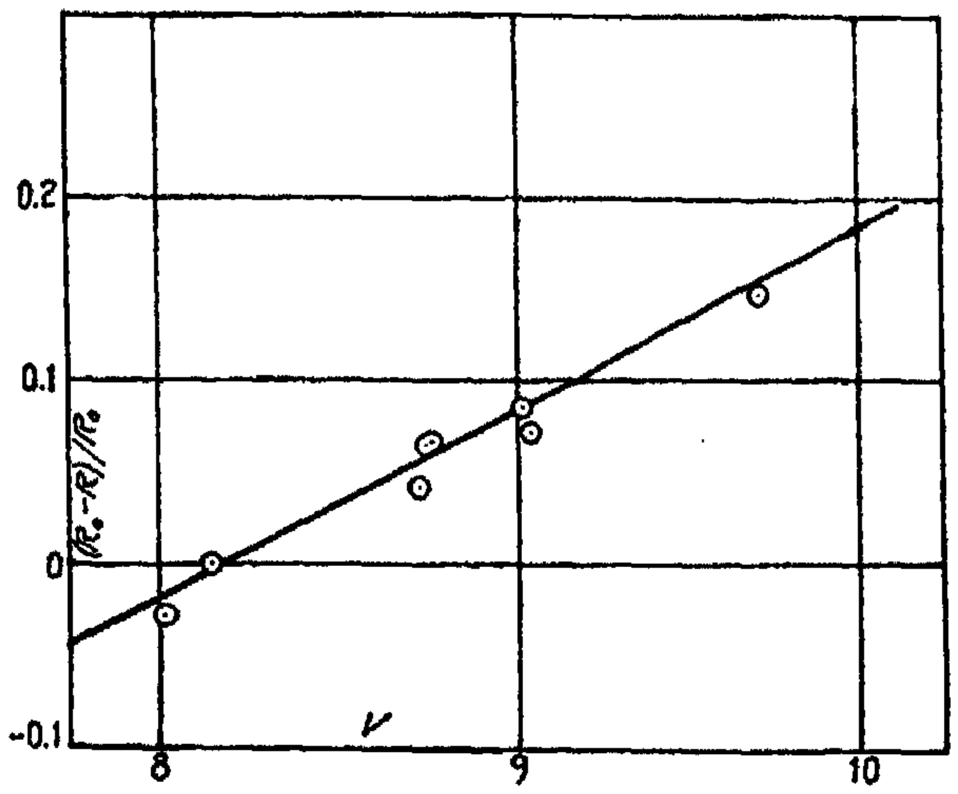

Fig. 5

In order to investigate the effect of trichloracetic acid on the evaporation rate under different conditions, the following scheme was adopted. A solution was made up by weight from a stock solution of trichloracetic acid (concentration known exactly), a stock solution of chlorine (concentration known approximately), and carbon tetrachloride. After determining the chlorine concentration of this solution by titrating a 10 cc. sample, the rate of evaporation was determined by carrying out a double run as described before. The solution was then poured back into the flask, thereby losing a little chlorine, and the chlorine concentration again determined. The rate of evaporation was then again determined, and this procedure was repeated until the concentration of chlorine fell below the lower limit of the range previously investigated.

Thus for each solution, a series of results was obtained corresponding to the same concentration of trichloracetic acid, but different velocities of air current and concentrations of chlorine. In each case the rate of evaporation corresponding to the same values of V and C (in absence of the acid) was calculated from curve *A* in Fig. 4 and the relation

$$R \propto C$$

This calculated rate was called R_0, and the fractional decrease in rate caused by the presence of the acid is given by

$$x = (R_0 - R)/R_0$$

where R = rate observed in presence of acid.

At first solutions containing about 10 grams of trichloracetic acid per 100 grams were used, but it was found impossible to obtain reproducible results. More dilute solutions were then used, and a series of preliminary experiments showed that the fractional reduction 'x' was dependent upon the velocity of the air current (as would be expected), but not upon the chlorine concentration. It was also found that for any one solution, on plotting the fractional reduction (x) against the velocity of air current (V), approximately a straight line was obtained in each case. A typical graph obtained in this way is shown in Fig. 5. After each of the tables of results which follow is given the linear equation obtained by applying the method of least squares to the experimental results for x and V. The values of x corresponding to V = 8.5 and V = 9.0 as calculated from this equation are also given in each case.

Results

In the following tables—

C = chlorine concentration in grams per litre.
V = velocity of air current in litres per minute.
R' = observed rate of evaporation in grams per second.
P_B = pressure over the liquid surface in millimetres of mercury.
R = rate of evaporation corrected to 760 mm., in grams per second.
R_0 = calculated rate of evaporation in grams per second.
x = fractional decrease in rate, i.e. $(R_0 - R)/R_0$.

TABLE IV

Solution H

Concentration of acid = 0.5253 grams per 100 grams

C	V	$R' \times 10^5$	P_B	$R \times 10^5$	$R_0 \times 10^5$	x
0.8598	8.15	5.286	758.6	5.277	5.302	0.005
0.8598	9.02	5.577	758.3	5.565	6.078	0.085
0.7554	9.04	4.978	759.7	4.976	5.357	0.072
0.5829	8.73	3.808	758.8	3.784	3.968	0.042
0.5829	8.02	3.617	758.9	3.612	3.510	−0.028
0.4994	9.72	3.263	759.0	3.259	3.813	0.146
0.4994	8.76	3.191	759.5	3.188	3.409	0.065

Equation of straight line is $x = 0.0983\ V - 0.806$

When $V = 8.50$ $x = 0.029$

When $V = 9.00$ $x = 0.079$

TABLE V

Solution J

Concentration of acid = 0.8594 grams per 100 grams

C	V	$R' \times 10^4$	P_B	$R \times 10^4$	$R_0 \times 10^4$	x
0.8702	8.93	5.580	761.7	5.593	6.081	0.080
0.8702	8.61	5.526	761.4	5.537	5.809	0.047
0.7739	8.21	4.691	759.1	4.686	4.755	0.015
0.6037	8.44	3.695	756.4	3.677	3.932	0.065
0.6037	9.97	3.910	756.5	3.892	4.246	0.106
0.5145	7.91	3.144	756.5	3.129	3.031	−0.032

Equation of straight line is $x = 0.115\ V - 0.934$

When $V = 8.50 \quad x = 0.045$

When $V = 9.00 \quad x = 0.104$

TABLE VI

Solution N

Concentration of acid = 1.165 grams per 100 grams

C	V	$R' \times 10^4$	P_B	$R \times 10^4$	$R_0 \times 10^4$	x
0.7543	8.63	4.576	761.4	4.584	5.054	0.093
0.7543	8.92	4.598	761.5	4.608	5.272	0.126
0.6829	8.11	4.062	760.3	4.065	4.181	0.036
0.6829	8.50	4.119	760.4	4.122	4.480	0.080
0.5500	8.39	3.312	759.8	3.311	3.545	0.066

Equation of straight line is $x = 0.116\ V - 0.907$

When $V = 8.50 \quad x = 0.079$

When $V = 9.00 \quad x = 0.137$

TABLE VII

Solution F

Concentration of acid = 1.375 grams per 100 grams

C	V	$R' \times 10^4$	P_B	$R \times 10^4$	$R_0 \times 10^4$	x
0.6616	8.66	3.894	760.0	3.894	4.455	0.126
0.6616	8.12	3.923	760.0	3.923	4.142	0.053
0.5619	8.33	3.302	759.6	3.299	3.583	0.079
0.5619	9.11	3.394	759.5	3.391	4.005	0.154
0.4820	7.94	2.732	758.2	2.726	2.856	0.047

Equation of straight line is $x = 0.102\ V - 0.857$

When $V = 8.50 \quad x = 0.099$

When $V = 9.00 \quad x = 0.150$

TABLE VIII

Solution K

Concentration of acid = 1.800 grams per 100 grams

C	V	$R' \times 10^5$	P_B	$R \times 10^5$	$R_0 \times 10^5$	x
0.5364	8.97	3.301	752.0	3.266	3.767	0.133
0.5364	8.11	3.114	752.1	3.082	3.315	0.070
0.4751	8.37	2.784	762.0	2.791	3.052	0.085
0.4751	8.87	2.840	761.7	2.847	3.294	0.136
0.4634	8.49	2.851	748.7	2.808	3.153	0.101

Equation of straight line is $x = 0.083\ V - 0.604$

When $V = 8.50$ $x = 0.100$

When $V = 9.00$ $x = 0.141$

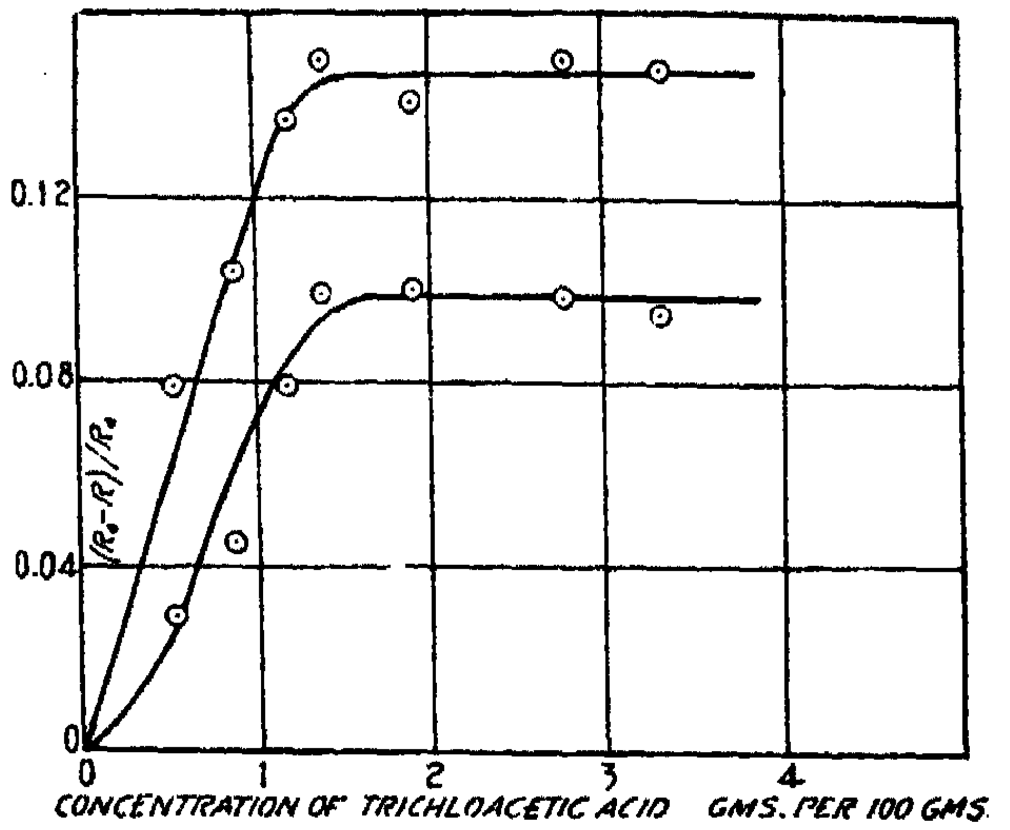

FIG. 6

TABLE IX

Solution M

Concentration of acid = 2.257 grams per 100 grams

C	V	$R' \times 10^5$	P_B	$R \times 10^5$	$R_0 \times 10^5$	x
0.8226	8.72	5.098	765.4	5.028	5.577	0.098
0.8226	8.65	4.790	765.5	4.826	5.524	0.126
0.7311	8.47	4.177	765.6	4.207	4.799	0.120
0.7311	8.35	3.322	765.7	4.348	4.696	0.074
0.6419	7.94	3.629	764.0	3.648	3.804	0.041
0.6419	9.12	3.843	764.1	3.864	4.597	0.159

Equation of straight line is $x = 0.108\ V - 0.822$

When $V = 8.50$ $x = 0.096$

When $V = 9.00$ $x = 0.150$

TABLE X
Solution L
Concentration of acid 3.302 grams per 100 grams

C	V	$R \times 10^5$	P	$R \times 10^5$	$R \times 10^5$	x
0.7879	8.67	4.792	763.0	4.805	5.307	0.095
0.7879	8.47	4.718	763.0	4.732	5.151	0.081
0.6987	8.48	4.241	761.9	4.252	4.566	0.069
0.5435	8.00	3.234	763.8	3.251	3.258	0.002
0.5435	8.25	3.283	763.6	3.298	3.445	0.043

Equation of straight line is $x = 0.130\ V - 0.919$
When $V = 8.50 \quad x = 0.095$
When $V = 9.00 \quad x = 0.148$
The values of x corresponding to $V = 8.50$ and $V = 9.00$ are plotted against the concentration of trichloracetic acid in Fig. 6.

Discussion of Results

The only equation previously obtained to express the variation of rate of evaporation with velocity of air current is that of Jablczynski and Przemski (Equation 2, Introduction). In terms of the present notation this becomes

$$\sqrt{V}\ \log_{10}\left\{\frac{VC_0}{VC_0 - 60R}\right\} = K \tag{3}$$

where C_0 = concentration of chlorine in saturated vapour, in grams per litre.
K = a constant.

This equation has been applied to the results of the first series of experiments. From the present data it is impossible to obtain an accurate value for C_0, but an approximate value has been obtained by extrapolating to V = zero the C − V curve calculated from the results, giving $C_0 = 7 \times 10^{-4}$ (approx.). This value was used in calculating the constants given in Table XI.

TABLE XI

V	$R \times 10^4$	x	V	$R \times 10^4$	x
8.00	5.19	1.63	10.00	6.76	1.76
8.50	5.68	1.71	10.50	6.96	1.72
9.00	6.11	1.76	11.00	7.08	1.63
9.50	6.48	1.78		Mean =	1.71

Thus an approximate constant is obtained although there is a distinct up and down trend in its value. (A similar degree of constancy is obtained by using values of C of 6.80×10^{-4} or 7.20×10^{-4}). It was not expected to obtain exact confirmation of this equation since it only applies strictly to the evaporation of a pure liquid, and takes no account of diffusion of a solute towards the surface. For a constant value of V, equation 4 leads to the relation

$$R \propto C_0$$

If we assume that the partial vapour pressure of chlorine is proportional to its concentration in solution, (a reasonable assumption since the solutions are dilute), this relation corresponds to that which was found to hold accurately in comparing the results of the two first series of experiments, namely,

$$R \propto C$$

where C = concentration of chlorine in solution.

Taking the partial vapour pressure of chlorine as corresponding to a concentration of 7×10^{-4} grams per litre, the Herz-Knudsen equation (Equation 1 Introduction) gives 2.0×10^{-3} grams per sq. cm. per second as the ideal rate of evaporation of the chlorine. The actual rates measured in the first series of experiments were about 2.0×10^{-5} grams per sq. cm. per second, so that the rates of evaporation measured represent about 1% of the ideal rate. The fact that reductions up to 15% were caused by the addition of trichloracetic acid shows that the rate of evasion must have been changed very considerably, either directly or indirectly.

The methods used for measuring the amount of the retarding effect caused by different concentrations of acid are purely comparative, so that the theory of the kinetics of evaporation is immaterial for this point. In calculating the values of the fractional reduction 'x' given in the tables, the only assumption is that

$$R \propto C$$

which relation has been shown to have both theoretical and experimental support.

The curves in Fig. 6 therefore represent the relation between the concentration of trichloracetic acid and the retarding influence of the film formed, under strictly comparable conditions. The points do not lie very well on the curves, but since an error of 1% in the determination of the value of R or C will cause an average error of 10% in the value of 'x' obtained, the results are as accurate as could be expected. The form of the curves for V = 8.50 and V = 9.00 is essentially the same in both cases, and the most important point is that for concentrations above about 1.4 grams per 100 grams the curve becomes parallel to the concentration axis: i.e., over this range the retarding power of the film is independent of the concentration of the acid. If we can take the retarding power as a measure of the surface density of the film, it seems very probable that this range corresponds to the existence of a stable monomolecular surface film of trichloracetic acid. This result is in agreement with the general evidence obtained from surface tension curves, and the results of previous work upon heterogeneous reaction velocity.[1]

It was mentioned in the practical part that preliminary experiments with solutions of trichloracetic acid containing about 10 grams per 100 grams failed to give reproducible results. The reason for this is not certain, but it is suggested that at these high concentrations a second, less stable, layer of molecules begins to form, which is partly destroyed by the slight agitation caused by the air current, thus giving erratic results.

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[1] Bell: loc. cit.

Besides any action caused by modification of surface conditions, the presence of trichloracetic acid will also have some effect upon the activity of the chlorine in solution, and hence upon its partial vapour pressure and its rate of evaporation. The order of magnitude of the effects observed is however much greater than would be expected from this cause, and the fact that a constant fractional reduction was observed over a range of concentrations makes it probable that this factor can be neglected. In two experiments (see results for solutions H and J), using abnormally small velocities of air current, a small but probably real negative value of x was obtained. It seems probable therefore that the addition of the acid causes a slight increase in the partial vapour pressure of the chlorine, and that with low velocities of air current the reduction in evaporation rate caused by the surface film is so small as to be masked by this secondary effect. Cases are known[1] in which the addition of a third component to a two-component system causes an increase in the activity of one of the components, and this is probably an example. In any case, the main conclusions with regard to the extent of adsorption are not affected.

If, as Langmuir[2] supposes, the primary factor in the reduction of rate of evaporation of solute by a surface film is a reduction in the rate of diffusion of the solute towards the surface, we should expect the reduction to be apparent at quite low rates of evaporation. In the present work it is found that the reduction becomes zero when the rate of evaporation is still nearly 1% of the ideal rate. This seems to show that at least in the present instance the reduction is primarily caused by the resistance of the film itself, as it must have been in Rideal's experiments on the evaporation of water.

Measurements of Surface Tension

In order to discover whether the conclusions arrived at above concerning the adsorption of trichloracetic acid from carbon tetrachloride solution were in accordance with the findings of the Gibbs adsorption equation, a series of surface tension measurements was carried out by the drop-weight method. The apparatus used was a modification of that described by Harkins.[3] In order to eliminate losses due to evaporation, each drop-weight was calculated by difference from two determinations in which the time taken was the same, but the number of drops different. In this way the drop-weight could be reproduced to within 0.5%. In Table XII, each value of the drop-weight represents the mean of five results, which showed an extreme divergence of less than 0.5% in each case.

Harkins[4] has shown that under the correct conditions, the surface tension is directly proportional to the drop-weight, so that the $w - \log_{10}c$ curve plotted in Fig. 7 has the same form as the $\sigma - \ln c$ curve. The Gibbs equation for adsorption is

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[1] Lewis and Randall: "Thermodynamics," p. 239 (1921).

[2] Irving Langmuir and D. B. Langmuir: loc. cit.

[3] Harkins and Brown: J. Am. Chem. Soc., 38, 246 (1916).

[4] Harkins and Humphrey: J. Am. Chem. Soc., 38, 228 (1916).

TABLE XII

w = drop-weight in grams.
c = concentration of acid in grams per 100 grams.

c	$\log_{10}c$	w	c	$\log_{10}c$	w
0.277	−0.558	0.02974	2.04	0.310	0.02934
0.458	−0.331	0.02965	3.26	0.513	0.02912
1.00	0.000	0.02957	5.15	0.712	0.02900
1.26	0.100	0.02946	6.61	0.820	0.02891

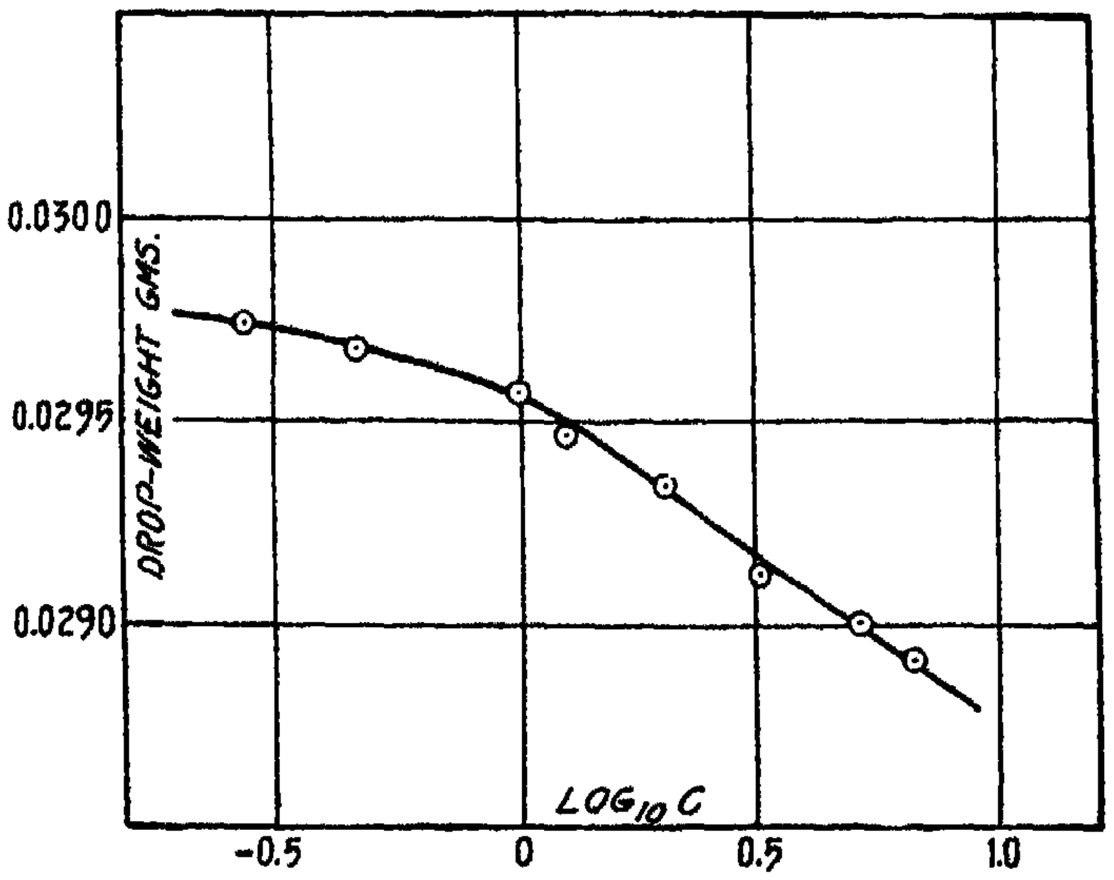

FIG. 7

$$\Gamma = -\frac{1}{RT}\cdot\frac{d\sigma}{d\ln C}$$

where Γ = excess concentration at the surface in gram-moles per sq. cm.
σ = surface tension
c = concentration of solute.

It is seen from Fig. 7 that the w − $\log_{10}c$ curve is a straight line for higher concentrations, while the slope falls off for low values of c. This means that for increasing values of c, $d\sigma/d\ln c$ and therefore Γ increases to a limiting value at which it remains constant, this limiting value presumably corresponding to the formation of a monomolecular layer. Owing to the small changes of surface tension involved, it is impossible to determine exactly where the curve becomes a straight line, but it is certainly between c = 1.0 and c = 1.6 grams per 100 grams, thus agreeing with the value found in the experiments on rates of evaporation, c = 1.4, as the minimum concentration necessary for the formation of a complete monomolecular layer.

Summary

(1). The possibility of employing measurements of velocity of evaporation for studying adsorption from solution has been discussed, and previous work on the subject reviewed.

(2). A method has been evolved for measuring the rate of evaporation of chlorine from its solution in carbon tetrachloride. Measurements have been carried out at 25C under different conditions of chlorine concentration and velocity of air current, and the results compared with previous equations for the kinetics of evaporation in a current of gas.

(3). The reduction in the evaporation rate caused by dissolving trichloracetic in the carbon tetrachloride has been measured under different conditions, and attributed to the surface adsorption of the trichloracetic acid.

(4). It has been deduced from these measurements that a saturated surface film of trichloracetic acid is formed at all concentrations greater than about 1.4 grams per 100 grams.

(5). Measurements of the surface tension of solutions of trichloracetic acid in carbon tetrachloride have been carried out by the drop-weight method. By applying the Gibbs adsorption equation to these results, it was found that the lower limit of concentration for the formation of a saturated film is between 1.0 and 1.6 grams per 100 grams, thus agreeing with the value previously found.

(6). It is suggested that the measurement of rates of evaporation may prove of general utility in the investigation of adsorption from solution.

In conclusion, the author wishes to express his best thanks to Sir Harold Hartley for his advice, encouragement and assistance throughout the work.

Physical Chemistry Laboratories,
Balliol and Trinity Colleges,
Oxford.
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THE BEHAVIOR OF NITROCELLULOSE GELS IN POLARIZED LIGHT

BY A. J. PHILLIPS

Introduction

From the time of Chardonnet[1] up to the present, numerous investigators have reported on the colors observed when nitrocelluloses of varying nitrogen content were examined, microscopically, in polarized light with crossed nicols. Each sought to establish a relation between the color observed and the nitrogen content of the nitrocellulose but no two observers agreed as to the color which represented any particular percentage of nitrogen..

A very extended investigation of this kind has been made by Tissot.[2] He observed that highly nitrated nitrocelluloses had a pale blue color in polarized light and as the nitrogen content decreased, the colors changed in the order—dark blue, indigo, violet, red, orange and yellow. Therefore from the color, the nitrogen content might be predicted. This exact conclusion was modified by the statement that the color did not depend solely on chemical constitution but was linked with the refractive index of the liquid in which the fibres were immersed, physical modifications in the structure of the fibre and the composition of the mixed acid bath used for nitration. The significant statements were made that it had not been found possible to link up the nature of the cellulose, the time of nitration or the temperature, with the color obtained and in addition that the method could not be applied to gelatinized nitrocellulose; that is to films or to smokeless powder grains.

There are a number of objections to the idea that the nitrogen content is the sole factor in determining what color will be seen in polarized light. Worden[3] points out that cellulose triacetate shows a light blue color in polarized light. Since the acetate contains no nitrogen, the latter cannot be the only factor in determining what color will be seen. Again De Mosenthal[4] has shown that cotton, wood cellulose, ramie and flax nitrated to the same nitrogen content, show entirely different colors in polarized light. Further more the colors vary with different immersion liquids, with the same liquid at different dilutions, with the degree of magnification and with the source of light. This is an indication that the physical condition of the nitrated material must be considered as well as the chemical constitution, in determining what color will be observed. Finally, a range of colors from light blue to brownish yellow has been observed frequently in thin sections of powder grains made from nitrocellulose containing 12.6% nitrogen. Unless it be assumed that this 12.6% nitro-

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[1] Chardonnet: Z. Angew. Chem., 20, 31 (1899).

[2] Tissot: Mém. des Poudres, 22, (1) 31-56 (1926).

[3] Worden: "Technology of Cellulose Esters," 1, (3) p. 1760.

[4] De Mosenthal: J. Soc. Chem. Ind., 26, 443-4 (1907).

gen material is a mixture of high and low nitrated material which undergoes segregation during mixing; then it becomes difficult to establish a connection between nitrogen content and polarized light color.

Color and Degree of Dispersion

A more satisfactory method of attack is a consideration of physical structure in relation to color. It has been pointed out that the composition of the mixed acid has an effect upon the color seen. Tissot (loc. cit.) has shown that in two series of nitrations in one of which the sulfuric acid is kept constant with variation in the nitric acid and water, while in the other series the nitric acid is kept constant; nitrocelluloses of the same nitrogen content from the two series, will not show the same polarized light colors.

Now Hake and Bell[1] have shown that sulfuric acid tends to reduce the particle size of the cellulose aggregates while nitric acid forms insoluble nitrates, the tendency being toward increase in particle size. The presence of water molecules tends to increase the complexity of the reaction, but as expressed by Wheeler,[2] nitration depolymerizes the cellulose complex, the action being masked by the entry of NO_2 groups.

If we assume as does Harrison[3] that cellulose is a dried-out gel, then mixed acid high in nitric acid alters the gel structure to produce a nitrocellulose with large particles and mixed acid high in sulfuric acid produces a nitrocellulose with small particles.

The relation of the different colors of the panchromatic metals (gold, silver and platinum) in the colloidal state, to their degree of dispersion, has been worked out. It has been found that the most highly dispersed metals are yellow or orange. As the particles become larger the color passes thru orange to red, violet, blue and finally green.[4] There is absorption of light by all the particles which is not uniform but which rises to a maximum in one portion of the spectrum. As the degree of dispersion decreases—as in high nitrated cellulose—the absorption maximum moves toward the red end of the spectrum and the light transmitted moves toward the blue end of the spectrum.

Tho these conclusions apply to the metals there are certain analogies which indicate that they apply likewise to the non-metals, the dielectrics. Bancroft[5] found that prolonged heating of Jena glass tubing produced colors varying from deep indigo thru pale blue to white. Keen and Porter,[6] Ritz[7] and Auerbach[8] found that sulfur precipitated from sodium thiosulfate by phosphoric acid transmitted yellow, red, violet, blue and gray light as the particles increased in size. Finally Breguet[9] found, by precipitating acetone

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[1] Hake and Bell: J. Soc. Chem. Ind., 28, 457 (1909).
[2] Wheeler: "Fifth Report on Colloid Chemistry," p. 5708.
[3] Harrison: "Second Report on Colloid Chemistry," p. 55.
[4] Ostwald-Fisher: "Theoretical and Applied Colloid Chemistry," 2nd Ed. p. 65.
[5] Bancroft: J. Phys. Chem., 28, 12-25 (1924).
[6] Keen and Porter: Proc. Roy. Soc., 98A, 370 (1914).
[7] Ritz: Compte Rendu, 143, 167 (1906).
[8] Auerbach: Kolloid-Z., 27, 22 (1921).
[9] Breguet: Rev. Gén. Coll., 3, 203-6 (1925).

solutions of nitrocellulose with increasing amounts of benzene, that each time a precipitate was formed a colored fluorescence accompanied the precipitation. With the first precipitate there was a bluish fluorescence, with the second a violet or red and with the third a yellow fluorescence. Viscosity measurements on each precipitate showed decreasing viscosities with presumably decreasing particle size. Thus a definite connection between particle size and color, is indicated.

Experimental

In support of the color-dispersion theory it was considered advantageous to show that there were exceptions in the color-nitrogen relation of nitrocelluloses in polarized light. For this purpose a series of commercial nitrocellulose samples were mounted in either glycerin jelly, Canada balsam or alcohol, and examined in polarized light with crossed nicols.

The glycerin jelly was made from

Commercial gelatin	20 grams
Distilled water	60 grams
Glycerin	120 grams

The jelly was melted in a watch-glass on a water-bath, the fibres immersed in the liquid, stirred to remove air bubbles, fished out, mounted on a warm slide and covered with a cover glass.

For the alcohol mounts, dry nitrocellulose was placed on a slide and covered with a coverglass. All but *a ⅛ in. opening of the* cover glass was sealed with a mixture of Canada balsam and paraffin wax. Thru the remaining opening, 95% grain alcohol was introduced by means of a capillary pipette.

For illumination two light sources were employed: one a substage lamp with a 15 watt Mazda bulb and ground-surface Corning-glass window, which was placed close to the plane mirror of the microscope. The other illuminant was a 6 volt, 108-watt tungsten filament bulb with a Corning daylight glass, which was located according to the following log. Both were equally satisfactory.

Beam width at face of nitrogen-filled lamp	4 cm.
Distance from glass face of lamp to glass of polarizing prism	31 cm.
Water-cooling cell 4 cm. thick between lamp and polarizing prism.	
Substage dropped	4 mm.
Nicol diaphragm opening	4 mm.
Achromatic objective	16 mm.
Eyepiece	15 X

A gypsum plate of such thickness as to give an interference color of 1st order violet, was mounted above the objective, with its principal direction at 45° to the vibration directions of the polarizing and analyzing prisms. A fibre placed in such a position as to be parallel to the slow ray, the C axis of the plate, is marked in the tables as parallel, while a fibre at right angles to the slow ray is marked vertical.

Colors of Nitrocellulose in Polarized Light

The results secured by such examinations are recorded in Tables I–IV. Analysis of these tables shows differences which may be classified under

TABLE I

Examination of Nitrocellulose in Polarized Light

High Nitrogen Specimen	Crossed Nicols	Glycerin Jelly Gypsum Plate with Crossed Nicols
1 Dupont 13.45% N.	Brilliant grayish white with bluish tint, extinguishing with a stronger bluish tint. Mottled extinction.	Parallel—brilliant pale yellow. Vertical—Light blue with pale greenish blue centers. Very few dark blues.
2 Hercules 13.34% N.	Brilliant grayish white, not uniform. Mottled extinction to a deep blue. Hercules 13.25 N. same, deep blue extinction not so marked,	Parallel—Canary yellow Vertical—Deep blue with lighter blue centers.
3 Picatinny 13.10% N.	Brilliant grayish white, Non-uniform, mottled extinction to a dark blue. Some pale yellow fibres extinguishing to a mottled black	Parallel—Dull yellow Vertical—Little darker blues with not so many light blue centers.
4 Picatinny Unpulped, long fibered 13.01% N.	Grayish white, dull colors. Extinguishing to a mottled dark color, no blues.	Parallel—Dull yellow. Vertical—Dull blues with no light blue centers.
5 Hercules 13.16% N.	Brilliant grayish white with mottled extinction.	Parallel—Clear yellows Vertical—Deep blue with many pale blue centers.
6 Nitrated Straw Cellulose 13.05% N.	Clear, grayish white. Uniform extinction.	Parallel—Clear yellow Vertical—Deep blue, very few pale blue centers
7 Picatinny 12.83% N.	Bluish white with uniform extinction.	Parallel—Dull yellow Vertical—Majority purple with a few deep blues.

TABLE II

Examination of Nitrocellulose in Polarized Light

Intermediate Nitrogen

Specimen	Crossed Nicols	Glycerin Jelly Gypsum Plate with Crossed Nicols
8 O'Bannon 12.63% N.	Clear grayish white extinguishing uniformly to a bluish white.	Parallel—Yellow Vertical—Bluish purple. Some dark blues with light blue centers.
9 Picatinny 12.62% N.	Bluish white, extinguishing uniformly to a brownish black.	Parallel—Canary yellow. Vertical—Purplish blue. Some dark blue with light blue centers. A few fibres rotating to light and dark green.
10 Dupont 12.62% N.	Bluish white, extinguishing uniformly to black.	Parallel—Yellow Vertical—Purple with very few blues.
11 Hercules 12.59% N.	Dull bluish whites with uniform extinction. Some dull browns and whitish grays with mottled blueish extinction.	Parallel—Very weak pale yellow. Vertical—Majority purple with a few deep blue centers.
12 Hercules Special Grade 12.4% N.	Brilliant blues extinguishing uniformly to deep browns and yellows.	Parallel—Clear yellow Vertical—Clear violet
13 Picatinny 12.3% N.	Dull whitish blues with mottled extinction Blues and browns with red inclusions.	Parallel—Dull yellow Vertical—Violets with very few blues.
14 Hercules 60–80 sec. 12.31% N.	Some deep blues, Majority deep yellow brown brown with brownish red, violet and indigo mottling.	Parallel—Greenish yellows, no clear yellows. Vertical—Dull purples, no blues.

TABLE II (Continued)

Examination of Nitrocellulose in Polarized Light

Intermediate Nitrogen		Glycerin Jelly
Specimen	Crossed Nicols	Gypsum Plate with Crossed Nicols
15 Celluloid Co. 12.32% N.	Browns, brownish reds, deep blues extinguishing to black. Strongly marked black central canals. Many blue bordered fibres with yellow white centers. All colors may be mixed in the same fibre.	Parallel—blue bordered fibres turn yellow. Yellow white centers turn purple, pale blue and red. Some yellow fibres. Vertical—Blues to violet, black canals to gray black. Many violet fibres.
Hercules R.S. 200-350 Secs. 12.20% N.	Deep blues, deep yellows, dark browns, uniform extinction.	Parallel—yellows, yellow violet and yellow fibres with a purple border. Vertical—yellow-browns.
17 Hercules R.S. 150-200 Secs. 12.20% N.	Deep blues, purples with some red inclusions, few yellow whites.	Practically all remained 1st order violet with complete revolution of stage.
18 Hercules R.S. 30-40 Secs. 12.20% N.	Mottled blues with few deep yellows. Mottled extinction to deep browns.	Parallel—Pale yellows and 1st order violet. Vertical—Purple with a few blues.
19 Hercules R.S. 5 Secs. 12.20% N.	Brilliant dark blues with light blue centers. Uniform extinction.	Parallel—Yellow Vertical—Purple. No blue centers.
20 Hercules R.S. ½ Sec. 12.20% N.	Very deep blues, mottled with pale blues, yellows and browns. No reds.	Parallel—Yellow browns and 1st order violet. Vertical—Purple and purple-violet.
21 Hercules Dynamite N.C. 12.18% N.	Very deep blues and deep yellows. Deep browns. Dull colors.	Parallel—Brownish yellow. Vertical—Purple tinted by 1st order violet of gypsum plate. Very dull colors.
22 Hercules R.S. 15-20 Secs. 12.10% N.	Brownish yellows extinguishing to mottled black with violets and deep blues.	Parallel—Yellow violet. 1st order violet tints fibres. Not much change on rotation of stage. Vertical—Few pale purples.

TABLE III

Examination of Nitrocellulose in Polarized Light

Low Nitrogen Specimen	Crossed Nicols	Glycerin Jelly Gypsum Plate with Crossed Nicols
23 Picatinny 11.96% N.	Dull yellows, with no whites. Mottled extinc-	Parallel—Purple with a few blues. Vertical—Yellow
24 Hercules A.S. ½ Sec. 11.65% N.	Pale yellow mottled with black. Very few blues. Some whitish yellows.	Parallel—Purple with many dark blue centers. Vertical—Yellow.
25 Hercules A.S. 15–20 Secs. 11.60% N.	Yellowish white, few yellows.	Parallel—Purple with few dark blue centers. Vertical—Yellow.
26 Hercules A.S. 30–40 Sec. 11.55% N.	Pale yellow with a few dark blues.	Parallel—Strongly marked in blue with many light blue centers. Very few purples. Brilliant colors. Vertical—Yellow.
27 27 Picatinny 11.23% N.	Yellowish white with black mottling. Very weak colors. Extinguishing to black.	Parallel—Majority purple. Many purples with light blue centers. Vertical—Yellow.

color, brilliance of color and method of extinction. Table I, showing the highly nitrated materials indicates little difference in the colors, making it difficult to distinguish between the samples. A rather sharp distinction however, may be made between grayish white and bluish white on a black background. The extinction of the 13.05% N material (#6) distinguishes it from the others.

The four pyro samples (#8, 9, 10 and 11) show differences where, according to the nitrogen content there should be similarities. The extinctions are also different where if the nitrogen content is the sole criterion, they should be similar. The gypsum plate shows green colors in the Picatinny sample (#9) while the O'Bannon (8) and Hercules (11) show differences in the light

TABLE IV

Examination of Nitrocellulose in Polarized Light

		Alcohol Mount
Specimen	Crossed Nicols	Gypsum Plate with Crossed Nicols
28 Hercules R.S. 200–350 Secs. 12.20% N.	Grayish white fibres with a few deep blues.	Parallel—Yellow Vertical—Purple with a few blues. Weak colors.
29 Hercules R.S. 150–200 Secs. 12.20% N.	Average is a dull bluish white, a few grayish whites, a few browns.	Parallel—Yellow Vertical—Purple
30 Hercules R.S. 30–40 Sec. 12.20% N.	Dull bluish whites, some browns.	Parallel—yellow Vertical—Purple, with a few blues. Fibres vary greatly in luminosity.
31 Hercules R.S. ½ Sec. 12.20% N.	Grayish white with very little blue tint. Very dull colors.	Parallel—Yellow Vertical—Very strong purple, no blues.
32 Hercules A.S. ½ Sec. 11.65% N.	Dull yellows, dull browns, no whitish yellows.	Parallel—Purple Vertical—Yellow masked by 1st order violet of Gypsum plate.
33 Hercules A.S. 15–20 Secs. 11.60% N.	Majority yellow white, few browns, very few blues. Uniform extinctions.	Parallel—Purple with some blueish inclusions. Vertical—Yellow
34 Hercules A.S. 30–40 Secs. 11.55% N..	Yellow and whitish yellows. Mottled extinction.	Parallel—Purple and purples with some blue centers. Vertical—Yellow with a few blues. Brilliant colors.
35 Picatinny 11.23% N.	Pale yellowish white, few deep blues. Mottled extinction.	Parallel—Purples with blue centers. Some deep yellows. Vertical—Deep yellow some violets.

and dark blue centers. The 12.3% N samples (#13, 14 and 15) show very marked differences with crossed nicols, with and without the gypsum plate. The Celluloid Co. sample (#15) is quite remarkable in its play of colors and attempts made to estimate its nitrogen content from the colors shown in polarized light, were failures.

The 12.20% N samples (#16, 17, 18, 19 and 20) showed most conclusively the exceptions sought for in the relation between nitrogen content and color. As it is known that these samples are pressure boiled, in order to reduce viscosity, it is plausible to link color with physical condition and degree of dispersion of the nitrocellulose aggregates. Samples #16 and 17 show red inclusions while #20 of the same nitrogen content, shows no reds. There are so many differences in these samples, that reference is best made to Table II.

The low nitrated materials likewise show marked differences. The 11.23 N sample (#27) shows light blue centers which are characteristic of highly nitrated materials. The 11.55% N sample (#26) with the gypsum plate shows light blues and a few purples, a characteristic of higher nitrated material while the 11.65% N material (#24)—a higher nitrated material, shows many purples with dark blues.

It may be noticed that in comparing the colors obtained with the gypsum plate, there is a change at a nitrogen content of 11.96% (#23). With more highly nitrated materials the colors are yellow-parallel and purple-vertical. This order is reversed at and below 11.96% N, the colors becoming purple-parallel and yellow-vertical. The change at this nitrogen content is associated with a change in sign of double refraction. Ambronn[1] has pointed out that at a low nitrogen content, nitrocellulose has a positive double refraction. With rising nitrogen content, the character of the double refraction changes at 11.8% nitrogen with monochromatic light and at a higher value with white light. The higher nitrogen nitrocelluloses are all negatively doubly refracting.

The change in color from yellow to purple, in changing from the position designated parallel to that of vertical is due to the orientation of the fibre with regard to the fast and slow rays of the gypsum plate. In one position an additive color is produced at the yellow end of the spectrum, while in the other position a subtractive color is produced at the blue end of the spectrum.

The variation in colors of a sample of definite nitrogen content is an indication of non-uniform nitration. This is shown very readily in polarized lights with crossed nicols when the gypsum plate is employed. The plate is of particular value in disclosing non-uniform nitration in a single fibre; if the nitrogen content is taken as a criterion of color, or better in indicating various degrees of dispersion in one and the same fibre. In addition to variations in the rate at which the fibres nitrate, resulting in varied colors; there is of course the possibility of the presence of a blend of high and low nitrated materials which results in the presence of vari-colored fibres in the same sample.

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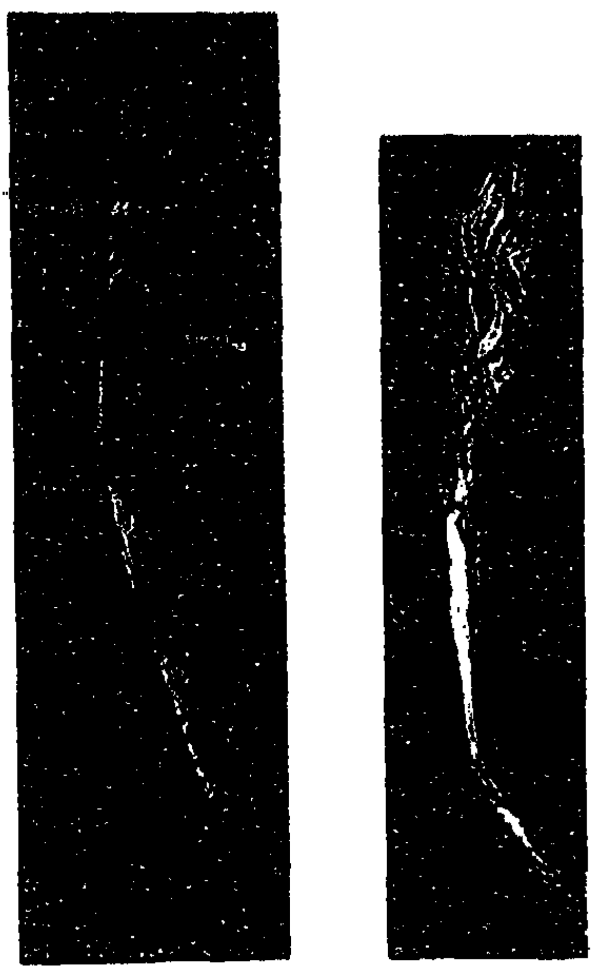
[1] Ambronn: Kolloid-Z., 13, 200 (1913).

Two photographs—Figs. 1 and 2 show variations in degree of dispersion within the same fibre. The first is from a nitrocellulose containing 12.63% of nitrogen (#8). With the gypsum plate is shown a purple border with a brilliant pale blue center. The greatest dispersion has taken place at the exterior of the fibre. It is only occasionally that this process is reversed with the greater dispersion within the fibre.



FIGS. 1 AND 2
O'Bannon nitrocellulose fibres, 12.63% N showing highly nitrated areas within the fibres. 100 × and 120 ×

Some very interesting results with regard to the nitration of the surface of a soluble nitrocellulose to produce an ether-alcohol insoluble material, have been presented by Craik.[1] The very slightly dispersed material on the outside of the fibre, which is insoluble, protects the more highly dispersed material within, from the action of the solvent. However modern beating practice is tending to produce material of the type shown in Fig. 3. The fibres are torn, shredded and split apart. They are photographed at the same magnification as those in Fig. 2 and show an enormously increased surface which permits more efficient action by the solvent. In this case a mechanical dispersion of fibres, which are apparently highly nitrated on the surface, will result in greater solubility, while no change in nitrogen content is necessarily indicated by the polarizing microscope.

Fig. 4 is a photograph of a fibre of Hercules ½ sec. nitrocellulose (#20). It has a deep blue color which is mottled with pale blues, yellows and brown. The yellows and pale blues photograph white, while the deep blues and browns are indicated by darker shades. This mixture of colors is not necessarily to be taken as an evidence of non-uniform nitration. In the light of the current theory it may be due to non-uniform dispersion during a viscosity reduction process. Some parts of the fibre may have been tendered during nitration and beating so that viscosity reduction resulted in more pronounced attack on these weak portions. This would result in variable dispersion with variable colors.

A color change as the result of heat, was found in the examination of fibres of pyro which had been exposed to the 135° heat test for 5 hours. It showed about equal amounts of dark blue and straw yellow fibres while normal pyro shows no yellow colors. The test was not conclusive since the sample showed red fumes and thereby indicated that nitrogen had been lost.

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[1] Craik: "Fifth Colloid Symposium Monograph," 272 (1928).

Fig. 3
Splitting, shredding and tearing of nitrocellulose fibres during beating.
150 ×

Fig. 4
Fibre of Hercules R.S.-1/2 sec., 12.20% N in polarized light, showing deep blues, mottled with pale blues, yellows and browns.
200 ×

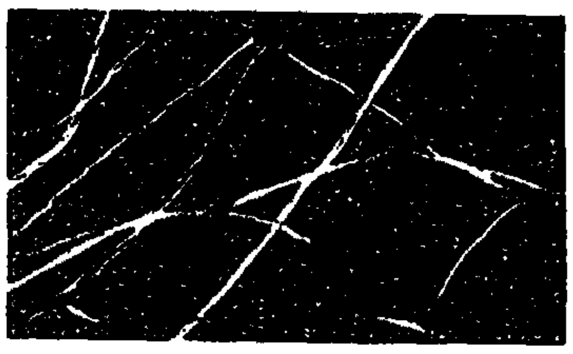

Fig. 5
Long-fibred gun cotton in polarized light with crossed nicols.
75 ×

Fig. 6
Same material swollen in acetone vapor and dried. Showing increase in size.
75 ×

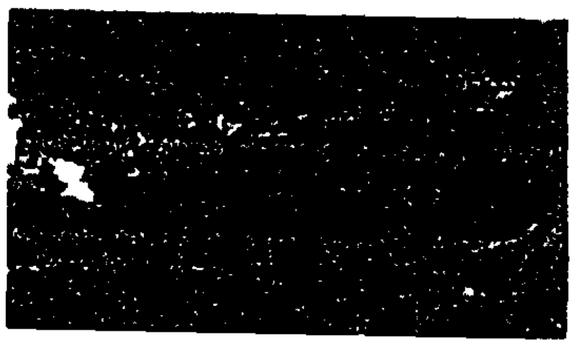

Fig. 7
Swollen material with crossed nicols in polarized light. Showing partial return of double refraction.
75 ×

A better but still inconclusive test was made by heating guncotton in the 135° test and removing it before the test paper turned salmon pink. The sample tested was long-fibered guncotton containing 13.5% of nitrogen. It showed a salmon pink color for the test paper in 35 minutes. A companion sample was removed from the bath at the end of 20 minutes, before there had been any change in the test paper. It showed an increase in the amount of blue colored fibres and the appearance of purples and violets with the gypsum plate.

A further test was made by exposing some of the guncotton on a slide, to the action of acetone vapors in a desiccator for 10 minutes at 30°. This length of time was sufficient to destroy the double refraction of the guncotton, so that between crossed nicols in polarized light it was almost indistinguishable from the background. It was then dried on a steam plate for eight hours to remove any volatile constituent and reexamined. Figures 5, 6 and 7 are photographs of this material.

The first photograph is of the untreated fibres showing their double refraction and size at 150 diameters. The second shows the fibres at the same magnification after the acetone vapor treatment and drying. The remarkable swelling which they have undergone illustrates the gelatinizing stage in the manufacture of smokeless powder. The third picture shows the dried, swollen fibres as they appear between crossed nicols. Some of the double refraction originally present, has returned. Either gelatinization was not complete or else strains set up in drying are responsible for the double refraction. Examination with a gypsum plate showed the presence of yellows, blues and violets in patches side by side, in between the light and dark-colored portions of the upper fibre. This indicated that sufficient acetone had condensed from vapor to liquid, on the surface of the fibre, to effect some slight dispersion, which was manifested by the play of colors noted.

Discussion of Results

It seems very probable that with uniform nitration, the range in colors would follow a spectrum wheel, such as that shown in Fig. 8, with the low nitrogen in the yellows and the high nitrogen in the blues. Apparently what really happens is that the colors follow the degree of dispersion. So that if a mixed acid bath high in nitric acid is employed, little dispersion of the cellulose aggregates results. At the same time there is some decided action, for the iridescence of the unnitrated fibres disappears. The iridescent play of colors in the raw material is caused by the resonance of particles of varying size. It seems obvious therefore that any type of nitration causes some readjustment in particle size. If a highly nitrated product is produced, a uniform grayish white or blueish white color is observed.

If however, a bath relatively high in sulfuric acid is employed to give a material of a relatively low nitrogen content, the dispersion of the cellulose aggregates is increased and the polarized-light colors, following the increased dispersion; appear on the red side of the spectrum. A result of the same kind is apparent if the nitrated material is treated with acids, alkalies, heat, superheated water, or ultra-violet light. The colors noted are therefore a record of the treatment which the cellulose aggregates have undergone whether within or outside of the nitrating bath.

A consideration of aggregate size and viscosity or of particle size and polarized-light color is sufficient to indicate why Tissot (loc. cit.) was unable to link up the nature of the cellulose, the time of nitration or the temperature with the color observed with the polarizing microscope. It is also indicated that the relationship which Punter[1] found to exist between the viscosity of the raw material and viscosity of the final product, will not hold if the nitrated material is subjected to viscosity reduction treatments. In other words there may be a change in the polarized light colors without a corresponding change in the nitrogen of the material. The conflicting elements in the situation are harmonized by a consideration of a statement by Kopaczewski[2] to the effect that according to the degree of dispersion of the substance under consideration we are sometimes confronted by chemical laws and sometimes by physical laws. In the case of nitrated cellulose the physical laws involving dispersion are more potent than the chemical laws relating to degree of nitration.

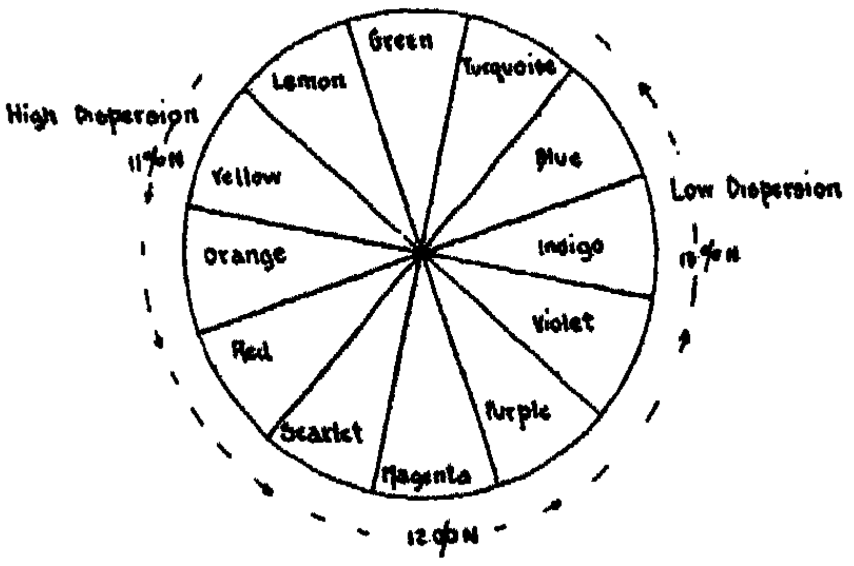

Fig. 8

Summary

The colors shown by nitrocelluloses of varying nitrogen content, in polarized light, are a function of the dispersion of the nitrocellulose.

The degree of dispersion and consequently the color observed is affected by the percentage of water in the nitrating bath, the ratio of nitric to sulfuric acid, the time and temperature of nitration, viscosity reduction treatments, ultraviolet light, heat and superheated water

The degree of dispersion effected by nitration to a definite nitrogen content, is a more powerful factor than the chemical constitution in determining what color will be seen in polarized light with crossed nicols.

Nitrocellulose is one of the dielectrics which transmit light ranging from red to blue, as the degree of dispersion decreases.

Research Laboratories,
Picatinny Arsenal,
Dover, N. J.

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[1] Punter: J. Soc. Chem. Ind., 33, 333T (1920).

[2] Kopaczewski: Alexander's "Colloid Chemistry," 1, 573.

THE APPROXIMATE PREDICTION OF VAPOR PRESSURE

BY JOHN CHIPMAN

The derivation of the Clausius-Clapeyron equation for the vapor pressure of a liquid,

$$d \ln P/dT = \Delta H/RT^2 \qquad (1)$$

involves two assumptions: (1) that the vapor behaves as an ideal gas; (2) that the volume of the liquid is negligible in comparison with that of the vapor. By introducing a third assumption, that the heat of vaporization is constant, we obtain the rule that log P is a linear function of 1/T. No one of these assumptions is ever strictly true; the deviations from all three are frequently very large, yet the linear relationship between log P and 1/T has been well established for many substances, notably those of the less-polar type. As an extreme example Dodge and Davis[1] have found for oxygen and nitrogen that log P is a nearly linear function of 1/T from the triple point to the critical temperature. Vapor pressures may therefore be expressed with a fair degree of accuracy over a considerable temperature range by the equation,

$$\log P = -A/T + B \qquad (2)$$

For the purposes of the following discussion this equation will be written:

$$\log P_{\text{atm.}} = -L'/2.303RT + L'/2.303RT_b \qquad (3)$$

where L′, the apparent heat of vaporization, is obtained by multiplying the slope of the log P against 1/T curve (at the boiling point) by 4.578. It is the purpose of this paper to present a method by which the value of L′ (and hence A and B) may be predicted when the boiling point and the chemical nature of the liquid are known.

The Heat of Vaporization

A number of empirical or semi-empirical equations have been proposed by which the heat of vaporization of an unassociated liquid may be estimated when its boiling point is known. The writer[2] has recently shown that the most reliable of these equations is that of Kistiakowsky,[3]

$$\Delta H_k = RT_b \ln(82.07T_b) \qquad (4)$$

For associated liquids the observed heats of vaporization are nearly always greater than ΔH_k defined by Equation 4. The ratios of the observed ΔH to ΔH_k for four classes of liquids are given in Table I. For the purpose of comparison it was thought best to employ data from a single source since the differences between two observers often exceed the sum of their apparent probable errors. The values used in Table I are accordingly taken entirely from the work of Mathews.[4]

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[1] Dodge and Davis: J. Am. Chem. Soc., 49, 610 (1927).

[2] Chipman: J. Phys. Chem., 32, 1528 (1928).

[3] Kistiakowsky: J. Russ. Phys. Chem. Soc., 53, 256 (1921).

[4] Mathews: J. Am. Chem. Soc., 48, 562 (1926).

TABLE I

Ratio of Observed to Calculated Heat of Vaporization

Substances	Number	$\Delta H/\Delta H_k$	Av. Deviation from Mean
Benzenoid Hydrocarbons	6	1.014	0.004
$C_aH_bX_c$*	13	1.030	0.016
Esters	16	1.072	0.013
Alcohols (Except Methyl)	6	1.296	0.012

* a, b, c, etc. = 1, 2, 3, etc. X = Halogen.

It is apparent from Table I that the Kistiakowski equation may be written,

$$\Delta H = 2.303\ aRT_b \log(82.07T_b) \qquad (5)$$

where the factor, a, is a constant for a given class of liquids.

The Vapor Pressure Equation

The quantity L′ of Equation 3 is not in general equal to the heat of vaporization although it approaches that quantity as assumptions 1 and 2 of the first paragraph approach validity. The ratio of L′ to ΔH is approximately constant for a given class of substances. Thus Parks and Barton[1] obtain the heat of vaporization of alcohols by multiplying the value of L′ (at the boiling point) by 0.96; similarly Mortimer[2] obtains an average value of 1.08 for the ratio L′/ΔH for a wide variety of liquids. In Table II are presented some of the values of this ratio obtained from vapor pressure data of the International Critical Tables[3] and heats of vaporization given by Mathews.

TABLE II

Ratio of Apparent to Observed Heat of Vaporization

Substances	Number	$L'/\Delta H$	Av. Deviation from Mean
Hydrocarbons	6	1.050	0.015
$C_aH_bX_c$	9	1.032	0.010
Esters	11	1.046	0.015
Alcohols	6	1.048	0.010

Since the two ratios $\Delta H/\Delta H_k$ and $L'/\Delta H$ are both approximately constant for a given class, it follows that $L'/\Delta H_k$ is also approximately constant. This ratio at the boiling point will be designated by the symbol g and may be called the "slope factor" for the substance since it represents *the ratio of the* actual slope of the log P against 1/T curve to the slope calculated by the Kistiakowsky and Clausius-Clapeyron equations. The actual slope will then be given by the equation,

$$A = L'/2.303R = gT_b \log(82.07T_b) \qquad (6)$$

When this value is substituted in Equation 3 a simple and very useful vapor pressure equation[4] is obtained:

$$\log P_{atm.} = -\ gT_b\log(82.07T_b)/T + g \log(82.07T_b) \qquad (7)$$

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[1] Parks and Barton: J. Am. Chem. Soc., **50**, 24 (1928).

[2] Mortimer: J. Am. Chem. Soc., **44**, 1429 (1922).

[3] "International Critical Tables," **3**, 201-246 (1928).

[4] An equation similar to this in which however the slope factor was omitted or considered unity was obtained by Kistiakowsky: Z. physik. Chem., **107**, 65 (1923).

TABLE III

Calculation of "Slope Factors"

Substance	T_b	Obs. Slope	$T_b \log(82.07/T_b)$	Slope Factor
Helium	4.2	7.30	10.65	0.685
Hydrogen	20.36	53.25	65.6	0.811
Methane	111.7	445.	443.	1.005
Ammonia	239.7	1255	1030	1.219
Sulfur Dioxide	263.1	1338	1140	1.173
Water	373.1	2160	1673	1.291
Formic Acid	373.6	1830	1675	1.093
Sulfur Monochloride	411.0	1880	1867	1.008
Mercury	629.8	3102	2970	1.043
Anthraquinone	652.9	3340	3090	1.081

TABLE IV

Slope Factors of Inorganic Substances

Substances	Number	Slope Factor	Av. Deviation from Mean
Rare Gases (except helium)	5	1.012	0.020
Nitrogen; Oxygen	2	1.045	0.004
Chlorine; Bromine; Iodine	3	1.085	0.002
Sulfur; Selenium	2	0.958	0.005
Mercury; Cadmium; Zinc	3	1.031	0.007
Calcium; Strontium; Barium	3	2.59	0.03
Sodium; Potassium; Rubidium	3	0.88	0.04
Bismuth; Antimony; Tin	3	1.21	0.04
HCl; HBr; HI; HCN	4	1.095	0.009
H_2S; H_2Se; H_3As	3	1.09	0.01
ClO_2; SO_2; N_2O; NOCl	4	1.15	0.01
$COCl_2$; $SeOCl_2$; CrO_2Cl_2	3	1.09	0.02
P, B, As, Sb, tri-halides (ex. fluorides)	7	1.08	0.03
P, B, tri-fluorides	2	1.19	0.005
$(CN)_2$; CNCl	2	1.14	0.01
CS_2; CSSe; C, Si, Ge, Sn, tetrachlorides	6	1.040	0.015
C, Si, Ge, Sn, P, hydrides	5	1.02	0.02
$Si_aH_bX_c$	6	1.07	0.01
$PbCl_2$; $PbBr_2$; PbI_2; $HgCl_2$; $HgBr_2$; HgI_2	6	1.13	0.05
AgCl; TlCl; TlBr; TlI	4	1.022	0.005
Cu_2Cl_2; Cu_2Br_2; Cu_2I_2	3	0.51	0.01
Alkali Halides	19	1.06	0.06

Miscellaneous: H_2F_2, 1.02; P, 1.01; CO, COS, 1.05; N_2H_4, 1.27; NO, 1.41; N_2O_4, 1.35; HgCl, 1.45; PF_5, 1.25; SO_3, 1.57; TlF, 2.05; (See also Table III).

The constants of Equation 2 are thus readily obtained when the boiling point and the slope factor are known. Table III shows the calculation of the slope factors for a few liquids whose vapor pressure curves have been accurately determined and which do not fit readily into the classifications of the subsequent tables. Substitution of the values of this table in Equation 7 reproduces the vapor pressure curves for the liquids within the limits of error of the assumption that log P is a linear function of $1/T$. Where this assumption is not valid the error becomes greater at temperatures farther from the boiling point. Thus for water which deviates largely from the linear assumption the error amounts to 0.9% at 80° and 2.4% at 60°. For the less polar liquids the errors are much smaller.

In Tables IV and V are summarized the average values of the slope factors for a wide variety of liquids. The data used were taken chiefly from the International Critical Tables but some other recently published data were also taken into consideration. Certain of the data of the I.C.T. had to be omitted where the points were not sufficiently concordant to determine even an approximate value of the slope. The deviation from the mean value of g within a well-defined class of substances is frequently less than that due to uncertainty of the experimental slope. The lowest member of an homologous series often has a different slope factor from the other members. Such exceptions are noted in the tables.

TABLE V

Slope Factors of Organic Substances

Substances	Number	Slope Factor	Av. Deviation from Mean
Ethane; Propane; n-Butane	3	1.032	0.002
Higher paraffines and olefines	18	1.053	0.020
Benzene; Toluene	2	1.082	0.002
Other benzenoid hydrocarbons	8	1.034	0.020
Naphthalene; Anthracene, etc.	6	1.084	0.022
Halogenated paraffines, benzenes, naphthalenes	28	1.070	0.015
Nitro compounds	6	1.120	0.011
Aliphatic Amines	5	1.13	0.03
Aniline and Toluidines	4	1.152	0.008
Alkyl anilines and toluidines, etc.	8	1.13	0.015
Ethers	6	1.10	0.015
Acetic Acid	1	1.18	
Acids (propionic to heptylic and benzoic)	7	1.365	0.085
Alcohols	10	1.352	0.020
Mercaptans	2	1.08	0.01
Phenols, Cresols, Benzyl Alcohol	5	1.31	0.07
Naphthols	2	1.145	0.005
Aldehydes	2	1.105	0.020
Ketones, Phenones	4	1.14	0.02
Esters	17	1.125	0.019

Correction of Boiling Points to Normal Pressure

In order to employ the methods here presented a knowledge of the normal boiling point is required. Frequently boiling points are observed at pressures more or less distant from normal and in such cases the foregoing considerations permit a very simple and accurate method of obtaining the normal boiling point. For this purpose Equation 2 may be put into the form used by Cragoe:[1]

$$\Delta T = (2.8808 - \log P_{mm})T/\Phi \qquad (8)$$

where ΔT is the correction to be added to the observed boiling point and

$$\Phi = g \log(82.07 T_b) \qquad (9)$$

This equation is most easily solved by successive approximations, the number of approximations depending upon the accuracy required and the magnitude of ΔT.

Summary

Relationships between ΔH (heat of vaporization), L' (apparent heat of vaporization from vapor pressure data) and ΔH_k (heat of vaporization by the Kistiakowsky equation) have been investigated. It is shown that for a given class of liquids the ratio between any two of these quantities at the boiling point is approximately constant.

The ratio, $L'/\Delta H_k = g$, called the "slope factor," may be estimated for nearly any liquid by comparison with the tables given. This factor and the normal boiling point are sufficient to establish the approximate vapor pressure equation.

A simple and reliable method of correcting observed boiling points to normal pressure is presented.

Department of Chemistry,
Georgia School of Technology,
Atlanta, Ga.

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[1] Cragoe: "International Critical Tables," 3, 246 (1928).

ADSORPTION OF POTASSIUM CHROMATE ON ZINC*

BY R. F. REED AND S. C. HORNING

Chromic acid and its salts are commonly used in lithographic etches. These etches are supposed to reduce the affinity of the zinc lithographic plates for ink and to increase their affinity for water. This change in the character of a metal surface in the presence of various substances can be shown in many ways. Iron which has been immersed in concentrated nitric acid, or zinc which has been immersed in chromic acid will no longer react immediately with copper sulphate. These phenomena have received various explanations, but all of the theories depend on the formation of a surface film having new properties. The data obtained shows that potassium chromate reacts with a zinc surface, imparting to it new properties by depositing on it a compound of chromium.

A qualitative measure of the extent to which the activity of a zinc surface is reduced by potassium chromate should be obtained by determining the effect of potassium chromate on the catalytic activity of zinc, adsorption on zinc, and on the chemical reactivity of zinc. Only the last two methods were investigated. The results obtained with these methods indicate that potassium chromate should act as a strong poison for zinc catalysts.

The amount of corrosion of zinc over a period of twenty hours was determined in three separate solutions, one of distilled water, one of .00286 M potassium chromate, and one of .00286 M chromic acid. These tests were made on two different samples of zinc, one sample containing 99.9 per cent zinc, and the other approximately 99.0 per cent zinc. The metal in each case was completely covered with the solution and aeration was continued throughout the tests. The plates in the distilled water became covered with a deposit of basic carbonate and were pitted, while the plates in both the potassium chromate and chromic acid solutions remained clean and retained their polished appearance. The losses in weight of the plates in chromic acid and in potassium chromate solutions were approximately equal, being about .01 mg. per square centimeter, while the loss in distilled water was more than .35 mg. per square centimeter. There was no noticeable difference in the rates of corrosion of the two grades of zinc of different purities.

A comparison was made of the amount of moisture adsorbed by clean zinc surfaces and surfaces which had previously been treated with a solution of potassium chromate. The moisture adsorbed was determined by first passing an inert gas saturated with moisture over the plates and then passing dry gas over the plates and collecting the water in calcium chloride tubes. The clean zinc adsorbed .0013 mg. of water per square centimeter, while the treated plates adsorbed .0009 mg. of water per square centimeter.

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* Institute of Scientific Research, University of Cincinnati, Department of Lithographic Research.

Three zinc plates were cleaned by rubbing with fine pumice powder and water. The first was allowed to dry and then immersed in a 2 per cent solution of methyl violet; the second was immersed, without drying, in the methyl violet solution; and the third was immersed, without drying, in a 15 per cent solution of potassium chromate and then in the methyl violet solution. The first was definitely colored a light blue, which could not be removed with water; the second acquired a deep blue bronze color, very similar to that of the methyl violet crystals, which changed on standing in air or on continued washing to the original color of the dye; while the third was not colored at all.

These experiments show conclusively that a zinc surface is changed in character through the action of potassium chromate. Since a reaction of some kind must occur, a determination was made of the amount of potassium chromate removed from solution by zinc and of the amount of chromium retained by the zinc surface.

Small plates of zinc were cleaned under water with pumice, and without drying were immersed in a dilute solution of potassium chromate. The error caused by the introduction of the moisture adhering to the zinc plates is much less than the experimental error involved. Using .00004 molar solutions, each square centimeter of zinc removed approximately .0001 mg. of potassium chromate from solution.

A clean zinc plate was treated with a 20 per cent solution of potassium chromate and the solution was allowed to dry on the plate. It was then washed in running water until all of the potassium chromate appeared to be removed. A determination of the chromium on the metal surface showed that as much as .003 mg. calculated as potassium chromate had been taken up per square centimeter. In each of the above cases the chromium was determined colorimetrically using diphenylcarbazide.

It has been shown that potassium chromate reacts with a zinc surface, depositing on it a compound of chromium and making it less active. The adsorbed compound is probably either zinc chromate or potassium chromate. This question could be decided if the potassium, in addition to the chromium retained by the zinc, could be determined.

IONIC EQUILIBRIUM IN COLLOIDAL SOLUTIONS

BY H. D. MURRAY

Since Perrin's work on endosmosis[1] it is generally accepted that the charge on colloid particles is due to ions at the surface of the particles. It is now suggested that several of the properties of these particles are to be expected from considerations based upon the law of Mass Action.

The process of the formation of the charge on colloid particles may be considered to take place in two stages. First, an adsorption of electrolyte upon the particle surface, and then the ionization of the electrolyte so adsorbed. It appears probable that adsorption of the stabilizing electrolyte is polar, that is to say that it is brought about by forces centred in one polar element of the electrolyte, so that subsequent ionization takes place in such a way that the ion remaining on the surface is of the same chemical nature as the particle itself. For example, metal particles stabilized by hydroxides appear to retain the cation on the surface, while sulphide particles stabilized by H_2S retain sulphur ions. Powis[2] has noticed that a $Fe(OH)_3$ sol which, when prepared in the usual way in the presence of excess $FeCl_3$, is positively charged by $Fe^{\cdot\cdot}$ ions may be obtained negatively charged by running a solution of $FeCl_3$ into a KOH solution. Another example is afforded by Lottermoser's experiments[3] on AgI sols. If $AgNO_3$ solution is added to excess of KI solution a negatively charged AgI sol is formed. If KI solution is added to excess of $AgNO_3$ solution a positively charged sol is formed.

If we write △AgI for colloidal silver iodide, the two sols would appear to be

$$\mathbf{O}\text{AgI.I}' + \text{K}^{\cdot} + \text{KNO}_3 \qquad \text{and} \qquad \mathbf{O}\text{AgI.Ag}^{\cdot} + \text{NO}_3' + \text{KNO}_3$$

for the first sol coagulates when a slight excess of $AgNO_3$ is present and the second sol when a slight excess of KI is present,

$$\mathbf{O}\text{AgI.I}' + \text{Ag}^{\cdot} \rightleftharpoons \mathbf{O}\text{AgI.AgI} \qquad \text{and}$$

$$\mathbf{O}\text{AgI.Ag}^{\cdot} + \text{I}' \rightleftharpoons \mathbf{O}\text{AgI.AgI}$$

This appears to be a general effect and may be summed up as follows:—When a colloidal precipitate is formed by mixing solutions of two electrolytes the precipitate will be positively charged when that electrolyte is present in excess which furnishes the cation of the precipitate and negatively charged when that electrolyte is in excess which furnishes the anion.

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[1] J. Chim. phys., **2**, 601 (1904); **3**, 50 (1905).

[2] J. Chem. Soc., **107**, 818 (1915).

[3] J. prakt. Chem. (2), **72**, 39 (1905); **73**, 374 (1906).

To say that the charge upon the particle is due to ionization of electrolytes from the surface gives a more static picture of what is known as formation of charge by selective adsorption. The conditions obtaining at equilibrium may be expressed graphically by:—

$$\mathbf{O} + \mathrm{AB} \rightleftharpoons \mathbf{O}_{\mathrm{AB}} \rightleftharpoons \mathbf{O}_{\mathrm{A}^{\cdot}} + \mathrm{B}'$$

If now a further quantity of electrolyte be added to the system, various effects may be observed.

(1) *When the particle surface is unsaturated.*

If the concentration of the stabilizing electrolyte AB is low and the particle surface has not adsorbed AB to saturation, that is to say if the balance of equilibrium lies to the right and left in the above equation, then addition of a further quantity of an electrolyte *ab* may result in the adsorption of *ab* upon the surface, subsequent ionization, and hence a slight increase in particle charge. This may be represented by:—

$$\mathbf{O}\,\mathrm{A}^{\cdot} + \mathrm{B}' + ab \rightleftharpoons \mathbf{O}^{\mathrm{A}^{\cdot}}_{ab} + \mathrm{B}' \rightleftharpoons \mathbf{O}^{\mathrm{A}^{\cdot}}_{a^{\cdot}} + \mathrm{B}' + b'$$

An increase of charge has often been observed when small quantities of univalent electrolytes have been added to comparatively pure sols. Some results by Burton[1] are given on the relation between the mobility of copper particles, and hence the charge on the particles, and the amount of KCl added to the sol.

Normality of Mixture	Mobility at 18°C
0.0	24.9×10^{-5}
17.0×10^{-6}	$25.7 \times$ "
38.0 "	26.2 "
74.0 "	22.8 "
154.0 "	18.7 "

The above process may be also offered in explanation of the fact noticed by Beans and Eastlake[2] that metal sols prepared by Bredig's method are more stable in the presence of traces of added electrolyte.

(2) *When the surface is saturated and little if any alteration of ionization occurs.*

Here there will be no immediate effect, but a slow rearrangement of adsorbed electrolyte on the particle surface will take place until the stabilizing electrolyte and the added electrolyte are in equilibrium with each other on the particle surface and in solution. Such an effect may be taking place in the phenomenon of acclimatization. There will be little alteration in the properties of the sol. If, however, a non-electrolyte be added to the system coagulation may ensue by replacement of the stabilizing electrolyte. This would explain the coagulation of sols by non-electrolytes when these are added in quantities insufficient to alter appreciably the physical condition of the system.

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[1] "Physical Properties of Colloidal Solutions," 2nd Ed., p. 167.

[2] J. Am. Chem. Soc., 37, 2667 (1915).

(3) *When the surface is saturated and ionization is repressed.*

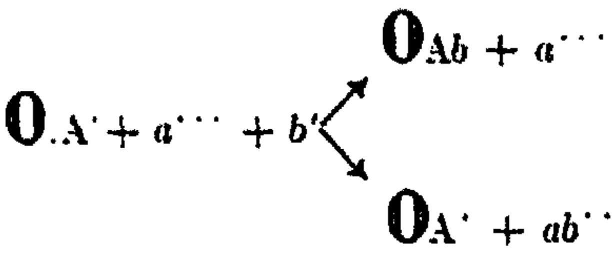
Consider the case where an electrolyte is added to the sol in such amount that the concentration of undissociated electrolyte on the particle surface increases. The problem is similar to that of calculating the degree of dissociation of the products obtained by mixing two dissimilar electrolytes in solution, but here we can confine our attention to two ions only. The anions of the added electrolyte will tend to combine with the cations on the particle surface. If the added anions are n-valent then the number of these which must combine with surface cations is equal to 1/n of the number of univalent anions required to reduce the effective charge on the particle to the same extent. In order to reduce the charge to the point where coagulation takes place, therefore, n times as many univalent anions must combine a n- valent anions. In addition, the force binding a polyvalent ion to a univalent is greater than that binding two univalent ions. This fact is apparent in the dissociation constants of a polyvalent electrolyte. Abbott and Bray[1] give the following values for H_3PO_4,

$$K_1 = 1.1 \times 10^{-2}$$
$$K_2 = 1.95 \times 10^{-7}$$
$$K_3 = 3.6 \times 10^{-13}$$

That is to say, a greater number of polyvalent anions will combine with surface cations than will univalent anions when an equal number are added to the system. Thus an electrolyte with, say, a trivalent anion, will bring about coagulation at a much smaller concentration than one third of that of an electrolyte with a univalent anion. This is in accord with well known facts. Burton[2] quotes some values for the concentrations in milligram-atoms per litre of different salts required to cause coagulation of arsenious sulphide sol, examples of which are as follows:—

LiCl	185.4	$CaCl_2$	2.06	$CrCl_3$	.316
NaCl	80.6	$BaCl_2$	1.68	$FeCl_3$	.123
KCl	97.9	$MgCl_2$	1.05	$AlCl_3$	.090

So far, only the effect of the anion of the added electrolyte has been considered: but the cation, especially when polyvalent, may also influence the coagulating power. As the concentration of the added electrolyte is increased the tendency of the anion to combine with surface cations is less when the added cation is polyvalent than when the latter is univalent. The former conditions may be represented:—



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[1] J. Am. Chem. Soc., 31, 729 (1909).

[2] Loc. cit., p. 158 et seq.

The balance of the equilibrium shifts to the lower reaction as the valency of *a* increases. Hence a greater concentration of added electrolyte is required to reduce the effective charge on the particle to the limiting value for coagulation. This effect is also shown in examples below quoted from Burton:

HCl	49.4	½H_2SO_4	80.0	1/3H_3PO_4 ca.	1290
KCl	49.5	½K_2SO_4	65.6	1/3K_3Citrate	240
$CaCl_2$	1.31	$CaSO_4$	1.60		
$MgCl_2$	1.14	$MgSO_4$	2.10		
$FeCl_3$	.136	½$Fe_2(SO_4)_3$	.216		
$AlCl_3$	.062	½$Al_2(SO_4)_3$	.074		

Returning now to the charged particle, it is obvious that, by the addition of sufficient electrolyte with univalent ions to the sol, it is possible to make the charge approach zero as dissociation of surface ions is repressed. But, if the anions of the added electrolyte is polyvalent the effect produced by its addition will depend upon its concentration. In small concentration the effective charge on the particle will be reduced,

$$O_{\substack{A^{\cdot}\\A^{\cdot}\\A^{\cdot}}} + b''' \rightleftharpoons O_{\substack{A^{\cdot}\\Ab''\\A^{\cdot}}}$$

In larger concentrations the effective charge will be reversed,

$$O_{\substack{A^{\cdot}\\A^{\cdot}\\A^{\cdot}}} + 3b''' \rightleftharpoons O_{\substack{Ab''\\Ab''\\Ab''}}$$

In still larger amounts the concentration of trivalent and divalent ions in solution becomes very small, and the effective charge on the particle is reduced, but not reversed, by combination of the surface cations with the univalent anions present,

$$O_{\substack{A^{\cdot}\\A^{\cdot}\\A^{\cdot}}} + 3a_2b' \rightleftharpoons O_{\substack{Aa_2b\\Aa_2b\\Aa_2b}}$$

All the above effects have been observed by Buxton and Teague.[1] Some of their results on the coagulation of a platinum sol by $Fe\,Cl_3$ are given below:—

Millimols	$FeCl_3$/litre		Effect	Direction of Cataphoresis
0	to	.0557	No coagulation	To anode
.0833	to	.2222	Complete coagulation	No cataphoresis
.3333	to	6.667	No coagulation	To cathode
16.33	to 666.7		Complete coagulation	No cataphoresis

The reversal in sign of the charge on particles has been noticed when polyvalent ions have been added to a sol, but not after the addition of univalent ions, except in some special cases where the ions is one of those of the electrolyte forming the body of the particle. On the above view, reversal of sign

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[1] Z. physik. Chem., 57, 72 (1906).

should only be possible with an added electrolyte having an ion, of opposite sign to the stabilizing ion on the particle surface, which is of greater valency than the stabilizing ion.

It would thus appear that those electrolytes are most efficient stabilizers of colloid particles which contain an ion in common with the substance of the particle, and that many of the typical properties of such particles may be explained on the assumption that these electrolytes are adsorbed at the particle surface and are free to dissociate dissociation taking place in such a way that the ion remaining attached to the particle surface is that of the same chemical nature as the substance of the particle.

Imperial College of Science and Technology.
South Kensington.

THE DIELECTRIC CONSTANTS OF SILVER SOLS WHEN DILUTED WITH VARYING AMOUNTS OF ETHYL ALCOHOL

BY GEORGE D. ROCK AND SIMON KLOSKY

In order to determine the charge on colloid particles, it is customary to measure the velocity at which they migrate under the influence of a known difference in potential. In the formula which shows the relation between these two quantities, the dielectric constant appears. It is usual to consider the dielectric constant of the sol equal to the dielectric constant of the medium; but as this is not always true[1] (for example, vanadium pentoxide) it was thought desirable to measure it in the case of silver sols especially in the presence of varying amounts of alcohol.

Preparation of the Liquids used

The silver sols were made by the method of Carmody[2] which consists in suspending freshly prepared and well washed silver oxide in water, heating to boiling, filtering hot as rapidly as possible, cooling and reheating to about 80°C, when the characteristic color of the Kohlschütter sols[3] appears and deepens on continued heating.[4]

Twenty liters of this sol were prepared.

Alcohol obtained from a widely known manufacturer was redistilled three times and a constant boiling fraction used to dilute the sol. This alcohol was not dried, but its density determined at 25° C. by pyknometer and the water content read from a table.[5]

In this way sols containing varying percentages by weight of alcohol were obtained. The silver content of all the sols was the same, namely, 25 milligrams per liter.

Standard liquids were now prepared. The methyl alcohol, acetone and carbon tetrachloride were analyzed samples from a prominent chemical firm. The nitrobenzene and bromobenzene were freshly distilled just before use and their refractive index, which was measured, indicated that they were very pure.

Apparatus[6]

The apparatus used in the experiment was arranged as an adaptation of the well-known heterodyne system and is illustrated in Fig. 1. The high-frequency oscillators were constructed according to the Hartley system and employed UX 210-A tubes as the vacuum tube oscillators. Large-capacity

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[1] Errera: Kolloid-Z., 31, 62 (1922).

[2] Unpublished Master's Thesis, Catholic University (1924).

[3] Kohlschütter: Z. Elektrochemie, 14, 49 (1908).

[4] Researches on the constitution of this micelle are in progress.

[5] "Smithsonian Tables," p. 124 (1921).

[6] Extract from Doctor's Dissertation of George D. Rock, Catholic University (1927).

storage batteries were used to heat the filament. This large capacity was necessary in order to minimize "drifting" caused by variation of filament current. Radio "B" batteries supplied the plate voltage.

The oscillator marked "B" in the diagram had four condensers in the high frequency circuit. A large fixed condenser K′ of 10,000 m.m.f. capacity was connected in parallel with the variable precision condenser K of maximum capacity 1500 m.m.f. These were in turn connected in series with condensers C and C′. The condenser C was a small fixed condenser and C′ was a fixed condenser containing the liquid under test.

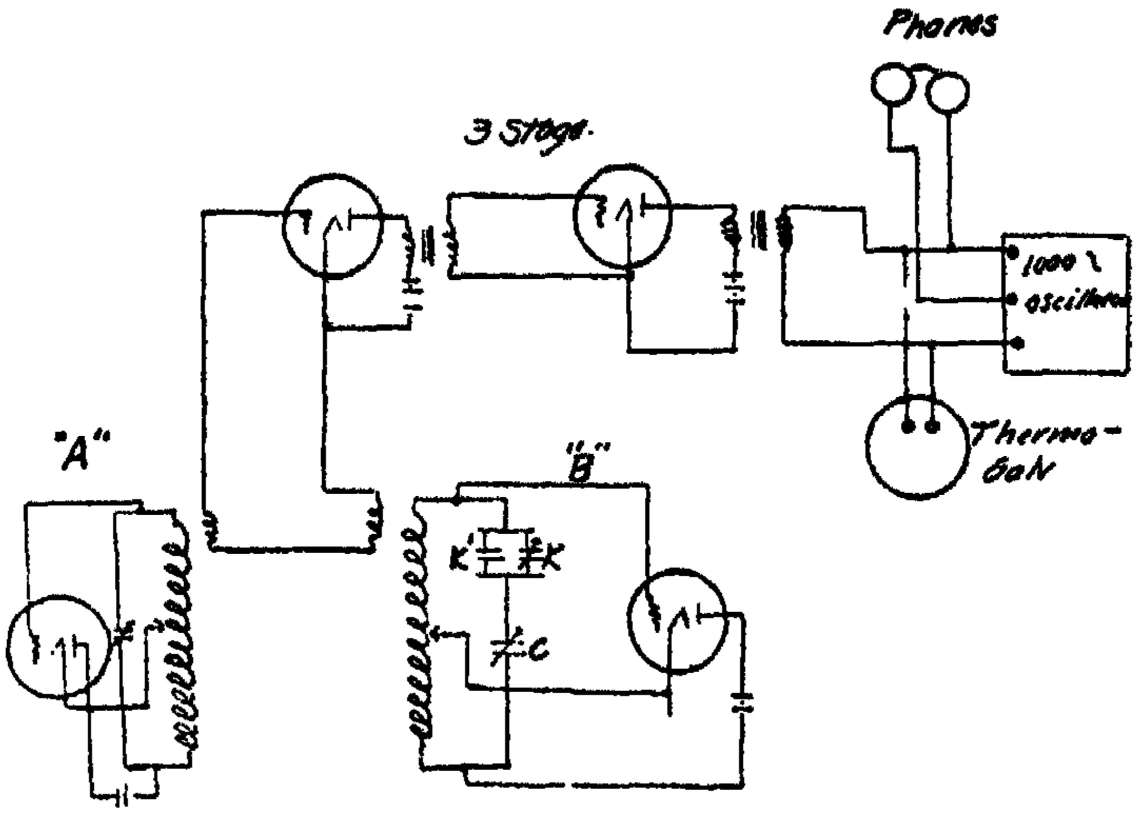

Fig. 1
Schematic Diagram of Electrical Connections

Oscillator "A" was essentially the same as "B" but had only one condenser in the oscillating circuit excepting the very small variable air condenser connected in parallel with the large condenser and arranged so as to compensate for the "drift" of the oscillators.

The detecting system consisted essentially of a three stage V.T. amplifier inductively connected to both "A" and "B" and having electrically connected in the output circuit of the third tube a 1000 cycle General Radio oscillator, a thermo-galvanometer and a pair of phones as indicated on the schematic diagram.

Procedure

The oscillator "B" was set to operate at 500,000 cycles as determined by a precision wavemeter. Oscillator "A" was then started and its frequency varied until zero beat was secured as evidence by no beat frequency in the phones. The 1000-cycle oscillator was then put into operation and "A" detuned from "B" by 1000 cycles. This result was secured by listening at the phones and noting the oscillations of the needle of the thermo-galvanometer. When nearing the 1000-cycle point beats could be heard and the needle of the galvanometer could be seen to oscillate slowly. At exactly this point the needle would remain at rest and the beat frequency was zero. The reading of the precision condenser was then noted. This system of detuning to a predetermined frequency resulted in very sharp balance points and entirely eliminated the tendency of the oscillators to fall into synchronism and give a very broad balance point. Precautions were taken to insure working on the same side of the zero point for all the readings.

A liquid with a known dielectric constant was then placed in the test condenser and the precision condenser varied until the total capacity of the oscillating circuit was the same as before, resulting i. the production of the same 1000-cycle beat note from the high frequency oscillators. The reading of the precision condenser was again noted and the entire operation repeated using another standard liquid. In this way data were obtained for a curve showing the relation between changes in condenser readings and the dielectric constants.

The solutions of alcohol in water for various concentrations were then placed in the condenser and the respective changes in the precision condenser noted. Then the liquids containing the silver were placed in the condenser and their changes noted.

Results

TABLE I

Standards used and Their Sources

Substance	Reading	Dielectric	Temp.	Observer
Carbon tetrachloride	2.917	2.25	18°C	Turner[1]
Water	10.980	81.1	18.6	Turner[1]
Bromobenzene	3.887	5.21	23.5	Walden[2]
Nitrobenzene	7.433	35.5	20.5	Walden[2]
Acetone	6.214	20.5	19.	Drude[3]
Acetone (25%)	9.334	67.0	19	Drude[3]
Acetone (50%)	8.596	50.6	19	Drude[3]
Methyl alcohol	7.298	31.5	18	Rudolph[4]
Air	2.130	1.0	20	Fritz[5]

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[1] Z. physik. Chem., **35**, 385 (1900).
[2] Z. physik. Chem., **70**, 569 (1910).
[3] Z. physik. Chem., **23**, 288 (1897).
[4] Diss. Leipzig (1911).
[5] Phys. Rev., (2) **23**, 345 (1924).

TABLE II

Dielectric Constants of Mixtures of Alcohol and Water

% Alcohol	Condenser Reading	D.E.K. (Curve)	% Alcohol (S)	D.E.K. (25°C) (S)
0	11.000	81.3	0.0	81.12
7.65	10.669	77.1	8.378	75.56
15.61	10.395	73.5	15.497	70.66
23.89	10.070	69.3	25.299	64.58
32.55	9.660	64.0	34.864	57.86
41.56	9.030	55.7	41.076	53.69

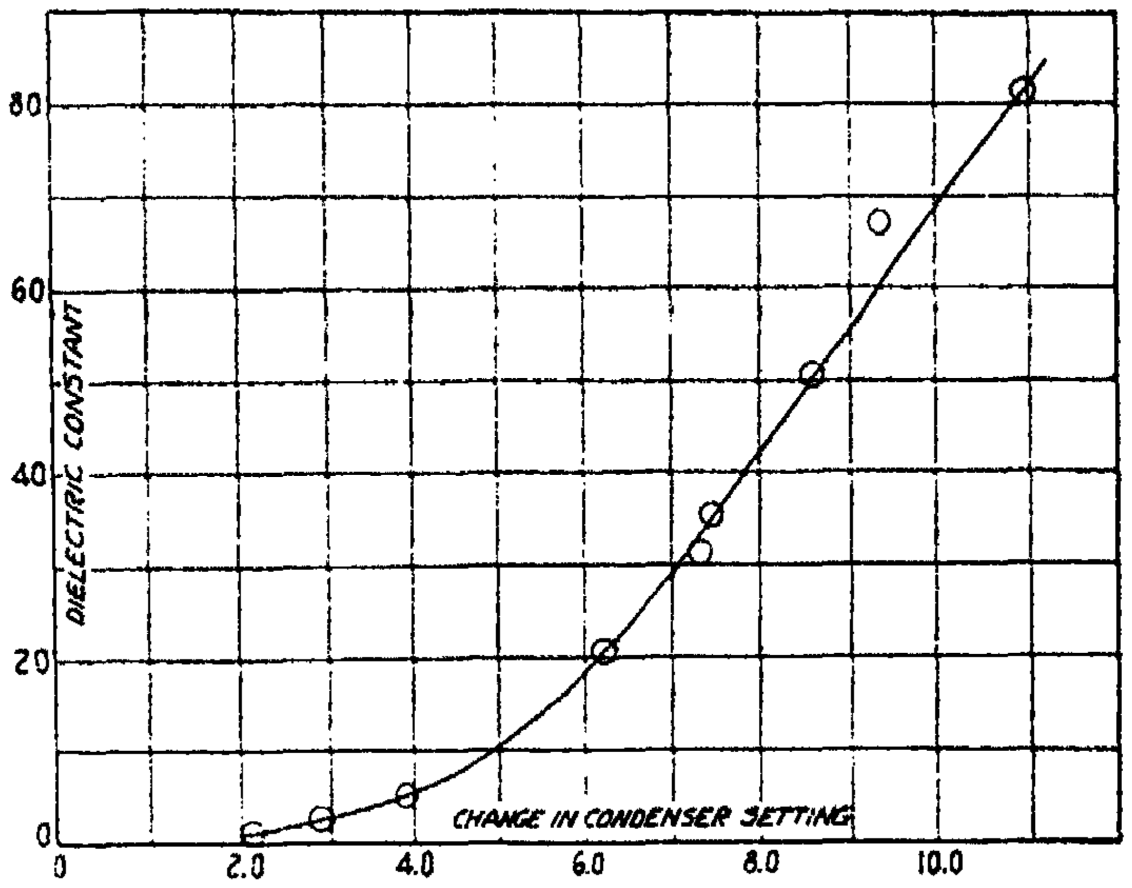

FIG. 2

TABLE III

Dielectric Constants of Silver Sols and Alcohol

Ag Sols.	% Alcohol	Condenser Reading	D.E.K. (Curve)
1	0.0	10.870	79.5
2	7.65	10.560	75.6
3	15.61	10.410	73.7
4	23.89	10.007	68.6
5	32.55	9.455	61.4
6	41.56	9.228	58.3

Discussion of Results

No provision was made for temperature control in these experiments. The temperature of the room was observed before and after each reading and in no case was it found to vary more than plus or minus one degree from 23°C.

As the temperature coefficient of the dielectric constant of ordinary liquids[1] at room temperature is only 0.005 units, no serious error is introduced by this procedure.

As can be seen from the curve, Fig. 2, the condenser readings for the standard liquids lie on a smooth curve with the exception of 25% acetone. No reason is known for the divergence.

The dielectric constants of the mixtures of alcohol and water lie on a smooth curve slightly higher than those of Salazar,[2] whose data are included in the columns marked (S) as the reference is rather inaccessible.

The dielectric constants of the silver sols are very close to those of the dispersion medium or slightly lower with the exception of 50% alcohol, which is higher. This is in agreement with the data of Errera[3] who found the dielectric constant of silver hydrolysols to be practically that of pure water.[4]

Summary

The dielectric constants of silver sols, to which varying percentages of ethyl alcohol were added, have been measured; and found to be substantially equal to the dielectric constants of the dispersion media.

The Catholic University of America,
Washington, D. C.
March 1928.

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[1] Turner: Z. physik. Chem., 35, 412 (1900).

[2] Salazar: Anal. Soc. Espan. Fis. Quim., 22, 275 (1924).

[3] Errera: Kolloid-Z., 32, 157, 244 (1923).

[4] Bibliographies on dielectric constant are given by Salazar and by Blüh: Physik. Z., 1926, 266.

THE PHOTOEXPANSION OF CHLORINE

BY W. H. MARTIN, A. F. W. COLE AND E. E. LENT

In 1871 Budde[1] observed that chlorine expanded on exposure to sunlight under conditions which caused no expansion in air. Since the gas absorbs light of certain colours such an expansion is to be expected if the absorbed light energy is degraded to heat energy. Budde sought to invent a mechanism to account for the expansion but his discussion is prejudiced by his belief that there was no corresponding rise in temperature of the chlorine. Any mystery surrounding this expansion of ordinary chlorine was dissipated by the work of Mellor[2] and Bevan[3] who showed that the expansion is quantitatively accounted for by the rise in temperature of the insolated gas.

The mysterious result on the expansion of chlorine is that of Shenstone and should not properly be called the Budde Effect. Shenstone[4] found that chlorine dried with phosphorus pentoxide did not expand on exposure to sunlight. It is difficult to be sure that anyone ever verified this remarkable result. Mellor may have done so. In his conclusion he says— "Dry chlorine does not exhibit the Budde Effect"; but in the paper no experiment is described and the only pertinent paragraph is— "If chlorine is dried by means of phosphoric oxide, there is no sign of Budde's expansion in sunlight. (Concentrated sulphuric acid may be used as index liquid.)......" which may well be a reference to Shenstone's work. Baker[5] certainly tried some experiments but does not describe them. "I have undertaken some experiments with unmixed chlorine, but I find that in this case there is absolutely no increase in volume (on exposure to light)". Baker neither here nor elsewhere says anything further about these experiments.

Yet almost everyone who has written on the photochemical reactions of chlorine accepts this result of Shenstone as proven. Theories of the mechanism of the hydrogen chlorine reaction have been built up using Shenstone's result as one of the foundation stones. Weigert[6] and Marshall[7] and many others accept and make use of this result in their theories.

If it be true that dry chlorine in sunlight does not increase in temperature, then what becomes of the energy of the absorbed light? All measurements on the absorption coefficients of dry and of wet chlorine[8] have failed to detect any difference between the two. It is true that Mellor[9] and Cordier[10] thought

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[1] Phil. Mag., (4) 42, 290 (1871); Pogg. Ann., 6, 477 (1873).

[2] J. Chem. Soc., 81, 1289 (1902).

[3] Phil. Trans., 202, 90 (1904).

[4] J. Chem. Soc., 71, 471 (1897).

[5] British Association Reports, 1894, 496.

[6] Z. physik. Chem., 106, 407 (1923).

[7] Trans. Am. Electrochem. Soc., 49, 143 (1926).

[8] Le Blanc: Z. Elektrochemie, 25, 234 (1919); Halban and Siedentopf: Z. physik. Chem., 103, 71 (1922); Kornfeld and Steiner: Z. Physik, 45, 325 (1927).

[9] J. Chem. Soc., 81, 1289 (1902).

[10] Wien. Monatshefte, 21, 655 (1900).

to have found that moist chlorine is more effective than is the dried gas in filtering out a constituent of the light which is active in promoting the reactions of chlorine with hydrogen and with silver. Recently, however, Weigert and Nicolai[11] have published a paper which casts grave doubt on these results.

If dry chlorine absorbs light without rise in temperature, then only two possibilities remain: either the chlorine must be changing—for which there is not the slightest evidence—, or the absorbed energy must be reradiated in some way. Weigert and Marshall speak of an "isochromatic fluorescence," by which they mean that the absorbed energy is reradiated as light of the same frequency as is the exciting light. It is unthinkable that visible light, thus reradiated, should not have been observed by any of the workers on dry chlorine.

One of us[12] has measured the light scattered by commercial chlorine and also by chlorine dried by long contact with phosphoric oxide and has found not the slightest difference in the intensities of their scattering. Indeed chlorine, wet or dry, scatters quite normally, that is, its intensity is as calculated from the Rayleigh formula: and this measured scattering is a thousandfold less intense than must be any hypothetical isochromatic fluorescence which would serve to explain Shenstone's result. Nor does lowering the pressure of chlorine result in any visible fluorescence. Iodine at low pressures fluoresces brilliantly and we have found it easy to observe this fluorescence which is a thousandfold more intense than the scattering. Bromine[13] fluoresces too at low pressures,—best at about 1 mm,—but the intensity is less than one percent of that of iodine.

We have tried to find a similar fluorescence in chlorine at low pressures when illuminated by a powerful beam from a carbon arc. The chlorine was dried intensively by long exposure to phosphoric oxide and the pressure was then lowered by condensing the chlorine into a side-arm by means of liquid air. As the pressure decreased the intensity of scattering also fell off gradually and disappeared without showing any increase which might be called fluorescence.

Mellor[14] tried to detect photographically a fluorescence in chlorine at atmospheric pressure but failed. "I find that no radiations capable of affecting the fastest 'Paget' sensitive plates are evolved by chlorine gas contained in thin glass tubes exposed for 1–5 hours to bright sunlight, limelight, or to a 600–1000 c.p. electric arc; nor does such a vessel of chlorine emit any rays capable of causing a perceptible influence on a sensitive mixture of hydrogen and chlorine."

Kistiakowsky[15] also sought to find fluorescence in dried chlorine; but neither visually nor with a thermopile did he obtain any evidence that the absorbed light was reradiated.

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[11] Z. physik. Chem., 131, 267 (1928).
[12] A. F. W. Cole: Trans. Am. Electrochem. Soc., 49, 135 (1926).
[13] Daure: Compt. rend., 183, 31 (1926).
[14] J. Chem. Soc., 81, 1287 (1902).
[15] J. Am. Chem. Soc., 42, 2104 (1027).

There appears then to be not the slightest direct evidence in favour of the reradiation hypothesis, so that Shenstone's result remains inexplicable. We have carried out the experiments described below in an attempt to verify his results.

The Purification and Drying of the Chlorine

The chlorine was taken from a steel cylinder of liquid chlorine supplied by the Canadian Salt Company. It contained almost one percent by volume of an impurity which was largely though not entirely soluble in alkali and was no doubt carbon dioxide with a little carbon monoxide. The first fractions taken from a new cylinder contained more than one percent of impurity, the last fractions very much less than this amount. The method of analysis was the usual one of absorbing the chlorine in mercury.

The chlorine was purified by a series of fractionations in the absence of air, using liquid air to condense the vapour and retaining the middle fraction each time. The purified gas was analysed by sealing up a sample in a tube of about 25 cc capacity and breaking off the tip under mercury. The top of the sampler tube was drawn out into a capillary, and it was estimated that with a hand lens a bubble of gas remaining after absorption would be visible if its volume were as great as .01 cubic millimetres. After a triple fractionation no bubble whatever remained and the chlorine certainly contained less than one part in one hundred thousand of impurity non absorbable in mercury.

Phosphoric oxide commonly contains lower oxides which react with chlorine. The oxide used in these experiments was distilled at about 400° over platinized asbestos in a current of oxygen. The product satisfied Shenstone and Beck's criteria for freedom from P_2O_3, namely,—it failed to reduce a 10% solution of silver nitrate when warmed and failed to reduce a boiling solution of mercuric chloride. It was largely volatile and could be easily distilled into the apparatus as required.

The Measurement of the Photoexpansion

The apparatus for drying the chlorine and measuring its photoexpansion is shown in Fig. 1. All was made of Pyrex except the Bourdon gauge which was more easily made from soft glass and was joined by a graded seal to the Pyrex. The gauge B was made by blowing a very thin-walled bulb and sucking in one side as symmetrically as possible. These gauges if thin enough to be sensitive will not stand a vacuum and were housed in the tube A which was connected to the rest of the apparatus by a capillary which could be sealed off at C after the system was filled with chlorine. The pointer of the gauge was observed by a very low power microscope with a micrometer eyepiece and calibration was made against a mercury manometer.

Phosphoric oxide, prepared as described above, was distilled from several sidearms into G. The whole apparatus was then tested for tightness and evacuated while baked out with a Bunsen flame. The expansion bulb E was baked out in an electric muffle at 425° for two hours under a high vacuum.

The evacuation was made with a mercury diffusion pump, kindly placed at our disposal by Professor Ferguson. The pump showed on a McLeod gauge a pressure certainly less than .0001 mm of mercury. The apparatus was then sealed up under this vacuum.

Chlorine, purified by fractionation, was admitted at D by breaking the seal with a plunger consisting of an iron rod sealed up in glass and operated by a solenoid. The apparatus was sealed off at L when filled with chlorine at atmospheric pressure. A sampler tube F was then removed and analysed and showed purity greater than 99.999%.

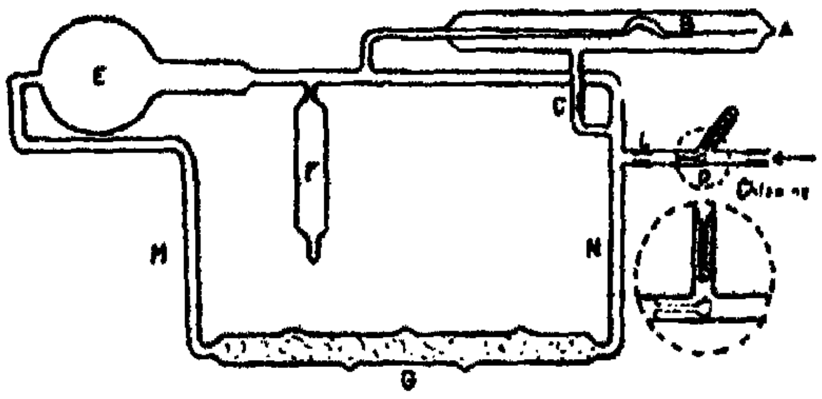

Fig. 1

The light from a powerful carbon arc lamp, after traversing a six-inch cell of water, was focussed on the bulb E (150 cc capacity) and the movement of the gauge was read. After chlorine was first admitted to the apparatus, the gauge showed, on illumination of the gas, an increase of pressure of 10.5 mm of mercury (the gauge is sensitive to about 0.5 mm). The pointer moves to its maximum reading about 30 seconds after the light is turned on and returns to its original position in about the same time after the light is extinguished. The same apparatus filled with air showed no expansion.

The chlorine was then dried by circulation over the phosphoric oxide, the circulation being effected by warming to about 34° the bulb E and tube M and cooling with running water to about 8° the tube N. An estimate of the rate of circulation was obtained by constructing a similar apparatus and measuring the rate of flow of a puff of smoke blown into the system. Circulation was at such a rate that the total volume of chlorine passed over the phosphoric oxide every 30 minutes.

Circulation was then carried for a period of 250 hours distributed over a total period of 30 days, circulation being carried on by day only. Readings were made from time to time of the photoexpansion and gave values such as: After 20 hours drying, 10.5 mm mercury; 50 hours, 9.5 mm; 100 hours, 11 mm; 200 hours, 9 mm. The variations were of course attributable to the arc lamp. There seemed to be no object in seeking a constant source of light and reproducible readings unless there was some indication of the expected great change in the photoexpansion. At the end of a month there was no change in the photoexpansion; the expected decrease in the photoexpansion did not occur.

Have the Walls of the Expansion Chamber any Effect?

It seemed a possibility that water might cling to the glass walls of E even though dried chlorine were circulated through it, so a second apparatus (Fig. 2) was made in which E could be first thoroughly baked out, and then the chlorine from the other part of the apparatus could be admitted for measurement only after thorough drying.

The expansion bulb was baked out at 425° under high vacuum for four days. The mercury diffusion pump was operated only about three hours each day to evacuate the apparatus completely and the tap turned off to hold the vacuum. It was then sealed up with the diffusion pump operating.

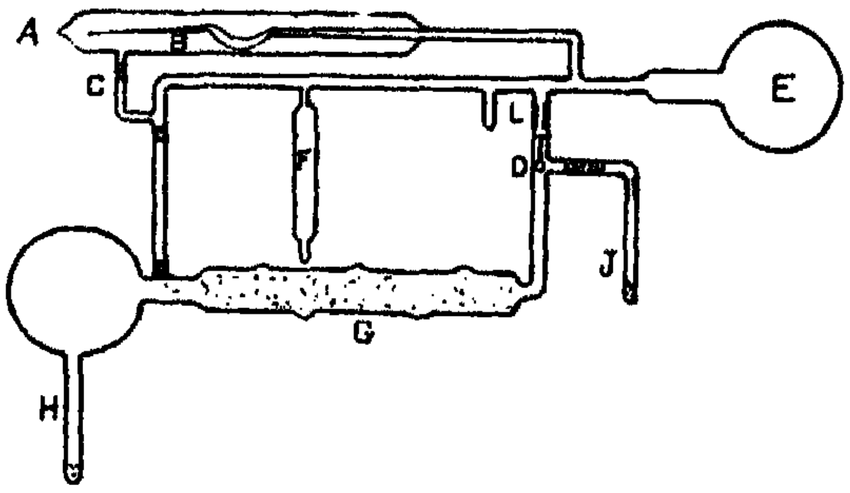

FIG. 2

Purified chlorine was admitted to the drying chamber where it was circulated over the phosphoric oxide by alternately condensing it with liquid air into H and J, which also contained a little phosphoric oxide. Drying was continued for 22 days, during which time the gas was circulated 20 times.

The dried gas was then condensed into H, the seal D was broken, the gas all condensed into F and the photoexpansion part sealed off at L. Since the drying section and the expansion section of the apparatus had been made the same volume, the pressure of chlorine is now atmospheric. A sampler tube F now showed perfect absorption by mercury.

On exposure to the arc light an increase of pressure corresponding to 15 mm of mercury was recorded. Again the expected decrease in expansion with drying did not occur.

It is difficult to explain the difference between these results and those of Shenstone. He prepared a very pure sample of chlorine electrolytically. His drying was carried out by a method not essentially different and he used as a manometer a thread of molten silver chloride which seems less satisfactory than an all-glass apparatus.

The Case for Bromine

Ludlam[16] and Lewis and Rideal[17] have studied the photoexpansion of bromine and find that a dry mixture of bromine and air does not expand in

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[16] Proc. Roy. Soc. Edin., **44**, 197 (1924).

[17] J. Chem. Soc., **1926**, 583.

light. Their experiments seem to be carefully done and those of Lewis and Rideal include quantitative measurements of the photoexpansion in which they find that, after drying with sulphuric acid, the expansion becomes less and after drying with phosphoric oxide it becomes zero. We had intended to repeat the above experiments with bromine replacing the chlorine and to withhold this paper on chlorine until the bromine had been studied; but a recent paper by Brown and Chapman[18] covers much the same ground as we had proposed to cover. They find that purified bromine dried for several days with phosphoric oxide, which had been freed from lower oxides, showed the same photoexpansion as ordinary somewhat moist and somewhat impure bromine. We are repeating the experiments on bromine with an apparatus of the type described above for chlorine.

Summary

The expansion of chlorine on exposure to light does not disappear nor is it greatly lessened on careful purification and drying of the gas. Nor has careful baking out of the walls of the insolation bulb before admission of the dried chlorine any effect on the photoexpansion.

Experiments reported here and in a previous paper show that dried chlorine at atmospheric pressure and at lower pressure shows no abnormal scattering nor any fluorescence which can be detected visually or photographically.

It is commonly assumed in papers on the theory of the photochemical reactions of chlorine that dry chlorine does not expand on insolation but that it reradiates the absorbed energy. The above experimental results are not in accord with these assumptions.

Chemical Laboratory, University of Toronto,
October 5, 1928.

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[18] J. Chem. Soc., 1928, 560.

NEW BOOKS

The Colloidal Salts. *By Harry B. Weiser. 21 × 15 cm; pp. xi + 404. New York: McGraw-Hill Book Co., 1928. Price: $5.00.* In the preface the author says: "Investigations on the colloidal character and applications of the inorganic salts are second in importance only to those on the hydrous oxides in the development of the modern theories of colloid chemistry. The present volume presents a critical summary of the colloidal behavior of the salts with particular reference to their role in the study of colloid chemical phenomena and to the theory underlying their technical applications." The subject is presented under the general headings: colloidal sulphides; colloidal sulphates; colloidal halides; colloidal ferrocyanides; colloidal silicates; miscellaneous colloidal salts.

"In determining the precipitation values of sols, a uniform procedure as regards stirring should be followed. Thus, if an arsenic trisulfide is shaken continuously, appreciable flocking will result in a given time with a concentration of electrolyte that will cause no flocking whatsoever without stirring. It has been observed repeatedly that the critical concentration of electrolytes does not cause agglomeration of the neutralized particles into a clump unless the mixture is shaken. What apparently happens is that the charge on the particles is reduced to the critical value but instead of agglomerating into a clump, the individual particles with their film of adsorbed water coalesce to a loose jelly structure that is readily broken up by stirring. If a concentration of electrolyte close to the critical value is used and the sol is allowed to stand quietly for a day or two, the surface of the precipitate as it settles appears to be a fairly strong, translucent, mobile film, strikingly similar in appearance to that of a copper ferrocyanide membrane." p. 36.

"Kruyt and van der Spek recognize the existence of two factors which determine change in precipitation value with dilution of sol: first, the smaller number of particles which will require the adsorption of *less* precipitating ion to lower the charge to the critical value; and second, the greater distance between the particles, which makes collision less probable, and so necessitates a greater reduction in particle charge by the adsorption of *more* of the precipitating ion. Since these two factors have opposite effects, it is only necessary to assume the predominating influence of one or the other to account for the results in a given case. Thus, for arsenic trisulfide Kruyt assumes the important factor to be the lessened chance of collision with potassium ion, and a decrease in the required amount to be adsorbed with barium and aluminum ions. If the decreased chance of collision were the only factor in preventing a weaker sol from coagulating in a given time in the presence of enough potassium chloride to coagulate a stronger sol, it would seem that complete coagulation of the weaker sol should result if sufficient time were allowed. As a matter of fact, however, enough potassium chloride to precipitate in 2 hours a sol containing 5 grams per liter will not precipitate a sol one-fourth as strong in several weeks. Other observations indicate that Kruyt attaches too much importance to the decreased chance of collision of particles on dilution of sol. Thus, the precipitation value varies almost directly with the concentration of sol for precipitating ions of high valence." p. 43.

"A satisfactory explanation of metallic conduction in compounds such as cupric sulfide is not available. Trümpler measured the potential of a number of solid conducting salts against a saturated solution containing the negative component of the salt in the free and ionic state. From the different behavior of metal-like and electrolytic conductors with respect to the influence of the negative component on the potential, a fundamental difference in internal structure is deduced. Thus it is assumed that in pure metallically conducting compounds, the space lattice points are occupied by atoms or molecules but not by ions; hence such compounds appear to be non-polar, in contra-distinction to electrolytic conductors. While this assumption may be true, it is not very helpful for it offers no explanation of the fact that metallic conductivity obtains with only a few salts. Moreover, it does not account for the very much greater metallic conductivity of cupric sulfide than other salts of the same kind. Since Bridgman has prepared a modification of phosphorus possessing metallic properties, it may be that a similar form of sulfur exists and that cupric sulfide is a compound of copper with this metallic form of sulfur," p. 69.

"In Becquerel's experiment, Freundlich points out that the two sides of the glass capillary will be oppositely charged by contact with the oxidising and reducing solutions on the two sides. Now, as already noted, copper sulfide is first formed in the capillary and this salt is a fairly good metallic conductor. Local currents will therefore be formed which flow in one direction through the capillaries and in the opposite direction through the copper sulfide as well. Just as in the case of electrostenolysis, an appreciable amount of metal can form on the cathodic portion of the capillary provided the conditions referred to above obtain," p. 71.

"Unlike cupric sulfide which is a pure metallic conductor, β-silver sulfide stable below 179° is a mixed conductor, about 80 percent of the current being carried by silver ions and 20 percent being conveyed as in a metallic conductor; the α modification, stable above 179°, is a pure electrolytic conductor," p. 76.

On p. 79 the author quotes the reviewer's explanation of the colors of colloidal metals. That was very polite of him; but unfortunately the reviewer was unquestionably wrong. All colloidal metals can be made to give the same colors and consequently the color in any given case depends on the size of the particles and not on the surface color.

The chapter on lithopone is extremely good and represents a real advance. The next chapter is on ore flotation because this "depends on the property of finely divided particles of the sulfides to concentrate preferentially at an interface," p. 137.

"In the preparation of the sulfide phosphors, relatively large crystals are formed by fusing the amorphous or submicroscopically crystalline mixture of sulfides, usually in the presence of a flux. The minute amount of heavy metal impurity is generally assumed to form a solid solution with the zinc or alkaline earth sulfide, which connotes a more or less uniform distribution of the impurity throughout the entire mass of the phosphor. Since the heavy metal sulfide possesses a crystal lattice different from that of the basic sulfide, it is probable that the crystals of the latter, which grow slowly during the ignition process, will be quite pure, most of the heavy metal impurity being adsorbed at the surface. On account of the very low concentration of heavy metal impurity, the latter will not be distributed over the entire surface but at points or "centers," as it were. From this point of view, a center in a zinc sulfide phosphor, for example, is a point on the lattice of a zinc sulfide crystal where a molecule or a minute crystal of copper sulfide is adsorbed. Since the lattices are different, there is a condition of strain at the interface which makes it easier for light to displace certain electrons. This condition of strain is augmented by distorting the lattice of the zinc sulfide by rapid cooling of the ignited substance. This concept of a center of phosphorescence accounts for a number of facts without the necessity of resorting to improbable assumptions," p. 170.

"When one considers that the luminescence bands are due entirely to the copper sulfide and that 9 copper sulfide molecules per million of zinc sulfide are sufficient, it seems altogether improbable that the few molecules of copper sulfide on the surface would account for the quantity of light emitted, assuming that the copper sulfide is dissolved, that is, distributed uniformly throughout the mass. On the other hand, if minute crystals of copper sulfide are adsorbed at points on the surface, which are not large for a given mass because of the size of the crystals, it is more easy to understand how such a small amount of active impurity can be so effective," p. 171.

"It is of interest that calcium sulfate gel played an important role in biology until comparatively recently. Mud dredged from the ocean and preserved in alcohol was found to contain a gelatinous substance which was believed to exist in great masses in the depths of the ocean and to consist of undifferentiated protoplasm. Regarding it as an organism which represented the simplest form of life, Huxley, in 1868, named it *Bathybius* (βαθὺς deep, βιος life). About 30 years ago Mobius showed that this Bathybius was nothing more or less than calcium sulfate gel precipitated by alcohol added to the muddy sea water," p. 202.

The author accepts the reviewer's distinction between an ultra-filter and a semipermeable membrane," p. 274.

"No ferrocyanide ion diffused through a certain ferrocyanide membrane into an isotonic sugar solution when the concentration was below 1.0 normal, and slightly alkaline water only was forced through a copper ferrocyanide ultrafilter from dilute solutions of potassium ferrocyanide. The explanation of this behavior is that copper ferrocyanide gel always contains adsorbed alkali ferrocyanide which is retained so tenaciously that the adsorption from moderately concentrated solutions may be regarded as almost irreversible. It is, therefore, strong negative adsorption by the adsorption complex which prevents the passage of both sugar and ferrocyanide ion through the membrane. As ordinarily prepared, one side at least of a copper ferrocyanide membrane is practically saturated with potassium ferrocyanide so that the positive adsorption is negligible from dilute solutions of the salt. The permeability of the membrane to relatively high concentrations of ferrocyanide ion is due to two facts: (1) the adsorption of ferrocyanide ion is not completely irreversible from strong solutions of potassium ferrocyanide and (2) the colloidal film is partially coagulated by the salt, opening up cracks at weak points in the membrane. The permeability of the membrane for a series of ions is in the order: chloride > sulfate > ferrocyanide, which is the reverse of the order of adsorption by the gel," p. 283.

The reviewer had not realized that Schwarz and Brenner had made out so good a case for the slow formation of a definite crystalline compound of alumina and silica in the wet way, p. 352. The author accepts, p. 354, the theory of plasticity outlined by Jenks in his Cornell thesis (1927).

When a new edition of this book becomes necessary, the reviewer hopes that Fig. 7 will be made smaller, so that it will go cross-wise on the page.

Wilder D. Bancroft.

The Physics of Crystals. *By Abram F. Joffé. 23 × 16 cm; pp. xi + 198. New York and London: McGraw-Hill Book Company, 1928. Price: $3.00.* This book contains the lectures given at the University of California in 1927. The titles of the lectures are: electrical theory of crystal lattices; equilibrium in a crystal lattice; the elastic after-effect; the elastic limit; the mechanism of plastic deformation; strength; conduction of electricity through crystals; the specific conductivity; electrolysis of crystals; dissociation in quartz; condensed polarization charge in calcite; electronic conductivity; photoelectric effect of dielectrics; the problem of dielectric losses; breakdown of dielectrics by heat; breakdown by ionization; the highest electric field.

"We believe that the unit of a crystal lattice is a system of electric charges and that no forces are to be expected other than electric and magnetic fields. We might see in a crystal a regular arrangement of smaller units than atoms, to wit, of positive nuclei and negative electrons. We must look for the minimum of energy of the whole system. The dimensions of the electrons and the nucleus are small relative to the distances between them. No more than the 10^{-15} part of the space is occupied by these elements. The crystal, from this standpoint, is an empty space with small charged particles distributed at enormous distances from each other. We believe that the quantum conditions inside the atoms are responsible for the dimensions of the electronic orbits and thus for the uneconomical disposition of space," p. 1.

"Contrary to the elastic after-effect and elastic fatigue, the plastic deformation may be observed, however, in a single crystal such as rock salt, gypsum, zinc, aluminum, etc. The effect is readily perceived when a crystal of rock salt is heated to about 600°C. and bent or twisted. The plasticity of salt at this temperature reminds one of wax. Still the bent or twisted crystal remains transparent and seems to form a unit, holding together as firmly as the normal crystal. When released, however, it fails to return to the original form and remains curved. A curved crystal lattice maintained without external forces obviously contradicts the idea of a lattice consisting of an arrangement corresponding to a minimum of potential energy. We may remark, of course, that a curved external shape is not necessarily bound to a curved internal lattice, since, for instance, we may cut from a normal single crystal a piece of any desirable shape without influencing the internal structure," p. 35.

"The stress at which the first change in the X-ray picture appears corresponds to some irreversible destruction of the lattice and may be called the destruction limit. Further investigation has shown that the first irreversible slip does not always occur immediately after the limit is reached, and the following slips are separated by time intervals. The measured limit is, therefore, to some extent dependent on the velocity of loading. This error, however, becomes less and less as we go to higher temperatures. Even at room temperature this error may be reduced to 1 per cent for rock salt.

"The existence of a definite limit has often been doubted. Experience with metals and glasses led to the opinion that everything flows more or less slowly. On this basis, a definite limit was considered unlikely. It is, of course, impossible to assert that a body does not flow unless the term 'flow' is limited by some minimum velocity. But we can state that at 500°C. not the slightest change in the X-ray picture could be observed after 24 hours if the load is 2 per cent below the measured limit and that at a load exceeding the limit by 2 per cent the change may be noticed within one second. This means physically that the limit has a definite physical value, even if the practically measured value exceeds the theoretical limit corresponding to an indefinitely long time.

"We further ascertained that the phenomenon depended on internal stresses and not on the size of the crystal. We chose crystals of the same crystallographic orientation but of different ratios of the cross-section to the perimeter. The limit measured at four temperatures between 20 and 600°C. was always proportional to the cross-sectional areas and independent of the perimeter. The limit was also the same for compression and tension. Rock-salt crystals of different origin, and consequently with different impurities, and with a surface treated in different ways—for instance, dissolved in water, polished, cleft, etc.—have all the same limit within 2 per cent. We may conclude, therefore, that the destruction limit measured by X-rays has a definite physical significance," p. 38.

"The coincidence of the melting point with the point where the destruction limit becomes zero may be supposed to have a physical significance, if we assume that the mechanism of fusion is equivalent to the same kind of destruction that is responsible for the limit at lower temperatures. When the slightest shear suffices to produce a destruction, the existence of a lattice becomes impossible and the heat absorbed by the crystal is applied to bring the atoms into a new form of equilibrium. Possibly this may explain why we do not know any example of superheated crystals while all other limits may as a rule be exceeded," p. 40.

"The destruction limit, as measured by the X-ray method gives the stress which produces an irreversible change in the structure of a crystal. The crystal becomes pulverized and the small fragments slip and turn in a quite irregular manner, while they continue to adhere to each other. The process of plasticity does not affect the transparency of the crystal; consequently there are no holes of the dimensions of a wave length of light or more produced in the destruction. Furthermore, the cohesion does not drop in value in a crystal so destroyed but, on the contrary, the rupture of a plastically deformed crystal requires a higher tension than for a single crystal. Thus, we must conclude that the separation involved in the plastic destruction does not exceed in magnitude the atomic distances. These conditions combined with the conditions for slip which is confined to one of the planes (110) only, and is limited to the direction of the shear, limit the irregularity of the arrangement of the fragments possible. The product of a plastic deformation after a compression or a tension is not like a compressed powder, but reminds one rather of a fibrous structure with a definite axis or a definite plane of symmetry. A complete recovery after such a destruction cannot be produced by an opposite deformation. The process involved in plasticity is irreversible, not only in the sense that the exerted work is transformed into heat, but also in the sense that, even by applying work in the opposite direction, we are unable to restore the initial state," p. 44.

"The tensile strength of single crystals is about five hundred times less than the calculated maximum for the cohesive forces and rupture occurs before an essential deviation from Hooke's law can be noticed. Even the strength of plastically deformed crystals is forty times less than we should expect. If the electric theory is not wrong in its fundamental assumptions, such a discrepancy should not exist. It is possible, however, that the usual phenomenon of rupture by tension has nothing to do with the true cohesive force. We can easily see that a *tearing* rupture would require a much lower force than a simultaneous rupture across the whole cross-section," p. 59.

"We were able to test Ohm's law in crystals in regard to the relation between the current and the applied potential difference up to fields producing breakdown. Ohm's law was thus checked for calcite, glass, and mica from a field of 0.1 volt per centimeter up to 5×10^6 volts per centimeter. Applying potentials increasing in an arithmetical progression for 0.1 sec. each, with time intervals of a few seconds between, we measured the corresponding currents by a string electrometer. These were photographed on a moving film and it was found that Ohm's law held for fields as high as 5×10^4 volts per centimeter, if properly applied," p. 79.

"We can thus state as a definite result of the measurements that (1) *the data of the last column of the table represent the true specific conductivity of electrically pure ammonium alum crystals at the corresponding temperatures.*

"Analogous experiments were repeated with copper sulfate, sodium nitrate, potassium nitrate, and sodium chloride with the same result. A successive crystallization always leads to standard values of conductivity which are less than the conductivity of the original crystals. The following conclusions in addition to (1) may be drawn from these standard conductivities.

2. The water of crystallization (12 molecules in ammonium alum and 5 molecules in $CuSO_4$) has no influence on the conductivity. As a matter of fact, those crystals are as good insulators as the crystals of $NaNO_3$ which crystallize without water," p. 84.

"While all phenomena so far considered have been due either to ions of the crystal lattice or to ions of some contaminating substance, we shall now take up the phenomena which are due to the electrons liberated in the lattice of a dielectric crystal. In 1903, I happened to find the first instance of the electronic type of conductivity in such crystals, while studying the influence of Röntgen rays upon the conductivity of various crystals. While the conductivity of quartz, calcite, and many other crystals increased distinctly under the unfluence of X-rays, the measurements on rock salt yielded utterly irregular and inconsistent results until I noticed that clouds covering the sun caused a diminution in the conductivity, in spite of the fact that the attempt to find an effect due to visible light on natural rock salt had failed completely. Rock salt first exposed to X-rays or radium rays, however, was found to become sensitive to visible light to such an extent as occasionally to increase the conductivity about 10^4 times the conductivity in dark. Rock salt thus sensitized to light by treatment with X-rays furthermore takes on a yellow-brown color indicating an absorption in the visible spectrum. This increase in conductivity by light will be shown to be due to electronic carriers," p. 127.

"Siedentopf was able to observe ultramicroscopic sodium particles both in the blue-colored rock salt produced by reduction at high temperature in hydrogen, and the natural blue rock salt. Although the brown crystals do not show particles of even ultramicroscopic size the analogy in the behavior leads one to suppose that neutral sodium atoms are also present in a still finer state of subdivision. The color is not due to any contamination, as it may be produced in the chemically purest crystals. It is brown for rock salt and violet for potassium chloride.

"The influence of light may be explained by the well-known photoelectric properties of sodium and potassium. While a free surface of sodium in vacuum possesses a photoelectric wave length limit of about 5000Å., the limit must be still lower for sodium particles in a medium of the dielectric constant 5.6 corresponding to rock salt. Thus, photo-electrons must be liberated by visible light from such atoms in the crystal treated by X-rays, and the electrons carry the electric current if they are mobile in the crystal lattice.

"In fact we have evidence that the conductivity of the illuminated rock salt is due to electrons in contradistinction to the ionic conductivity of the normal crystals. While the ionic conductivity decreases at low temperatures and becomes too small to measure for most dielectrics and especially for rock salt at liquid air temperatures, the conductivity produced by light is practically unchanged by a cooling to the liquid air temperature. It is thus more convenient to work at liquid-air temperatures as the normal dark conductivity of rock salt vanishes at those temperatures and the only current observed is that due to light," p. 129.

Wilder D. Bancroft

The Discovery of the Rare Gases. *By Morris W. Travers. pp. vii + 128. London: Edward Arnold and Co., 1928. Price: 15 shillings.* "Early last year Lady Ramsay and her daughter asked me to arrange Sir William Ramsay's scientific papers, which had not been touched since his death in 1916. Among the papers was a complete series of laboratory notebooks, most of which contained little more than numerical data, with the briefest of descriptive notes. However, with the commencement of the work which led to the discovery of argon, the notebooks took on an entirely different character; experiments were described in detail, and were illustrated by accurate and vigorous drawings, made as the work proceeded. It seemed as if Ramsay had suddenly become aware of the historic importance of his work." 13

"It was at first my intention to annotate the notebooks, and then to draw up a summary of the contents, such as would enable the future historian of the chemistry of our times to make full use of them. Gradually my notes expanded, and, in the form of a manuscript volume, illustrated by photostatic reproductions from the notebooks themselves, it came into the hands of friends and colleagues, who insisted that the work should be published."

The above quotation from the author's preface gives the *raison d'être* for the publication of his book. The discovery of the rare gases was an event, or rather a series of events, which aroused the greatest enthusiasm among chemists and others at the time, although sceptics were not wanting. It is difficult for present-day students to visualise the conditions which then existed, although the time is not so very far back; and it is a matter of congratulation that Dr. Travers, who was so intimately concerned in the discoveries of Ramsay, was entrusted with the task—rather was it the pleasure—of telling the story of those days in a manner which was made possible only by his access to the original notebooks, and by his personal recollections. Controversial matters are handled very discreetly and sympathetically.

Some personal touches which have no direct connection with the subject are retained, since the work was not primarily intended for publication. They serve in many cases, however, to illuminate not only the personality of the author, but also that of Ramsay.

It may be mentioned that there are several facsimile reproductions of Ramsay's own sketches of apparatus used, and also of pages of his note books.

The book should find a wide circulation, and for this reason it is to be regretted that more care was not taken in the proof reading. Misprints occur, the worst of them being the head of chapter X as "May and June, 1908; the date should have been 1898. At times the English of the author is capable of improvements, as may be instanced by the following sentence: "The chamber for the gas A, into which projects through a rubber stopper a piece of unglazed tobacco pipe stem sealed at the lower end in the oxyhydrogen blowpipe, connects through a rubber tube L with the mercury reservoir I, through a cock E with a syphon, by means of which gas, stored over mercury in the tube K, and communicating with the Töpler pump F, direct through the cock D, and through the porous pipe stem by the cock C."

T. Slater Price

Atomic Structures as modified by Oxidation and Reduction. *By William C. Reynolds. 23 × 14 cm; pp. vi + 128. London: Longmans, Green and Co. Price: 7 shillings, 6 pence.* To those who like unorthodox views this book can be thoroughly recommended. The author accepts "the Rutherford atom with its central positive charge, surrounded by extranuclear electrons in number equal to the figure indicated by Moseley's rule"; but he says that "electrons moving in planetary fashion around central nuclei, or in Cassinian 1 curves about two, have yet to testify chemical consideration." Most of them, according to him, rotate in pairs or quartets about a few symmetrically placed centres outside the nucleus and they follow spiral paths round their orbits. Electrons are divided into three classes, Valence electrons, Potential Valence electrons and those in Radial quartets or pairs, the maximum number of potential valence electrons ever found in an atom being six and of valence electrons seven. Potential valence electrons can become valence electrons and vice-versa, while radial pairs can split up into a valence and a potential valence. Oxidation and Reduction, to which especial importance is attached, and chemical reaction generally are considered in such terms and electronic structures, which the author deems satisfactory, are attributed to all the elements, free use of assertion and assumption being made. Besides dealing with the constitution of matter the author also discusses that of the electron, the proton and the ether, the last chapter of 26 pages being devoted to this theme.

H. Bassett

Handbuch der biologischen Arbeitsmethoden. *By Emil Abderhalden. Section I. Chemical Methods, Part 2, Second Half, No. 2. 25 × 18 cm; pp. 1339-1908. Berlin: Urban and Schwarzenberg, 1928. Price: 32 marks.* This volume is written by Franz Bachér of Rostock and deals with "Chemical Reactions of Organic Compounds in Ultraviolet Light and in Sunlight." The book is divided into a general and a special part. In the first the sub-heads are: photochemical reactions; the experimental set-up for investigations with short wave-lengths; and reacting mixture; the working up of the reaction products. In the special part the author discusses the photochemical behavior of hydrocarbons, alcohols, ethers, aldehydes, ketones, quinones. carbohydrates, acids, derivatives of the acids; acid nitriles; amino-compounds; substances with nitrogen in the ring, including the alkaloids; nitro-compounds; nitroso-compounds; azoxybenzenes; halogen compounds; sulphur compounds; phosphorus compounds; chlorophyll; unsaturated compounds; oximes. There are also a few remarks on photochemical changes of dyes.

The book is invaluable as a collection of facts and will be used as a starting point by everybody who is interested in this subject. Unfortunately it is nothing but a compilation of data. The author does not know at all why light acts as it does in any given case and apparently does not care. It seems almost incredible that anybody could have worked up this enormous mass of data without asking himself the why and wherefore of the reactions which he records.

Wilder D. Bancroft

Calculations in Physical Chemistry. *By J. R Partington and S. K. Tweedy. 18 × 12 cm; pp. viii + 152. London: Blackie and Son, Ltd. Price: 7 shillings, 6 pence.* Of the value of problem work for students of physical chemistry there can be no doubt, and from this point of view the present volume will be found extremely helpful. The ground covered is indicated by the headings of the chapters:—Thermodynamics, Characteristic Equations, Liquids and Solutions, Equilibrium, Electrochemistry, Nernst's Heat Theorem. In each chapter, or in each section of a chapter, a number of problems are proposed for solution, while at the end of the volume a hundred miscellaneous exercises are added. At the beginning of each section there is a reasonable amount of theoretical introduction, and the question of units, which presents difficulties to many students, is expounded at appropriate points. In this connection it may be pointed out that the pressure of 10^6 dynes/cm.^{2} which the authors term a 'megabar', is called a 'bar' by the International Meteorological Committee. The volume can be warmly recommended to students of physical chemistry.

James C. Philip

THE POTENTIAL OF THE NICKEL ELECTRODE*

BY M. M. HARING AND E. G. VANDEN BOSCHE**

1. Introduction

That a careful revision of the standard potential of the nickel electrode is highly desirable will be evident from the following considerations.

Nickel is one of the most important metals from the standpoint of the electroplating and electroforming industries. Therefore the need for an accurate value of its electrode potential requires no comment. However, a review of the literature furnishes a multiplicity of values for the normal potential[1] of this element ranging from −0.138 to −0.621 volts[2] calculated to the standard hydrogen electrode as zero.[3]

Most of these values are based on work involving no special precautions, such as temperature control, purity of materials, oxygen-free conditions, etc. Futhermore, in practically every case, the solutions used were 1.0 N., i.e., relatively concentrated, solutions of nickel salts, and the values reported for the electrode potential, so far as can be ascertained, were those actually measured in these 1.0 N solutions.

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* Part of a thesis submitted by E. G. Vanden Bosche in partial fulfillment of the requirements for the degrees of doctor of philosophy in the graduate school of the University of Maryland.

** Contribution from the Dohme Laboratory of Physical Chemistry of the University of Maryland.

[1] By normal potential we shall be understood to mean the electrode potential when the solution bathing the electrode contains one gram equivalent of the ion in question per liter of solution.

[2] Throughout this paper the sign of the electrode potential will be governed by the convention adopted by the Bunsen Gesellschaft, the American Electrochemical Society and the U. S. Bureau of Standards. That is, if we write the element Me/Me^+ and the electrons tend to pass through the junction from right to left, the sign is negative.

[3] Throughout this paper, unless otherwise specified, all electrode potential values will be based on the standard hydrogen electrode as zero. A standard electrode potential is defined as the potential developed by an electrode in a solution containing the ion in question at unit activity.

We wish to take this occasion to protest against the careless and prevalent misuse of the terms standard electrode potential and normal electrode potential. The following examples, culled at random from well known works of very recent date, will illustrate the existing confusion of thought in the matter.

"Thus we shall define the normal electrode potential as that obtaining *when the activities of the reacting substances are unity.*"

"*When the concentration of the ions is molal,* the potential of any reversible electrode is called . . . the normal electrode potential."

"The normal electrode potential of a metal is the potential against a solution *normal in respect to the metal ion.*"

"The difference of potential at a reversible electrode, *when the concentration of the ions of the electrolyte is molar,* is known as the normal electrode potential."

To avoid this confusion we have explicitly defined the two terms mentioned. We believe the term "normal" used in connection with solutions, should invariably signify gram equivalents per liter of solution.

Based on the *standard* hydrogen electrode the *normal* calomel electrode has been taken as having the value + 0.2822 volts at 25°. (Lewis and Randall: "Thermodynamics," page 407.) This value has been used in reducing the literature values to the hydrogen basis.

Gerke,[1] in his critical review of the standard potentials of the elements, evidently does not consider the accepted value of nickel to have sufficient accuracy for inclusion in his tabulation, for it does not appear. Finally, some recent work by H. E. Haring[2] seems to indicate that the true electrode potential of nickel is somewhat more negative than the value of −0.198 volts accepted at present.

2. Review of Literature

Neumann[3] used a nickel amalgam electrode. This was prepared by plating nickel from a nickel chloride-boric acid solution, rubbing with mercury, plating again, and so on until a thick amalgam was obtained. His values were:

1.0 N $NiSO_4$	−0.256 volt
1.0 N $NiCl_2$	−0.258 volt
1.0 N $Ni(NO_3)_2$	−0.218 volt

Küster[4] studied the electrolytic separation of iron and nickel from solutions of their sulphates. He found that nickel began to be deposited from neutral 1.0 N nickel sulphate solution at −0.521 volt. He believed this to be the true electrode potential of nickel.

Siemens[5] used a nickel electrode polarized alternately, anodically and cathodically. He found the value −0.222 volt.

Euler[6] pointed out that roughened nickel gave more nearly reproducible values than smooth nickel. He etched Kahlbaum's nickel with sulphuric acid and electrolyzed a 1.0 N solution of nickel sulphate at a low current density, using the etched nickel alternately as the anode and cathode. After this treatment, the electrode was allowed to stand for a few days before making measurements. With 1.0 N nickel sulphate solution he obtained the value −0.184 volt and with 0.2 N nickel sulphate solution −0.190 volt. Assuming 1.0 N nickel sulphate solution to be 0.11 N in nickel ions, he calculated the normal potential of nickel to be −0.178 volt. Using Mond nickel, he found the normal potential to be −0.184 volt. Euler pointed to the desirability of excluding air in such measurements but took no special precautions in this respect himself. He makes no mention of having worked at a controlled acidity.

Muthmann and Fraunberger[7] believed the true potential of nickel to be obtainable only in the absence of all passivizing influences. To realize this condition, they polarized their nickel with hydrogen in distilled water. Then the polarized electrode was rapidly transferred to a 1.0 N nickel sulphate solution for measurement. They found the value −0.601 volts.

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[1] Chem. Rev., **1**, 377 (1925).

[2] Trans. Am. Electrochem. Soc., **46**, 209 (1924).

[3] Z. physik. Chem., **14**, 215 (1894).

[4] Z. Electrochemie, **7**, 257 (1900).

[5] Z. anorg. Chem., **41**, 249 (1904).

[6] Z. anorg. Chem., **41**, 93 (1904).

[7] Sitzungsber. Bayr. Akad. Wiss., **34**, 201.

Schweitzer,[1] using as electrodes pure powdered nickel and nickel sheet in 1.0 N nickel sulphate solutions, and working in an atmosphere of hydrogen, found potentials of −0.331 and −0.308 volt respectively. With a powdered nickel electrode and a 1.0 N solution of nickel chloride, he obtained −0.314 volt.

Pfanhauser[2] found the value −0.237 volt, using a 1.0 N nickel sulphate solution.

Schoch[3] made quite a comprehensive study of the electrode potential of nickel, and his value of −0.198 volt has been accepted rather generally up to the present time. He worked in vacuo and also in an atmosphere of nitrogen so as to remove the influence of oxygen and other gases. The electrodes used were commercial sheet nickel, Kahlbaum's electrolytic nickel, an electrolytic nickel of his own preparation, and powdered nickel (made by heating Kahlbaum's nickel nitrate, followed by reduction with hydrogen). The electrolyte was a solution of 1.0 N nickel sulphate. The powdered nickel, which must have contained some adsorbed hydrogen, gave a potential of −0.308 volt after standing 36 hours. On subsequent boiling out to remove this hydrogen, the potential became −0.240 volt. The interpretation of this experiment is complicated by the fact that nickel, reduced from its oxide by hydrogen, is strongly pyrophoric. Such nickel nearly always contains a little oxide. With the other electrodes, Schoch obtained values ranging from −0.183 to −0.205 volt. Spongy electrolytic nickel showed −0.238 volt even after standing. To show the effect of hydrogen on the potential of nickel, he boiled a piece of sheet nickel in concentrated NaOH solution and then placed it in concentrated HCl for the same length of time. The electrode was then carefully rinsed in distilled water and placed in the 1.0 N nickel sulphate solution for measurement. A value of −0.593 volt was obtained. Nickel sheet, over which hydrogen was bubbled while immersed in 1.0 N nickel sulphate solution, gave a value of −0.338 volt. On boiling out and standing for three weeks, this value dropped to −0.198 volt. Schoch therefore concluded that −0.198 volt was the true reversible potential of nickel. Nickel in contact with 1.0 N nickel chloride solution, gave the value −0.138 volt.

Smits and de Bruyn,[4] on the basis of the theory of electromotive equilibrium developed by Smits[5]; came to the conclusion that when the potential of nickel is measured in an acid solution, in an atmosphere of hydrogen, the result should be dependent on the hydrogen ion concentration of the solution and should be equal to the potential of a hydrogen electrode in the same solution. They measured the potentials of nickel and hydrogen electrodes in a solution saturated with hydrogen, and found that the potentials of both electrodes became constant at —0.640 volt. Later they measured the

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[1] Z. Elektrochemie, 15, 607 (1909).

[2] Z. Elektrochemie, 7, 698 (1901).

[3] Am. Chem. J., 41, 208 (1909).

[4] Proc. Acad. Sci. Amsterdam, 20, 394 (1918).

[5] "Theory of Allotropy," p. 325.

potential of a nickel wire in a 1.0 N nickel sulphate solution (oxygen and hydrogen having been removed by evacuation and boiling) and found the value −0.198 volt, in agreement with that of Schoch. The present study has shown that nickel of this form, even with careful evacuation and boiling, becomes coated, after standing a short while, with what is apparently a black oxide. It is not at all inprobable that the potential obtained by both Schoch and by Smits and de Bruyn may have been affected by this oxide.

Thompson and Sage,[1] using spongy nickel made by electrolyzing 0.5 N nickel chloride solution at 90°, obtained the value −0.390 volt with neutral molal nickel sulphate as the electrolyte. Spongy nickel, made by electrolyzing at 20° a solution consisting of 60 grams, $NiSO_4.6H_2O$, 20 grams, $(NH_4)_2SO_4$ and 40 cc. concentrated NH_4OH per liter, showed a potential of −0.295 volt against the same electrolyte as that used in the first experiment. No special precautions were taken to remove air or hydrogen.

Very recently Murata[2] published his work on the electrode potential of nickel. He reduced NiO (made from purified $Ni(NO_3)_2$) with hydrogen at 300° in the electrode vessel itself. The latter was then filled with 0.05 or 0.005 M nickel sulphate solution in an atmosphere of hydrogen. This solution had been freed of air previously by prolonged passage of hydrogen through it. The reference electrode was a 0.1 N calomel electrode with saturated KCl salt bridge. Four cells were studied, two each at the two different concentrations. The potentials measured were fairly constant and reproducible over a period of 60 hours. Measurements were made at 18° and 25°. E_0 at 18° was found to be −0.249 volt and at 25° −0.248 volt ±0.002 volt (based on individual ion activities) or −0.251 and −0.250 volt (based on ion concentrations from conductivity measurements). Murata claims to have shown (details in a paper to appear shortly) that hydrogen has no effect on the potential of nickel.

In connection with this work, the following comments seem justified. Such reduced nickel must have contained a great deal of adsorbed hydrogen. The experience of other investigators, as well as our own, points to the marked influence of hydrogen on the electrode potential of nickel. Nickel powder produced by this method is very active catalytically. There is at least a reasonable doubt that such active nickel may not represent the most stable form. A liquid potential was present in the cells studied. Although a KCl salt bridge reduces this, it does not remove it.[3]

No attempt was made to correct for this potential. Only two cells were studied at each concentration of electrolyte. This was certainly too small a number on which to base a claim of reproducibility. Finally, the activity coefficients used were those of individual ions. Our present knowledge of these values scarcely warrants their use in the calculation of precise potentials.

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[1] J. Am. Chem. Soc., 30, 714 (1908).

[2] Bull. Chem. Soc., Japan, 3, 57 (1928).

[3] Lewis and Randall: "Thermodynamics," page 399.

The literature reveals many other conflicting values and opinions. Thus Bonsdorff[1] states his inability to obtain a reproducible electrode. Coffetti and Foerster[2] found that nickel was deposited from a 1.0 N nickel sulphate solution at a cathode potential of −0.621 volt. They incline to the value found by Muthmann and Fraunberger (loc. cit.)

Schildbach,[3] while working on the potential of cobalt, assumed the potential of nickel to be −0.198 volt. Glasstone,[4] working on the overvoltages found in electrodepositing iron, nickel and cobalt from solutions of controlled acidity on a copper cathode at 15° concluded that nickel began to be deposited at a cathode potential of about −0.288 volt, and that this was nearly independent of the hydrogen ion concentration.

For convenience the values discussed above are collected in Table I. Unless otherwise specified, the electrolyte is understood to be $NiSO_4$, the electrode non-polarized and the temperature that of the room.

TABLE I

Investigator	"Normal" potential	Comments
Neumann	−0.256 volts	
"	−0.258 "	$NiCl_2$ solution
"	−0.218 "	$Ni(NO_3)_2$ "
Küster	−0.521 "	Electrolysis measurements
Siemens	−0.222 "	
Euler	−0.178 "	
"	−0.184 "	
Muthmann and Fraunberger	−0.601 "	Electrode polarized cathodically
Schweitzer	−0.331 "	
"	−0.308 "	
"	−0.314 "	$NiCl_2$ solution
Pfanhauser	−0.237 "	
Schoch	−0.198 "	
"	−0.138 "	$NiCl_2$ solution
Smits and de Bruyn	−0.198 "	
Thompson and Sage	−0.390 "	
" " "	−0.295 "	
Coffetti and Foerster	−0.621 "	Electrolysis measurements
Glasstone	−0.288 "	at 15°
Murata	−0.250 "	at 25°
"	−0.251 "	at 18°

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[1] Akad. Abhandl. Helsingfors, S 17 (1904).

[2] Ber., 38, 2934 (1905).

[3] Z. Elektrochemie, 16, 977 (1910).

[4] J. Chem. Soc., 1926, 2887.

In comparing the values given above, one should keep in mind the following factors. Few of the values given in the literature have been calculated on the basis of a solution 1.0 N in nickel ions. Assuming 1.0 N nickel sulphate to be ionized to the extent of 31% (as are other salts of this type) the values given for potentials obtained in 1.0 N nickel sulphate solutions should be about 0.015 volt more positive. As a matter of fact, neither the activity nor the ion concentration (determined from conductivity measurements) being accurately known for such concentrated solutions, it is not really worth while to make the calculation mentioned. Liquid junction potentials, ignored in much of the work quoted, add their item of uncertainty. Nickel is a very stiff metal and therefore measurements made on any but finely divided nickel are apt to be affected by errors due to strain. Oxygen very certainly produces results that are too positive. Hydrogen, just as certainly, produces results that are too negative. In few cases were adequate precautions taken to insure absence of these gases. Finally, since nickel can displace hydrogen from an acid by immersion, any free acid in the electrolyte will tend to vitiate the results of the potential measurements.

3. Theoretical Discussion

The cell used in this research

$$Ni \mid NiSO_{4(x\ \text{molal})} \mid Hg_2SO_4 \mid Hg$$

involves no liquid junction. When it operates to produce two faradays of electricity, the reaction occurring is

$$Ni + Hg_2SO_4 \rightleftarrows NiSO_4 + 2\ Hg.$$

The equation connecting the E.M.F. of the cell with the activities of its components is

$$E = E_0 - \frac{RT}{2F} \ln \frac{a_{NiSO_4}\, a^2_{Hg}}{a_{Ni}\, a_{Hg_2SO_4}} \tag{1}$$

Nickel, mercurous sulphate, and mercury, being in their standard states (i.e., solid, solid and liquid respectively at 25°C and under one atmosphere pressure) are at unit activity. Consequently equation (1) simplifies to

$$E = E_0 - \frac{RT}{2F} \ln a_{NiSO_4} \tag{2}$$

But by convention $a_{NiSO_4} = a_{Ni''}\, a_{SO_4''}$ and $a_{\pm} = \gamma m$.

Hence equation (2) becomes

$$E = E_0 - \frac{RT}{2F} \ln (\gamma m)^2, \tag{3}$$

Which at 25°C and for Briggs logarithms simplifies to

$$E = E_0\ 0.05912 \log \gamma m. \tag{4}$$

By the use of equation (4), the measured E.M.Fs. can be calculated to E_0 for the cell. Combining E_0 for the cell with the E_0 value for the reference electrode gives at once E_0 for the nickel electrode.

There appeared to be a possibility that the accepted value for the potential of nickel might be low due to the presence in the electrolytes used of ions of metals more positive than nickel, e.g. copper. Nickel would displace a more positive metal from solution by immersion and, if the displaced metal coated over the nickel electrode in a layer even one molecule thick, would tend to show a potential more positive than its standard value. If the coat were impervious (a very extreme and improbable case) the potential exhibited would be that of the coating metal against its own ions. To investigate this possibility, it was decided to attempt the removal of such impurities by fractional electrolysis. It should be possible to do this by electrolyzing at a cathode voltage equal to the static potential of nickel, (i. e. the voltage exhibited by a nickel electrode against the solution in question when no current is flowing.). However, nickel is more negative than hydrogen, and so hydrogen will be discharged in the process, although probably at a pressure less than one atmosphere. This would reduce the efficiency of electrolysis with respect to the impurities in question. To improve this efficiency, hydrogen, at a pressure of one atmosphere, might be bubbled over the electrode (which should be of platinized platinum), thereby making it more difficult for hydrogen ions to be discharged. The use of a cathode of a metal having a high hydrogen overvoltage, e.g. mercury, should likewise improve the efficiency of purification. Mechanical difficulties with the latter method of purification made it desirable to try the first method of purification.

4. Experimental Details

a. Preparation of Materials.

Water. This was the best product of a Barnstead still. It had a pH of about 6.9.

Nickel sulphate. A considerable quantity of high-grade nickel sulphate was thrice recrystallized at room temperature. The product was redissolved to make a 2.0 N solution and shaken with $Ni(OH)_2$ for a day. By this means the pH of the solution was automatically adjusted at 6.8. From the clear supernatant liquid, the more dilute solutions used in this work were prepared.

A 2.0 N nickel sulphate solution, made from that just discussed, was electrolyzed for 200 hours at a cathode voltage equal to the static potential of nickel in the solution named. The cathode was of platinized platinum and was kept saturated with hydrogen.

Nickel sulphate was also prepared by the electrolysis of dilute sulphuric acid, using an anode of Mond nickel and a cathode of platinum foil. The salt so obtained was further purified by recrystallization, then made up to a 2.0 N solution and shaken with $Ni(OH)_2$ as described.

Nickel hydroxide. A solution of the recrystallized $NiSO_4$ was treated with a dilute NaOH solution until precipitation was complete. The precipitate was washed by decantation until the washings were neutral and sulphate free. It was then sucked to a paste on a Buchner funnel and preserved in a glass stoppered bottle.

Plating solution. The nickel plating solution was one commonly used in the electroplating industry. It was 1.0 N in $NiSO_4$, 0.25 N in NH_4Cl and 0.25 M in H_3BO_3.

Nickel chloride. This salt was made by electrolyzing a dilute HCl solution, using a Mond nickel anode and a platinum foil cathode. The solution so obtained was evaporated to dryness to remove the excess HCl. The residue was thrice recrystallized at room temperature. The purified salt was then made up to a 2.0 N solution and agitated with $Ni(OH)_2$ as usual. (This $Ni(OH)_2$ had been made from $NiCl_2$ instead of $NiSO_4$).

Nickel. Nickel from five different sources was used in this research.

1. This was a pure nickel wire obtained in the open market.

2. This was nickel plated on platinum under varying conditions.

3. This was thin electrolytic sheet nickel obtained from the Bureau of Standards. It had been stripped off of brass sheet.

4. This was the finely divided nickel that was used for all except preliminary measurements. It was prepared by electrolysis at high current density from the plating solution described above. Prior to electrolysis, the solution was boiled under reduced pressure so as to remove as much oxygen as possible. Electrolysis was carried out at 70° with a current of 1.6 to 2.0 amperes. A number 24 B. and S. gauge platinum wire about 8 mm. long served as the cathode and a considerably longer platinum wire as the anode. Merely touching the cathode with a glass rod served to detach the fluffy masses of nickel that formed there. These masses invariably crumbled to an extremely fine powder as they fell through the solution. The nickel so prepared was thoroughly washed with some of the solution on which measurements were to be made, and was then allowed to stand in some of the same solution for two days before being introduced into the electrode vessel. These solutions were always well boiled out before being allowed to touch the nickel. The nickel itself was never exposed to the air. Whenever transfers from one vessel to another were necessary, they were carried out very rapidly and the nickel was kept completely immersed in the boiled out solutions. Electrolysis of a pure 1.0 N nickel sulphate solution invariably gave a greenish deposit,—probably $Ni(OH)_2$ mixed with the nickel. Such deposits could not be used. The plating solution yielded nickel deposits free from such contamination.

5. This was a nickel amalgam prepared by electrolyzing a 1.0 N nickel sulphate solution for one hour at a current density of about 5 amps./dcm.^{2} The cathode was pure mercury and the anode a platinum wire. The amalgam so formed always separated into three parts,—a liquid portion, a putty-like portion and a finely divided solid portion that was apparently pure nickel. These amalgams were washed with water and kept under water for four days before use.

Mercury. The mercury used was purified according to the method of Hulett and Minchin.[1] Ordinary laboratory mercury was passed several

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[1] Phys. Rev., 21, 388 (1905).

times through a long column of 1.0 N HNO_3 and 0.5 N $Hg_2(NO_3)_2$ solution in the form of a fine spray. This washed mercury was then distilled several times in a current of air under reduced pressure in an apparatus made in one piece of Pyrex.

Mercurous sulphate. This salt was prepared according to the method described by Hulett.[1] 1.0 N H_2SO_4 solution was electrolyzed at a current density of 0.9 amps./dcm.,[1] using a platinum foil cathode and a pure mercury anode. The mercury surface was kept clean by a rotating glass arm. The product was preserved under 1.0 N H_2SO_4 solution in a glass stoppered bottle in the dark. Before use it was thoroughly washed until free of acid.

Mercurous chloride. This salt was prepared by the method of Lipscomb and Hulett.[2] The apparatus and technique were exactly similar to that employed for the Hg_2SO_4, save that 1.0 N HCl solution was used as the electrolyte. The calomel so prepared was washed until free of HCl, after which it was preserved in a glass stoppered bottle in the dark.

Hydrogen. The hydrogen used in the electrolytic purification of the $NiSO_4$ solution was prepared in an electrolytic generator similar in all details to the one described by Clark.[3]

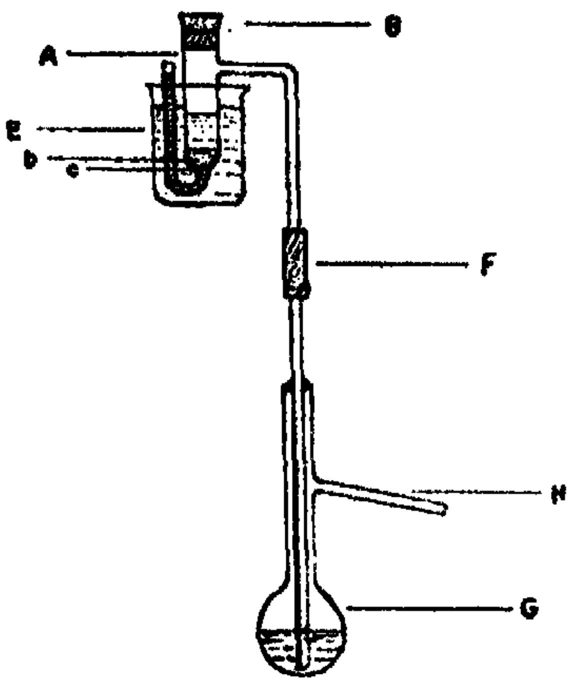

FIG. 1

b. *Apparatus.*

For the potential measurements, a Leeds and Northrup student potentiometer, lamp and scale galvanometer (sensitive to 0.025 microamperes) and an Eppley standard cell were used. The standard cell was carefully compared with a Bureau of Standards cell and its value found to be correct as stated. All volumetric apparatus and weights were carefully calibrated. An air thermostat adjusted to 25° ± 0.5° was used. The thermometer had been calibrated by the Bureau of Standards. The same electrode vessels were used for both reference and nickel electrodes. A half cell, with its filling device, is shown in Fig. 1. (Illustrated and described under "d. Procedure.")

c. *Preliminary studies.*

A considerable number of cells were studied by way of orientation as to type of vessel, electrode material, technique, etc. A normal calomel electrode was used throughout the preliminary work as the reference electrode. The saturated KCl salt bridge used was of the type described by H. E. Haring.[4] The other half cell was similar to that described by Smits (loc. cit.) and was

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[1] Phys. Rev., 32, 257 (1911).

[2] J. Am. Chem. Soc., 38, 21 (1916).

[3] "The Determination of Hydrogen Ions," 3rd Ed. page 350.

[4] Trans. Am. Electrochem. Soc., 49, 417 (1926).

TABLE II
Preliminary Measurements

	Time in Days							
Cell	1	2	3	4	6	8	10	12
1	.451	.457	.463					
2	.452	.457	.460					
3	.444	.445	.458					
4	.453	.468	.471		.474	.475		
5	.492	.516	.517		.512	.510		
6	.493	.517	.521		.523	.522		..
7		.400			.457		.463	
8	.435	.452			.452		.468	
9	.445	.458			.467		.468	
10	.460	.470			.472		.468	
11		.545			.557			.555
12		.530			.542			.535
13	.525		.525					
14	.523		.523					
15		.571	.577		.577			.577
16		.587	.580		.591			.591
17		.520		.520		.544		
18		.530		.542		.543		
19		.540		.541		.545		
20		.553			.550			.552
21		.565			.563			.561
22		.565			.563			.561

Cell	15	18	20	22	24	30	35	48
1								.455
2								.451
3								.460
4								.470
5								.502
6								.492
7		.452		.471	.465			
8		.469		.470	.472			
9		.469		.470	.472			
10		.471		.471	.472			
11		.555	.556		.555	.552	.552	.550
12		.532	.530		.526	.518	.523	.500
13						.532		.532
14						.531		
15		.577	.576		.574			
16		.586				.576		
17	.546	.550			.550	.551		
18	.542	.544			.542	.544		
19	.545	.547			.547	.547		
20		.555			.555	.557		
21		.560			.556	.556	.557	.555
22		.560			.556	.554	.556	.550

filled according to his procedure. Nickel electrodes from various sources were used, but the electrolyte, with the exception of that used in cells Nos. 5 and 6, was 1.0 N nickel sulphate solution, purified and adjusted for acidity as described. Measurements were continued for many days,—in some cases for nearly seven weeks. The results are displayed in Table II. All values recorded in this table are those actually obtained from the measurements, i.e. they are really half-cell potentials if we take the normal calomel electrode as zero.

The electrodes of cells Nos. 1, 2, 3, and 4 were nickel wire. The wires were inserted directly through the rubber stoppers of the cells. The electrodes of cells Nos. 5 and 6 were thin electrolytic sheet nickel that had been exposed to the air for some time. Previous to use, the metal was polished with pumice powder and thoroughly washed. Strips of it were inserted between the rubber stoppers and the walls of the electrode vessels. The electrolyte in these two cases was the plating solution mentioned above. To it had been added sufficient NaOH solution to bring the pH to 6.8, i.e. the precipitation point of $Ni(OH)_2$ from a 1.0 N nickel sulphate solution. The electrode of No. 7 was made by sealing a piece of the thin electrolytic sheet into a glass tube and inserting this through the stopper. The electrodes of cells Nos. 8, 9 and 10 consisted of the nickel amalgam. No. 8 contained the liquid portion, No. 9 the putty-like portion and No. 10 the finely divided solid portion. Contact was made in the usual manner through a platinum wire sealed into a glass tube.

The electrodes of cells Nos. 11, 12, 13 and 14 consisted of platinum foil, thinly plated with nickel from the plating solution at a current density of about 1.5 amps./dcm.^{2} Nos. 11 and 12 were washed and boiled in water and then allowed to stand in 1.0 N nickel sulphate solution for two days previous to use. Nos. 13 and 14 were allowed to stand in distilled water, exposed to the air, for several days before use. After 30 days, No. 11 was made the anode in electrolysis so that oxygen was discharged on the nickel and No. 12 was made the cathode so that hydrogen was discharged. Oxygen apparently did not affect the potential but hydrogen caused a change of 0.515 volts for just a short time. After 30 days, No. 14 was opened for just an instant. Its potential immediately dropped to 0.450 volts, showing the effect of air. When opened for just a second or two longer, it dropped still farther to 0.350 volts. The electrodes of Nos. 15 and 16 consisted of a "tree" of nickel plated on a small platinum wire from the plating solution. No. 15 was washed and used at once while No. 16 was kept in water for two weeks previous to use.

The electrodes of cells Nos. 17 to 22 inclusive consisted of a small platinum wire, plated with nickel, completely covered with the finely divided nickel described above. The pulverulent nickel for cells Nos. 17, 18 and 19 was allowed to stand in contact with 1.0 N nickel sulphate solution for four days before filling the electrode vessels. The powdered nickel in No. 20 was used as soon as made. The electrode material in Nos. 21 and 22 was allowed to stand in contact with 1.0 N nickel sulphate solution for two days prior to filling the cells. After 28 days No. 22 was emptied and refilled with fresh N-$NiSO_4$ solution.

The table shows clearly the marked influence of the method of preparation of the electrode, its history, presence of air or hydrogen, etc. It is especially noteworthy that cells Nos. 11 to 22 inclusive, all of which had electrodes of electrolytic nickel of some variety, show quite noticeably higher values than Nos. 1 to 10. In the case of cells used immediately after plating the electrodes, the potential given may have been affected, to some extent, by hydrogen, but it is highly improbable that nickel, which has been exposed to the air, or which has been allowed stand in contact with water or nickel sulphate solution, would still contain hydrogen in sufficient amount to account for such consistently high values. In the case of the amalgam electrodes, it is probable that air was not entirely excluded, for they took a long time to reach equilibrium and the values rose steadily. The rapid attainment of equilibrium and the reproducibility of those cells utilizing the finely divided nickel electrodes was so marked, that it was decided to use such electrodes exclusively in the final measurements.

d. *Procedure.*

Some of the solution to be studied, previously boiled out, was poured into A and G (Fig. 1).

A is a 2 × 15 cm. test tube with side arm and mercury contact arm sealed on as shown. B is a solid rubber stopper carefully sealed in with Khotinsky cement. C is a #24 B. and S. gauge platinum wire sealed in through the bottom of A. The end inside A is nickel plated. D is the finely divided nickel. E is a 600 cc. beaker filled with water. F is a short piece of very carefully cleaned suction tubing. G is a 200 cc. Pyrex distilling flask with sealed in connection as illustrated. H is connected to a good water jet pump.

The fine nickel, carefully washed with the boiled solution, was rapidly transferred in the manner described previously to A and the stopper B at once sealed in. Sufficient nickel was introduced to cover the nickel plated platinum wire C completely. Connection between A and G was made by means of F. H was connected to the pump and a vacuum produced. At the same time the liquid in A and G was made to boil vigorously by heating E and G. When boiling had continued for some time, the vacuum was broken beyond H. The liquid in G immediately rushed up into A, filling it completely. This procedure effectually removed all hydrogen and air. When cool, F was removed from A and the outlet tube of the latter placed immediately in a beaker of the same solution. A quantity of the purest mercury had been placed in the bottom of the beaker and the outlet of A dipped into this, thus effectually sealing A from the air. The outlet of the reference electrode also dipped below this mercury. To make measurements, it was only necessary to raise both half cells slightly so that they communicated through the solution.

The reference electrodes were mercury-mercurous sulphate electrodes with the particular nickel sulphate solution under investigation (saturated with mercurous sulphate) as the electrolyte. They were filled in the manner usual with such electrodes. Several of these electrodes were made at the same time for each concentration and they invariably checked within 0.0001 volt, both immediately and during the whole experiment. After assembly, the cells were kept in the darkened thermostat during the whole period of the experiment. The mercury seal was broken only for the very short periods of time required for the E.M.F. measurements.

Since boiling affected the concentration of the various nickel sulphate solutions, they were always analyzed after the equilibrium potential had been determined. A volume of solution equivalent to 0.2 to 0.3 grams of nickel was taken and analyzed according to the electrolytic method described by Treadwell and Hall.[1] This method proved very satisfactory. Completion of electrolysis was always proved by the use of dimethylglyoxime. Molalities (mols salt per 1000 grams water) being desired in this work rather than normalities, it was also necessary to determine the density of each solution. This was done by constructing a graph of densities plotted against normalities ranging from 0.05 N to 1.00 N. Landolt-Börnstein[2] furnished a few values. The balance were determined with the aid of a 50 cc. pyknometer at 25°/4°. Table III gives the density values, all of which fall on a very smooth curve.

TABLE III

Density of $NiSO_4$ Solutions.

Normality	D 25/4	Source
0.050	1.0010	Experimental
0.100	1.0051	Experimental
0.125	1.0067	Landolt-Börnstein
0.175	1.0109	Experimental
0.200	1.0132	Experimental
0.250	1.0168	Landolt-Börnstein
0.300	1.0209	Experimental
0.500	1.0360	Landolt-Börnsetin
1.000	1.0741	Landolt-Börnstein

5. Data

The data are exhibited in the tables following. To calculate E_0 it was necessary to know the activities of the various nickel sulphate solutions. No data were available from which the activity coefficients could be calculated. The values for $CuSO_4$ at the same concentrations were assumed, therefore, to be approximately correct. (As with the densities, a graph was constructed from which the desired values could be read off.) The data were taken from Lewis and Randall's "Thermodynamics" (loc. cit. pages 344 and 362). The justification for this procedure was three-fold. First, bi-bivalent salts as a class have nearly the same activities at the same concentrations. Thus Lewis and Randall, (loc. cit) give values for several salts of the type $MeSO_4$, where

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[1] "Analytical Chemistry," Fifth Edition, Vol. 2, page 138.

[2] "Physikalische-Chemische Tabellen," Fifth Edition, Vol. 1, page 410.

$MeSO_4$ stands for Mg, Zn, Cd or Cu sulphates. These are practically uniform throughout the class, especially for the more dilute solutions such as were used. Second, Hampton[1] assumed the activity coefficients of $FeCl_2$ to be similar to those of $BaCl_2$. The results justified his assumption. Third, the constancy of the E_0 values tabulated below, based on the assumption mentioned, is perhaps the best evidence that nickel sulphate acts similarly to salts of the type $MeSO_4$.

Table IV gives the data for cells where recrystallized nickel sulphate was the electrolyte.

TABLE IV
Recrystallized $NiSO_4$ as Electrolyte.

Cell No.	Molarity	Malality Calc.	E.M.F. Measured	γ	E_0 Calc.
26	0.0507	0.0508	0.968	0.215	0.852
27	0.0510	0.0511	0.968	0.214	0.852
28	0.0503	0.0504	0.967	0.215	0.852
29	0.0505	0.0506	0.968	0.215	0.852
30	0.0515	0.0516	0.968	0.213	0.852
31	0.1016	0.1018	0.958	0.157	0.852
32	0.1050	0.1052	0.958	0.154	0.852
33	0.1015	0.1017	0.958	0.157	0.852
34	0.1018	0.1020	0.958	0.156	0.852
35	0.1022	0.1024	0.958	0.156	0.852
36	0.1501	0.1504	0.954	0.129	0.853
37	0.1613	0.1617	0.954	0.120	0.852
38	0.1540	0.1543	0.953	0.127	0.852
39	0.1540	0.1543	0.952	0.127	0.851
40	0.1516	0.1519	0.953	0.128	0.852
41	0.1500	0.1503	0.953	0.129	0.852

Table V gives the data for cells where the nickel sulphate was prepared from Mond nickel.

TABLE V
$NiSO_4$ from Mond Nickel as Electrolyte.

Cell No.	Molarity	Molality Calc.	E.M.F. Measured	γ	E_0 Calc.
42	0.0511	0.0512	0.967	0.214	0.851
43	0.0508	0.0509	0.967	0.215	0.851
44	0.0510	0.0511	0.967	0.214	0.851
45	0.0503	0.0504	0.967	0.215	0.851
46	0.0505	0.0506	0.967	0.215	0.851

Table VI gives the data for cells where the electrolyzed nickel sulphate was the electrolyte.

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[1] J. Phys. Chem., 30, 980 (1926).

TABLE VI
Electrolyzed $NiSO_4$ as Electrolyte.

Cell No.	Molarity	Molality Calc.	E.M.F. Measured	γ	E_0 Calc.
47	0.0514	0.0515	0.970	0.213	0.854
48	0.0514	0.0515	0.968	0.213	0.852
49	0.0503	0.0504	0.969	0.215	0.853
50	0.0506	0.0507	0.971	0.215	0.855
51	0.0524	0.0525	0.971	0.212	0.854

Table VII is given to show the rapidity with which equilibrium is reached and the constancy with which it is maintained.

TABLE VII
Change of Potential with Time

Cell	Time in Days					
	1	2	4	6	12	18
36	0.952	0.954	0.953	0.953	0.953	0.952
37	0.951	0.953	0.954	0.954	0.954	0.952
38	0.952	0.953	0.953	0.953	0.952	0.951
39	0.947	0.952	0.952	0.953	0.952	0.951
40	0.950	0.953	0.953	0.953	0.953	0.952
41	0.952	0.953	0.953	0.953	0.953	0.953

The measurements given represent only a part of the total number made. Thus five other cells were studied, using recrystallized nickel sulphate solution (0.0625 molar) as the electrolyte. These gave a value for E of 0.966 volts ± 0.001 volt. This is in excellent agreement with the values in Table IV. Other cells were measured using 0.15 molar solutions. Their values also agreed to ± 0.002 volts with the average value for cells with an electrolyte of the concentration mentioned. Twelve other cells, containing 0.05 molar electrolyzed nickel sulphate solution, were measured. The potentials of all of them fell within the limits of Table VI. Accidents, lack of time, etc. prevented the determination of the nickel content after equilibrium was reached, and so E_0 could be calculated for none of the cells just mentioned.

The mean value of E_0 for cells Nos. 26 to 51 inclusive is 0.852 volts. Lewis and Randall (loc. cit. page 407) give 0.6213 volts at 25° as the value of E_0 for the electrode $Hg/Hg_2SO_4(S)/SO_4''$, based on E_0 for hydrogen equal zero. Hence it follows that E_0 (the standard potential) for nickel at 25° is -0.231 volts. The *normal potential* then is about -0.245 volts (assuming the degree of ionization of 0.05 molar nickel sulphate to be about 41%).

6. Errors

All weights, volumetric apparatus, thermometers, etc. were carefully calibrated and, as shown, the voltage of the standard cell was found correct to 0.0001 volt, while the reference electrodes always checked to 0.0001 volt at any given concentration. However, a critical examination of other possible sources of error reveals the following. Although the potentiometer was guaranteed accurate to 0.0005 volt, and it was very easy to read and check to 0.0001 volt, all values recorded are rounded off to 0.001 volt. The thermostat temperature limits of ± 0.5° can produce a maximum deviation of but 0.0001 volt in the measured potentials. The concentration of each solution, as determined by the analysis, is accurate to ±0.0005 molarity units. Densities are accurate to ±0.1%. Consequently neither of these factors can appreciably affect the final values.

Although all materials were very carefully purified, a sample of the purified nickel sulphate and of the nickel sulphate prepared from it by subsequent electrolytic purification were analyzed spectroscopically through the courtesy of the U. S. Bureau of Standards. Arc spectra of each sample were photographed, the sample being burned on graphite electrodes. Neither sample was found to contain copper. The non-electrolyzed sample showed as impurity, only a small quantity of cobalt. The electrolyzed sample showed no cobalt at all, but small traces of Al, Mn and Na were found. NaOH had been added to the electrolyte to make a small quantity of $Ni(OH)_2$. The purpose of this was to maintain a pH of 6.8 during the electrolysis. The Al and Mn probably came from the Pyrex dish in which the electrolysis was carried out. The complete removal of the cobalt is very interesting. It suggests either that cobalt is more positive than nickel (which is contrary to the order accepted at present) or that it shows less cathodic polarization than nickel. The matter is now under investigation in this laboratory. The excellent agreement between the E_0 values from the non-electrolyzed nickel sulphate, the electrolyzed nickel sulphate and the nickel sulphate from Mond nickel shows that the impurities mentioned can have but very slight effect.

This same reproducibility attests the practically complete removal of oxygen by the technique finally used. The effect of oxygen is shown conclusively in the preliminary results. The values obtained are not reproducible and the potentials usually drop with time, while intentional introduction of air produces a large drop immediately. Furthermore, in the preliminary studies when the finely divided nickel was removed from the electrode vessel, it was always found to be blackened (probably by oxide formation), whereas the nickel used under the more carefully controlled final conditions was invariably a metallic gray (its original color), even after standing several weeks.

That hydrogen was removed by our technique seems certain. Long standing in contact with the solution before use should permit practically complete removal by diffusion of any hydrogen formed in the electrolytic preparation of the nickel. Followed by the thorough boiling and evacuation, this removal must have been complete. Hydrogen tends to raise the potential of nickel. This is because the hydrogen electrode at one atmosphere pressure, immersed in a solution of pH 6.8, shows a potential of −0.403 against the standard hydrogen electrode. Of course if the partial pressure of the hydrogen is smaller than 1 atmosphere, this value will be smaller, i.e. more positive. At pH 6.8 the partial pressure of the hydrogen required to give a potential of

-0.231 volt (i.e. the E_0 value for nickel found by us) would be 2×10^{-6} atmosphere. This, for all practical purposes, would represent complete removal of hydrogen. Again, within a very short time after cathodic polarization, cells Nos. 11 and 12 returned to their equilibrium values, showing how rapidly hydrogen really does leave nickel so prepared. Finally, Lewis and Lacey[1] proved that a finely divided copper electrode, prepared by electrolysis, did not function as a hydrogen electrode. They added a small quantity of free acid to the electrolyte. There was no appreciable change in the voltage of the cell. However, because nickel displaces hydrogen from free acid, we were unable to make this test in the present case.

There is every reason to believe that the metal was in its most stable state. It was very finely divided, had been allowed to stand in contact with the electrolyte for some time, and was free from oxide. Any nickel prepared by the reduction of its oxide with hydrogen is almost sure to contain some oxide if exposed to the air at all. Metals prepared by high current density electrolysis seem to be free from surface strains, either immediately or on standing in contact with the electrolyte for a very short time.[2] This process was used successfully by Lewis[3] in his study of the silver electrode, by Lewis and Lacey (loc. cit.) in their work on copper, by Hampton (loc. cit.) in connection with the potential of iron, and by others.

That the electrode studied was truly reversible was shown by the following facts.

(1) The relation between potential and concentration was that predicted theoretically. (2) Anodic and cathodic polarization and short circuiting of the cells produced a temporary disturbance, the equilibrium value being quickly regained.

For these reasons we assign to the standard nickel electrode the value -0.231 volts ± 0.002 volts at 25°.

7. The Potential of Nickel against Nickel Chloride

It was hoped that several cells of the type $Ni|NiCl_2(0.05 \text{ molal})|Hg_2Cl_2|Hg$ might be studied. They contained no liquid junction and should have been amenable to the same technique as that used with nickel sulphate. The relation connecting cell voltage with electrolyte concentration for such cells would be

$$E = E_0 - 0.02956 \log 4\,(m\gamma)^3 \qquad \text{and}$$

the activity coefficients for the bi-univalent electrolyte should be approximately the same as those of $BaCl_2$ at the same molality.

As a matter of fact, thirteen of these cells were set up and studied, but extensive hydrolysis, accentuated by the boiling, produced so much free acid and nickel hydroxide (and in a few cases visible hydrogen) that equilibrium values were unobtainable. Addition of free acid to suppress the hydrolysis

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[1] J. Am. Chem. Soc., **36**, 804 (1914).

[2] Allmand-Ellingham: "Applied Electrochemistry," 2nd Ed., page 126.

[3] J. Am. Chem. Soc., **28**, 158 (1906).

defeated its own purpose, as might have been expected. For any given pH the cell potentials were moderately reproducible, although they did not become constant for at least 16 days. The data obtained (which are not produced here to economize space) serve merely to emphasize the deleterious effect of free acid and hydrogen on the potential of the nickel electrode.

7. Summary

(1) The standard potential of nickel has been determined to be −0.231 volts ± 0.002 volts at 25°.

(2) As in many previous cases, nickel prepared by electrolysis at high current densities has been found most satisfactory for such work.

(3) The necessity of excluding oxygen and hydrogen in potential measurements has been reemphasized.

(4) Cobalt has been shown to be either more positive than nickel or less polarized.

(5) Nickel chloride, due to hydrolysis, has been found to be an unsatisfactory electrolyte in potential measurements.

It gives us pleasure to acknowledge the interest shown in this work by Dr. William Blum, of the U. S. Bureau of Standards, and Mr. H. E. Haring, of the Victor Talking Machine Company, and their cooperation in certain phases of it.

32.90

NITROCELLULOSE DIFFUSION EXPERIMENTS*

BY R. O. HERZOG AND D. KRÜGER

The following communication deals with experimental work which was performed several years ago and which is not yet concluded.

If cellulose is nitrated with so-called mixed acid, nitrocellulose products are obtained which differ according to the conditions employed (concentration of the mixed acid, time and temperature of the action). We have dissolved the nitrocelluloses made from cellulose of various botanical origins in suitable liquids and determined their diffusion coefficients, finding as was expected that the diffusion coefficient is dependent upon the raw material employed as well as upon the conditions of nitration.

An essential difference revealed itself however in the course of the investigation, which consisted of several hundred single experiments, namely, only in a relatively few number of experiments was the diffusion coefficient constant within a single experiment, i.e. for the four different heights in one diffusion cylinder; by far the majority of determinations displayed a deviation from Fick's law of diffusion.

If, on the assumption that this law holds, our values for the concentration in the various layers of the diffusion cylinder are calculated by the use of Stefan's derived tables for the Graham determinations, one finds in these anomalous cases always the same trend: the coefficients for the topmost layer and, for the second layer from the bottom is too great; the coefficient of the lowest and of the third layer from the bottom are approximately equal. (An indication of this trend is present also in the cases where the coefficients of all four layers may be considered as equal.) This trend in the values of the coefficients of diffusion indicates that the conditions on which the validity of Fick's law is based, i.e. that the solution is homodisperse and that the coefficient of diffusion does not depend upon the concentration, are not fulfilled in the present case. In addition to heterodispersity, the extent of which will be determined by the nature and pretreatment of the raw material, the conditions of nitration and dispersion etc., a splitting off of larger particles into smaller ones in the course of the diffusion process must be taken into consideration. This tendency to disaggregate on dilution will also vary with the kind of the cellulose material and other factors.

As a matter of fact, certain experiments which one of us (H) has performed together with Mr. Lange, namely the investigation of nitrocellulose solutions by means of depolarized Tyndall-light point to such a disaggregation on dilution.

In this communication only those experiments are recorded in which the "heterodispersity" of the nitrocellulose solution may be disregarded.

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*From the Kaiser Wilhelm Institut für Faserstoffchemie, Berlin-Dahlem.

Experimental Procedure

Nitration

The conditions of nitration were so chosen that the destructive action of the nitrating acid upon the raw material was as small as possible, this is the case where the reaction is carried out at a low temperature and with acid containing but little water. An acid consisting of 71.70% H_2SO_4, 18.65% HNO_3 and 9.63% water was used at 0°C. The ratio by weight of fibre to mixed acid was 1:100. The fibres were in part scoured by a simple boil in 1% soda solution and in part especially purified in the manner described below.

The "purified" materials were heated as follows: 20 grams of the cellulose material, previously freed from impurities, was introduced into 400 cc of boiling 1% soda solution and boiled for two hours with the cellulose submerged below the surface of the liquid. The hot liquor was then gradually displaced by cold water. The expressed cellulose was next treated at 35°C for two hours with 400 cc of a bleaching powder solution containing 2.7 gm Cl of per liter, soured with ½% hydrochloric acid and washed with water until acid free. Then followed in the same manner a second boil with 1% soda solution, a second bleaching with chloride of lime solution containing 2 grams of Cl per liter, a third boil in 1% soda and a third bleach in 1.3 gram per liter Cl and finally one more boil in 1% soda. The cellulose after washing in running water until free of alkali was dried in the air.

Experiments were also carried out with only one 1½ hour boil in 1% soda solution.

Experiments on different materials (hemp and alkali cellulose) show that within rather wide limits (10 minutes to 3 hours treatment) the diffusion coefficient is independent of the duration of the nitration. In all further experiments the nitration period was three hours unless otherwise noted. Determination of the velocity of nitration under the same conditions indicated that after 15 minutes some 7% N had been taken up, while the maximum N content was reached after about 1½ hours. Those products which were nitrated for shorter periods were only partly soluble in acetone.

The N content of the product produced by a three-hour nitration with a mixed acid containing 71.7% H_2SO_4, 18.65% HNO_3 and 9.63% water at 0°C amounted in the case of nitrated cotton, regardless of its preliminary treatment (mercerization, action of acids) to 12.8 – 12.9%; in the case of nitrated wood cellulose the N content was lower (11.8 – 12.3%) which is in accord with previous observations.

The nitrocelluloses produced in this manner are easily soluble in acetone, methylethylketone, amylacetate, nitrobenzol, pyridine and chloroform. The solutions produced in the cold are highly viscous or jelly-like even with concentration of less than 1% nitrocellulose. The solutions in hot acetone or methylethyl ketone also show high viscosities. The viscosity varies considerably according to the nature and preparatory treatment of the raw material.

In ether-alcohol or methyl alcohol these nitrocelluloses are insoluble, Unstabilized nitrocellulose decomposes gradually when kept at ordinary temperature with the splitting off of nitrogen oxide, In order to determine to what extent the properties of the above described nitration products are altered in storage, the following experiments were carried out. The nitrates were first washed thoroughly with cold water. For nitrated hemp, after storage for seven months only a small increase in the diffusibility was observed, while in the case of nitrated pulp no change had occurred after four months.

Since commercially produced nitrates, of the sort here in question, also remain (for our purpose) unchanged for a long time without any special stabilizing treatment, this procedure was omitted in the experiments dealing with the comparison of different raw materials, and the nitrates were simply washed with cold running water, until a blue litmus paper when pressed against the fibres showed no tendency to turn pink. This method was also chosen because after-treatment of nitrocellulose may affect considerably its colloid-chemical properties.

By boiling nitrocellulose in water preferably in the presence of an acid or alcohol, not only the stability increases, but also the viscosity of the subsequent solution in acetone (a fact which is well known). The increase in viscosity by this method of stabilization was also observed in a few experiments on nitrated cellulose as follows:

Cellulose was nitrated for 1 hour at 20°C with an acid mixture of the composition: 61.53% H_2SO_4, 20.02% HNO_3 and 18.45% water. The nitrocellulose was first thoroughly washed in cold running water, a part of it was then further washed for 1 hour in water, twice boiled for periods of one hour in 1% soda solution, then boiled for an hour in water (the water from this first water boil gave a neutral reaction with litmus.) The nitrocellulose was then dissolved by heating with acetone for one hour under a reflux condenser and the period of flow of the solution at 20°C was determined with the Ostwald viscosimeter.

	Concentration g/100 cc acetone	Discharge Time (seconds)
Unstabilized nitrocellulose	1.74	18.1
Stabilized nitrocellulose	1.63	34.8

In the industry no such energetic stabilization as boiling with 1% soda solution is employed. By this treatment a considerable quantity of substances which are regarded as nitro-oxycelluloses and nitro-hydrocelluloses and which form the less dispersible part of nitrocellulose are dissolved out.

In general the nitrocelluloses were used within a few days of their production.

Solvents

The choice of suitable solvents for diffusion experiments on nitrocellulose is limited by the following considerations:

1. The solvent must be sufficiently pure and stable and must not react with the nitrocellulose.

2. Solvents which are specifically heavier than nitrocellulose (chloroform for example) can not be used without altering the method.

3. Very low boiling solvents are inconvenient for practical reasons.

We used principally acetone (Bp. 56.3°) and methyl-ethylketone (Bp. 81°), occasionally also other solvents such as amylacetate. The commercial ester was freed from acid, dried and distilled; in the case of the other solvents, the pure preparations of Kahlbaum were used directly. The presence of moisture within certain limits was without effect upon the results, therefore in general air-dried nitrocellulose was employed.

The nitrocelluloses prepared as described gave even in small concentrations with cold acetone, amylacetate, etc. (insofar as the raw material had not received extensive chemical pretreatment), highly viscous gelatinous solutions which were difficult to maintain homogeneous. It was therefore found advisable to effect the solution by heating with the solvent concerned. Experiments with methyl-ethylketone solutions indicated that the duration of heating (2-4 hours) was without influence.

The question as to what extent the different solvents cause aggregation must be reserved for further investigation.

The nitrocelluloses were produced therefore, when not expressly otherwise stated, by a three-hour nitration with a mixed acid whose composition was 71.70% H_2SO_4, 18.65% HNO_3 and 9.63% H_2O, washed with cold water and dried in air. The air dry nitrocellulose was dissolved by treatment for four hours with the boiling solvent, usually acetone or methyl-ethylketone and the solution finally centrifuged.

Diffusion

The diffusion was carried out in the apparatus of Oeholm[1]. The experiments were conducted in a cellar whose maximum temperature variation in the course of a day was 0.1° and in the course of the whole experimental period 0.5°.

Because of the volatility of the solvents employed, special precaution were taken to limit as far as possible the evaporation during the long time required for the experiments. To the capillary tube on the upper part of the diffusion cylinder, a bent glass tube with a blown bulb in it was connected and this tube was drawn out to a long fine capillary. This dipped into a vessel which was filled with the solvent and which was connected to the outer air only through a capillary tube.

The diffusion coefficients at t° in organic solvents when calculated to the diffusion coefficient in water at 20° (D_{w20}) give within the limits of experimental error, equal values for solutions in acetone, methyl-ethyl ketone, ethyl formate and methyl alcohol.

After tapping off, the nitrocellulose content of the four layers was determined by evaporation in vacuum to constant weight. From the amount of substance thus found the diffusion coefficient was ascertained by the use of Kawalki's tables and curves.

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[1] L. W. Oeholm: Z. physik. Chem., 50, 309 (1904).

TABLE I

	Temp. ($t°$)	Time in days (z)	Content of layer mg.	Content of layer %	D.	D_{w20}
Nitrocellulose from purified hemp, 12.8% N, dissolved in hot methyl-ethyl ketone.	13.2	47	143.9	40.9	0.039	0.018
			109.0	31.0	0.039	0.018
			60.0	17.1	0.037	0.017
			38.8	11.0	0.042	0.019
			Σ = 351.7	Mean	0.039	0.018
The same nitrocellulose kept at room temperature seven months and then dissolved in hot acetone.	13.6	19	162.4	48.7	0.068	0.024
			107.4	32.2	0.071	0.025
			41.1	12.3	0.056	0.019
			22.7	6.8	0.083	0.029
			Σ = 333.6	Mean	0.069	0.024
Nitrated ramie, 12.8% N, dissolved in hot methyl-ethyl ketone	12.8	29	117.8	54.8	0.032	0.015
			68.3	31.8	0.029	0.014
			19.2	8.9	0.026	0.012
			9.5	4.4	0.043	0.020
			Σ = 214.8	Mean	0.032	0.015
Nitrated flax, 12.8% N, dissolved in hot methyl-ethyl ketone	12.8	29	127.4	46.5	0.047	0.022
			88.9	32.4	0.039	0.018
			37.5	13.7	0.040	0.019
			20.4	7.4	0.059	0.027
			Σ = 274.2	Mean	0.046	0.021
Nitrated cotton, 10.7% N, dissolved in cold acetone	14.2	38	98.5	39.9	0.054	0.019
			77.7	31.5	0.045	0.016
			43.8	17.8	0.046	0.016
			26.6	10.8	0.054	0.019
			Σ = 246.6	Mean	0.050	0.017
The same, dissolved in hot acetone	14.2	38	102.6	41.6	0.049	0.017
			77.6	31.4	0.045	0.016
			41.2	16.7	0.042	0.015
			25.2	10.2	0.051	0.018
			Σ = 246.6	Mean	0.047	0.016

TABLE I (Continued)

	Temp. (t°)	Time in days (z)	Content of layer mg.	%	D.	D_{w20}
Nitrocellulose from sulfite pulp, 12.3% N, dissolved in hot acetone	13.3	28	147.1	46.5	0.045	0.016
			100.3	31.7	0.052	0.018
			41.5	13.1	0.036	0.013
			27.4	8.7	0.057	0.020
		Σ =	316.3	Mean	0.047	0.017
Nitrocellulose from German sulfite pulp, 12.3% N, dissolved in hot methyl-ethyl ketone	12.9	34	128.6	48.1	0.041	0.019
			84.1	31.5	0.052	0.024
			29.3	1.0	0.029	0.014
			25.2	9.4	0.059	0.027
		Σ =	267.2	Mean	0.045	0.021
Nitrated α-cellulose from sulfite pulp[1], 12.5% N, dissolved in hot acetone	13.3	27	110.8	36.7	0.98	0.034
			88.7	29.4	1.02	0.036
			58.9	19.5	0.90	0.031
			43.1	14.3	1.04	0.036
		Σ =	301.5	Mean	0.97	0.034
Nitrated viscose silk, 12.7% N, dissolved in hot methyl-ethyl ketone	12.9	34	125.5	44.0	0.056	0.026
			88.0	30.8	0.070	0.033
			43.9	15.4	0.050	0.023
			28.1	9.8	0.067	0.031
		Σ =	285.5	Mean	0.061	0.028
Nitrated alkali-cellulose[2] which has been ripened 28 days. Dissolved in hot acetone. Nitration time 10 min.	13.3	27	112.8	41.3	0.069	0.024
			81.4	29.8	0.091	0.032
			46.8	17.2	0.064	0.022
			31.9	11.7	0.082	0.029
		Σ =	272.9	Mean	0.076	0.027

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[1] The α-cellulose from sulfite pulp was obtained from artificial silk wood pulp according to the instructions of Schwalbe, the other α celluloses as well as the β cellulose according to the process of Lenze, Pleuss and Mueller. According to their instructions, a three-fold treatment with alkali is necessary to remove the hemicelluloses. A lengthening of the alkali treatment is however useless, since by each increase in time only small and approximately constant quantities go into solution and these consist of the soluble products formed by the action of the alkali itself.

[2] By alkali cellulose is meant here as in the artificial silk industry—wood pulp which has been soaked in approximately 16% NAOH liquor, pressed until it weighed about three times as much as the original pulp and stored for a certain period.

(Table I Continued)

	Temp. (t°)	Time in days (z)	Content of layer mg.	Content of layer %		
Ditto, nitration time 60 min.	13.3	27	0.1421	38.1	0.076	0.027
			0.1120	30.0	0.076	0.027
			0.0708	19.0	0.065	0.023
			0.0484	13.0	0.085	0.030
		Σ =	0.3733	Mean	0.076	0.027
Ditto, nitration time 3 hours	13.3	28	133.8	40.9	0.067	0.023
			99.0	30.3	0.076	0.027
			57.5	17.6	0.063	0.022
			37.0	11.3	0.069	0.024
		Σ =	327.3	Mean	0.069	0.024

The diffusion time was reckoned from the beginning of the admission of the solution into the cylinder to the beginning of the drawing off of the first layer. The filling of the cylinder required at least 30 minutes, the tapping off of each layer an average of 20 minutes.

The duration of the diffusion was usually so chosen as to be most favorable for the evaluation (with regard to the slope of the concentration-time-curve) of the first, third and fourth layer; in the second layer, on the other hand, the quantity of material present was usually in the maximum region or in the flat part of the curve after the maximum; the D values of the second layer are for this reason less trustworthy than the rest.

The concentration used seldom reached 1% nitrocellulose. For every solution, two parallel experiments were made. In the tabulated data, the result of one experiment only is given in each case.

Experiments

In Table I the solvent, the diffusion time in days (z), the temperature (t), the content of the layer in milligrams and in percent of the total content are given. Under D stands the calculated diffusion coefficient for the layer and under D_{W20} the coefficient calculated for water at 20°C (for comparison of the solvents and of the numbers independent of temperature).

We add here another group of experiments, Table II, which refer to the influence of the duration of nitration by a mixed acid considerably richer in water content. They are taken from the dissertation of E. Kausmann whose work was performed in our Institute.

The composition of the acid was 20% HNO_3, 61.5% H_2SO_4, 18.5% H_2O; and the nitrating temperature 20°C.

TABLE II

	Temp. ($t°$)	Time in days (z)	Content of layer mg.	%	D	D_{w20}
Nitrated cotton dissolved in hot acetone. Time of nitration 35 min.	11.5°	31.1	70.0	36.9	0.086	0.031
			58.2	30.7	0.071	0.025
			85.0	18.5	0.070	0.025
			26.4	13.9	0.089	0.032
		$\Sigma =$	239.6	Mean	0.079	0.028
Ditto, nitration time 60 min.	12.5	34.0	51.7	35.1	0.080	0.029
			41.9	28.4	0.089	0.032
			28.6	19.4	0.065	0.023
			25.3	17.2	0.093	0.033
		$\Sigma =$	147.5	Mean	0.082	0.029
Ditto, nitration time 65 min.	11.5	31.1	76.3	36.7	0.077	0.028
			62.7	30.2	0.070	0.025
			39.5	19.0	0.066	0.024
			29.4	14.1	0.079	0.028
		$\Sigma =$	207.9	Mean	0.073	0.026

The following summary of the diffusion coefficients calculated for water at 20°C. shows that the natural fibres yield values between 0.015 and 0.021.

The values for alkali cellulose (see below) are not different from those for viscose, so that the diminution in particle size in the manufacture of artificial silk must occur chiefly in the "preripening" process.

The last three series of experiments show that under other than the above specified conditions of nitration greater values are obtained for the same raw material: D_{w20} increases from 0.016 to 0.028 (the particle diameter is inversely proportional to the diffusion coefficient). For our purposes it was most expedient to work under conditions which would lead to the smallest practicable change in the particle size, Table III, as against the cellulose crystallite.

TABLE III

			D_{w20}
Cotton	0.016	Sulphite pulp[1]	0.019
Hemp	0.018	"Alkali cellulose"	0.026
Ramie	0.015	α-Cellulose	0.034
Flax	0.021	Viscose silk	0.028

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[1] Because of the impurities in sulfite pulp experiments with it cannot be considered positively dependable.

TABLE IV

Nitrated cotton (12.8% N) in acetone.

Diffusion time days (z)	Temp. (t°C)	Content of the layers mg.	%
2.8	13.5	80.2	74.5
		16.0	14.9
		7.1	6.6
		4.4	4.1
		Σ = 107.7	
4.0	12.8	81.6	74.1
		15.8	14.5
		7.5	6.8
		5.1	4.6
		Σ = 110.0	
6.0	12.8	81.3	73.9
		15.5	14.2
		7.8	7.1
		5.3	4.8
		Σ = 109.9	
25	12.7	62.7	57.0
		26.0	23.6
		11.5	10.4
		9.9	9.0
		Σ = 110.1	

Nitrated mercerized cotton in acetone.

Diffusion time days (z)	Temp. (t°C)	Content of the layers mg.	%
7	14.0	93.5	73.3
		26.8	21.0
		4.6	3.6
		2.6	2.0
		Σ = 127.5	
19	14.0	76.0	59.6
		33.3	26.1
		10.0	7.8
		8.3	6.5
		Σ = 127.6	

It remains to give the results of further experiments which are not recorded in the foregoing tables.

The content of so-called α-, β- and γ-cellulose does not stand in any easily understood relation to the observed diffusion distribution. In this regard the diffusion coefficient of the nitrate from α-cellulose is always smaller than that for nitrated β-cellulose.

Mechanical treatment, for example in a Hollander mill, increased the diffusion coefficient.

Fig. 1
Concentration gradient after different time periods. (Photometric determination of the Tyndall-cone on the surface between solution and solvent).

Two series of experiments remain for discussion. If as for example in the following experiments the diffusion coefficient be calculated for the lowest layer for different time periods on the assumption that Fick's law is valid, it decreases sharply with time, while—under the same assumption—the coefficient for the topmost layer increases. With increasing time the values for D in the different layers approach nearer to equality.

It appeared possible that disturbances which are present at the beginning, immediately after the two liquids brought in contact might be caused by the nitrocellulose solution swelling as it stands beneath the pure solvent, in other words: that the true diffusion of the particles does not occur immediately but rather that the solution at first increases in volume by the absorption of solvent, therefore the lowest layer is lifted, so to speak, into the second. Such a process has been observed by R. O. Herzog and R. Gaebel[1] when viscose is covered by a layer of alkali. In the experiments with nitrocellulose to be sure such a disturbance is not so probable because of the small concentration used. Its absence was in fact proven in the following manner.

In a small bulb 1% nitrocellulose solution (in acetone) was carefully pipetted under acetone with the aid of a fine capillary. At first every ten minutes, later every 30 minutes and finally every hour the Tyndall-cone on the intersurface of the solution and solvent was photographed and the photograph evaluated.

If swelling occurred then the Tyndall-cone should have raised in relation to a mark on the bulb. This however was *not* the case, the photometer curves on the contrary, from which the concentration distribution at various heights of the bulb could be read (since the Tyndall cone represents a relative measure of the concentration of colloid particles), showed a normal course. Immediately after mixing a normal concentration gradient began, which with time mounted even higher in the bulb. The following graph represents such photometer curves (somewhat smoothed out) curve I was obtained 5 minutes after the two liquids were brought in contact, II after 20 minutes more, III

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[1] Kolloid-Z., 35, 193 (1924); 39, 252 (1926).

one hour later, IV $1\frac{1}{2}$ hours after III. For the execution of such experiments we must thank Mr. H. Kunze.

The particle sizes, which were calculated from the diffusion coefficients of the nitrocelluloses made by the mild process described above, lie approximately *in the neighbourhood of the values found from the width of the X-ray interferences* for natural cellulose as well as for the nitrated fibres.[1]

The cellulose crystallite therefore holds together under certain conditions of nitration 1) in fact the single crystallites disintegrate but little or not at all, even when the nitrated fibre is dissolved. The colloid particles in the nitrocellulose solution correspond to the cellulose crystallite in the fibre.

This behavior is the more surprising since dilute (1-2%) solutions are stable for 6 weeks and longer. It seems to us of particular interest to search farther for the causes which determine this cohesion and to seek an exacter understanding of the laws of the disintegration of colloid particles,—whether they be static or controlled by a dynamic equilibrium[2]).

One must expect here in the case of organic colloids quite different reactions, and chemical action also must be carefully considered. For these reasons we have begun to extend our investigation with the aid of an ultracentrifuge.

Summary

Diffusion experiments with nitrocellulose in different solvents are described.

The diffusion coefficients obtained when calculated to water at 20°C as the dispersing medium, lie mostly between 0.015 and 0.021 for the natural fibres.

Methods for obtaining such solutions are described; these methods however do not suffice to guarantee the production of a homodisperse solution of the indicated particle size, still less to explain more exactly the true causes of the cohesion and dispersion.

A few disturbances are pointed out and the line of future investigation is indicated.

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[1] For example, in the case of ramie the particle diameter of the natural fibre is found to be 128×10^{-8} cm., and after nitration and subsequent denitration, 130×10^{-8} cm., i.e. constant. R. O. Herzog: Svensk Pappers Tidning, **1927**, 231 (contains a misprint).

[2] M. Volmer: Z. physik. Chem., **125**, 151 (1927).

THE CONDUCTIVITY OF SOLUTIONS OF SOME ALIPHATIC ORGANIC ACIDS IN WATER AND ETHYL ALCOHOL*

BY HERSCHEL HUNT WITH H. T. BRISCOE

Many investigations have been made to determine the nature of solutions, and many of these have dealt with conductivity measurements. But much remains to be done, before our knowledge, particularly of non-aqueous solutions, is complete. This paper deals with the conductances of solutions of various fatty acids and their substitution products in water and in ethyl alcohol. The effect of the substituent upon the conductivity of the acids in both alcoholic and aqueous solutions and the relative effects of the substituent upon the conductivities of the acids in solutions of the two solvents constitute the chief interests of this paper. Both the character and the position of the substituent have been considered. In so far as conductivity data will serve the purpose, the data have been used to measure the relative ease with which H may be dissociated from the remainder of the acid molecule in each of the two solutions. The effect of substitution upon the strength of the bond has been observed.

It is planned to continue and extend these studies to include conductivity determinations of solutions of aliphatic, aromatic, and unsaturated acids, both mono- and dicarboxylic, in various solvents. The dielectric constants, viscosities, and other physical constants of such solutions will be determined. Such data as we hope to collect may be expected to throw some light upon the relation of the character of solute and solvent molecules to the properties of their solution mixtures.

Much work has already been done on the conductances of aqueous solutions of organic acids. One may mention the work of Ostwald[1] who studied the electrical conductivity of aqueous solutions of some 240 organic acids. Jones[2] has studied the conductivity of solutions of many organic acids as affected by temperature and dilution.

Very little work has been done on solutions of organic acids in other solvents. Wightman, Wiesel, and Jones[3] made conductivity measurements of nine organic acids in ethyl alcohol. Lloyd and Wiesel[4] extended this work to include twenty-nine other acids, most of which were of aromatic character.

The study of the conductivity of alcoholic solutions of acetic and other fatty acids and their substitution products has been neglected and avoided because of the extremely low conductivity of such solutions and the difficulty of at-

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* This paper is a part of a thesis presented by the first named author as a partial fulfillment of the requirements for the degree of Doctor of Philosophy in Indiana University.

[1] Ostwald: Z. physik. Chem., **2**, 561 (1888); **3**, 170, 241, 369 (1889).

[2] H. C. Jones: Am. Chem. J., **44**, 159 (1910).

[3] Wightman, Wiesel, and Jones: J. Am. Chem. Soc., **36**, 2243 (1914); Carnegie Inst. Wash. Pub., No. 210, Chap. III, (1915).

[4] Lloyd and Wiesel: Carnegie Inst. Wash. Pub., No. 230, Chap. VII (1915).

taining a sufficiently sharp minima to make the reading on the bridge possible. Using cells with very low constants and observing the best methods and all the precautions of modern methods of conductivity measurements, we have been able to obtain easily read minima in all the solutions reported herewith.

Experimental

Reagents

Eastman's and Kahlbaum's purest acids were further purified and thoroughly dried by standard and well-known laboratory methods. Purity was tested by melting points and boiling points.

The water used in the investigation had a specific conductivity of 1.2–0.91 × 10^{-6} and was prepared by distillation (1) from alkaline permanganate, (2) from barium hydroxide, and (3) from Nessler's reagent in a block tin still which was fitted with a block tin condenser. Not all the steam of this final distillation was condensed. The distillate was caught in a quartz container.

Ethyl alcohol was treated with sulphuric acid, distilled, and then refluxed for several hours with lime. The lime was prepared by heating hydrated lime for six hours in an electric muffle furnace at a temperature of 600°–700°C. Five hundred grams of this lime were used for each liter of alcohol. After distillation from the lime the alcohol was fractionally distilled using a long fractionating head and a block tin condenser. In all this work cork stoppers were carefully wrapped with pure tin foil. The alcohol prepared in this way was found to have a specific conductance of 75 × 10^{-9}. In all cases the measurements of conductivity were made on solutions for which the solvents had been prepared on the same or the preceding day. Specific conductivity determinations for solvents were made, of course, directly preceding the preparation of the solutions.

Solutions were made up by weight and the various concentrations were prepared by dilution of the mother solutions. Care was taken to make all transfers of liquid away from contaminating air and to prevent evaporation during preparation. In each case at least two mother solutions were prepared. Subsequent dilutions were made from each of them. Data were not accepted unless two such independent determinations agreed within less than 0.2%. The solutions were made in carefully calibrated Jena glass vessels at 25°C. Hence, a correction for the expansion of the solution from 25–30° had to be made. The precautions of Morgan and Lammert[1] were observed in cleaning and filling the cells. All glassware used was first carefully treated and steamed to remove soluble impurities.

The Kohlrausch bridge assembly was employed in the determinations. A Leeds and Northrup Kohlrausch slide wire bridge with extension coils, tunable telephones, a microphone hummer and carefully calibrated resistances were used. A thermostat filled with water was kept constant to within 0.01°C. Beckmann and 0.1° thermometers were used in measuring temperatures in all the work. These were all calibrated by the U. S. Bureau of

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[1] Morgan and Lammert: J. Am. Chem. Soc., **45**, 1693, (1923).

Standards. All parts of the bridge assembly and all wiring were protected by properly grounded shields.

The cells used were of the Washburn type. Their constants were determined by the methods employed by Kraus and Parker.[1] The values of these constants varied from 0.0300 to 0.8752. Cells with the larger constants were used only for water solutions.

All parts of the apparatus, especially the cells, were frequently checked to observe variations. Readings for each solution were made at three different known resistances, time allowance being made for temperature adjustments. The assembly and procedure in making up solutions were tested by repeating conductivity measurements of solutions of organic acids in water. Such determinations checked the results of Jones, Ostwald, and others very closely. The specific conductances of solutions were corrected for the specific conductance of the solvent.

TABLE I
In Alcohol 30°

Dilution	Acetic	Propionic	Butyric	Iso-Butyric	N-Valeric	Iso-Valeric
2	0.003947	0.003060	0.002967	0.002876	0.002860	0.002498
8	0.015226	0.013730	0.013476	0.012689	0.011744	0.009340
32	0.057696	0.045407	0.043380	0.042663	0.041154	0.039056
128	0.218384	0.156912	0.144452	0.134718	0.121265	0.111400
512	0.855070	0.585798	0.553142	0.546366	0.522752	0.500019
1024	1.329120	1.281607	1.253376	1.209628	1.145629	1.000042

Sp. Cond. of alcohol 75 – 214 × 10^{-9} reciprocal ohms.

TABLE II
In Water 30°

Dilution	Acetic	Propionic	Butyric	Iso-Butyric	N-Valeric	Iso-Valeric
2	2.3918	1.9676	1.9498	1.8678	2.7044	
8	4.9456	4.2792	4.4296	4.2472	4.0088	4.4880
32	9.9256	8.5664	8.9664	8.6400	8.2048	9.1936
128	19.6480	17.0112	17.8302	17.1008	16.3840	18.3296
512	38.1952	34.0582	34.5497	34.1555	32.6004	36.5875
1024	53.0125	45.0150	46.2029	46.1414	47.2678	51.8553
2048	77.2301	62.0338	68.5670	63.7337	63.4880	74.5267

Sp. Cond. of water 0.94 – 1.56 × 10^{-6} reciprocal ohms.

TABLE III
In Alcohol 30°

Dilution	N-Caproic	Iso-Caproic	Monochlor-Acetic	Dichlor-Acetic	Trichlor-Acetic	Bromo-Acetic
2	0.003086	0.009444	0.059246	0.253086	2.04740	0.081805
8	0.008192	0.017804	0.111056	0.457648	3.68048	0.156424
32	0.035664	0.041125	0.220464	0.895856	6.59040	0.302099
128	0.152128	0.141914	0.480947	1.761972	11.77165	0.668147
512	0.635136	0.631603	1.195091	4.336896	20.65433	1.342223
1024	1.136128	0.682199	1.636352	7.622686	27.38585	1.614028

Sp. Cond. of EtOH 161 – 200 × 10^{-9} reciprocal ohms.

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[1] Kraus and Parker: J. Am. Chem. Soc., **44**, 2422 (1922).

TABLE IV
In Water 25°*

Dilution	N-Caproic	Iso-Caproic	Monochlor-Acetic	Dichlor-Acetic	Trichlor-Acetic	Bromo-Acetic
2	—	—	—	—	—	—
8	—	—	—	—	—	—
32	7.45	—	72.4	253.1	323.0	68.7
128	14.89	—	127.7	317.5	341.0	122.30
512	29.00	—	205.8	352.2	353.7	199.20
1024	40.31	—	249.2	360.1	356.0	241.20

* Ostwald: Z. physik. Chem., 3, 170 (1889).
Ostwald's values are in Siemens' units.

TABLE V
In Alcohol 30°

Dilution	Cyan-Acetic	Glycollic	Iodo-Acetic	Thioacetic	Pyruvic	Amino-Acetic
2	0.20735	0.041606	0.065808	0.080107	0.16019	—
8	0.32930	0.071616	0.117980	0.147508	0.31040	—
32	0.58054	0.121032	0.213873	0.287508	0.59485	—
128	1.09895	0.252320	0.483904	0.581939	1.19232	—
512	2.16512	0.606464	1.045504	1.165056	2.64090	—
1024	3.01822	0.907161	1.581466	1.600717	3.44064	—

Sp. Cond. of EtOH 127 – 161 × 10^{-9} reciprocal ohms.

TABLE VI
In Water

Dilution*	Cyan-Acetic	Glycollic*	Iodo-* Acetic	Thioacetic*	Pyruvic*	Amino-* Acetic
2	—	—	—	—	30.104	0.27678
8	—	—	—	—	59.025	0.33164
32	105.3	24.79	50.60	42.05	105.644	0.43891
128	176.4	47.50	94.31	79.84	169.454	0.66816
512	260.9	88.00	164.50	139.10	236.707	2.14016
1024	297.3	116.70	207.00	176.80	257.720	2.45453

* 30° values in reciprocal ohms.
** Ostwald: Z. physik. Chem., 3, 170 (1889). 25°

TABLE VII
In Alcohol 30°

Dilution	a-Bromopropionic	b-Bromopropionic	a-Bromo-butyric	a-Brom-iso-butyric	a-Brom-Valeric	a-Bromo-iso Valeric
2	0.037452	0.022487	0.03856	0.02790	0.02760	0.05653
8	0.077060	0.036360	0.07103	0.05604	0.05871	0.08955
32	0.157320	0.062784	0.13853	0.10804	0.13952	0.14861
128	0.328614	0.117760	0.36422	0.26541	0.33139	0.27960
512	0.727219	0.303129	0.78080	0.53391	0.74393	0.59241
1024	0.854784	0.656607	1.38404	1.20934	0.77629	0.84408

Sp. Cond. of EtOH 135 – 226 × 10^{-9}.

TABLE VIII
In Water 30°

Dilution	a-Bromopropionic**	b-Bromopropionic*	a-Bromo-* butyric	a-Bromo-iso Butyric	a-Bromo-Valeric	a-Bromo-iso Valeric
2	—	—	—	—	—	—
8	—	—	—	36.84	—	40.34
32	—	19.48	—	83.81	—	79.51
128	110.4	37.36	109.0	157.79	—	138.80
512	185.3	70.66	180.0	262.63	—	225.84
1024	225.0	95.25	218.0	330.70	—	271.08

*P. Walden: Z. physik. Chem., 10, 638 (1892).
Walden's values are given in Siemens' units at 25°.

Discussion of Results

Variations in the conductivity of the same substance in different solvents are usually explained by differences in dielectric constants, viscosities, association factors, and molecular complexities of the solvents. The results of this investigation show that the molecular conductivity in aqueous solution is 40–1000 times as great as the conductivity of the same acid in ethyl alcohol. When one considers the conductance of strong electrolytes in alcoholic solutions, these great variations in conductivity values are difficult to explain on the basis of the above-named properties of the solvents.

TABLE IX
Organic Radicals in the Order of their Effect upon Conductivity

Temperature 30° Alcoholic Solutions	Concentration N/512 Aqueous Solutions
1. CH_2BrCH_2 --	1. $CH_2(NH_2)$ --
2. $CH_3CH(CH_3)CH_2$ --	2. $CH_3CH_2CH_2CH_2CH_2$ --
3. $CH_3CH_2CH_2CH_2$ --	3. $CH_3CH_2CH_2CH_2$ --
4. $CH_3CBr(CH_3)$ --	4. CH_3CH_2 --
5. $CH_3CH(CH_3)$ --	5. $CH_3CH(CH_3)$ --
6. $CH_3CH_2CH_2$ --	6. $CH_3CH_2CH_2$ --
7. CH_3CH_2 --	7. $CH_3CH(CH_3)CH_2$ --
8. $CH_3CH(CH_3)CHBr$ --	8. CH_3 --
9. CH_2OH --	9. CH_2BrCH_2 --
10. $CH_2(CH_3)CH_2CH_2CH_2$ --	10. $CH_2(OH)$ --
11. $CH_3CH_2CH_2C_2H_2CH_2$ --	11. CH_2I --
12. CH_3CHBr --	12. CH_3CH_2CHBr --
13. $CH_3CH_2CH_2CHBr$ --	13. CH_3CHBr --
14. CH_3CH_2CHBr --	14. CH_2Br --
15. CH_3 --	15. CH_2Cl --
16. CH_2I --	16. $CH_3CH(CH_3)CHBr$ --
17. CH_2Cl --	17. CH_3CO --
18. CH_2Br --	18. $CH_2(CN)$ --
19. $CH_2(CN)$ --	19. $CH_3CBr(CH_3)$ --
20. CH_3CO --	20. $CHCl_2$ --
21. $CHCl_2$ --	21. CCl_3 --
22. CCl_3 --	

The effect of increase in dilution is to increase the molecular conductivity. The increase in conductivity in most cases is almost proportional to the volume. This relation is shown graphically in Fig. 1

For the purposes of interpolation and extrapolation the values of the molecular conductances at different concentrations are plotted against the cube root of the concentration. It is not possible to estimate the molecular conductivity at infinite dilution from these graphs because sufficiently high dilutions of these weak acids could not be run in alcohol to determine accurately where the curve cut the Y-axis. We expect later to determine the percentage ionization of these acids in alcohol.

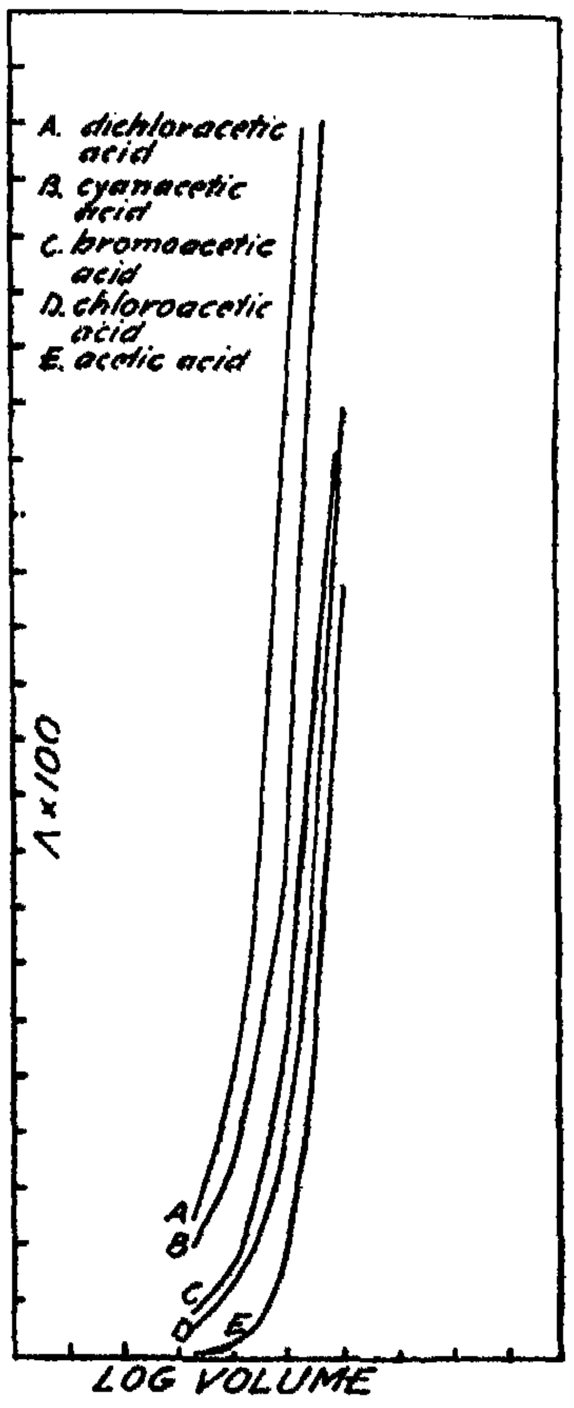


FIG. 1

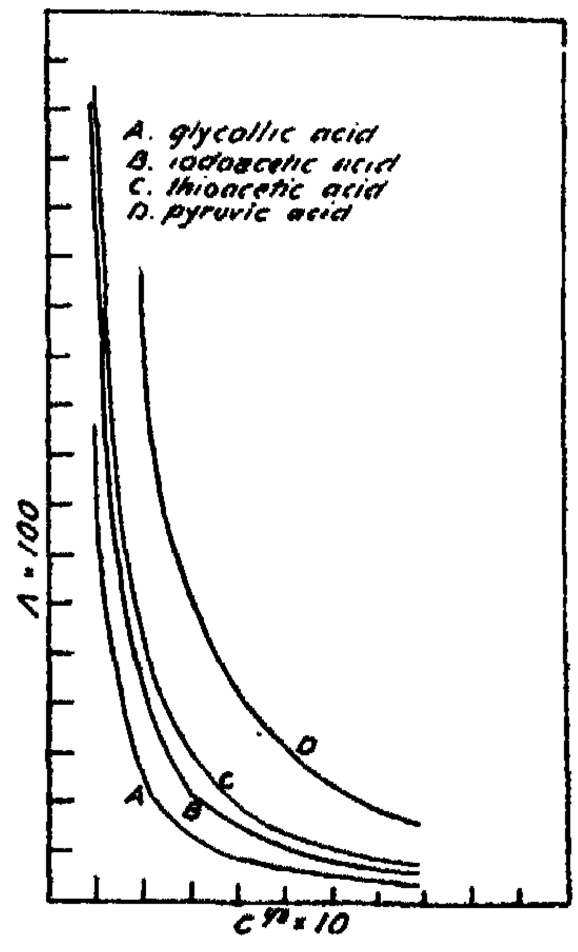


FIG. 2

In Table IX we have arranged the acids in the order of their conductances in the two solvents. This was done in order that we may emphasize the important effect which constitution of the molecule of the solute has upon its conductance in the same and in different solvents. Acetic acid, for instance, stands fifteenth in the alcoholic series and eighth in the water series. Although beta-bromopropionic acid is the poorest conductor in alcoholic solutions it conducts better than eight other acids in the water solutions. In many cases decided shifts in the order are to be noted. The greatest differences are found in solutions of those acids containing the groups $CH_3CHBrCH_2-$; $(CH_3)_2CBr-$; $(CH_3)_2CHCHBr-$; and $C_5H_{11}-$.

With an increase in CH_2 groups one would look for a simultaneous decrease in conductivity. This is true in alcoholic solutions until we reach caproic acid, which has a conductance greater than either propionic, butyric, or valeric, and iso-caproic has a conductance greater than normal caproic in concentrated solutions but falls below caproic in a N/512 solution. Even this regularity is not found in aqueous solutions.

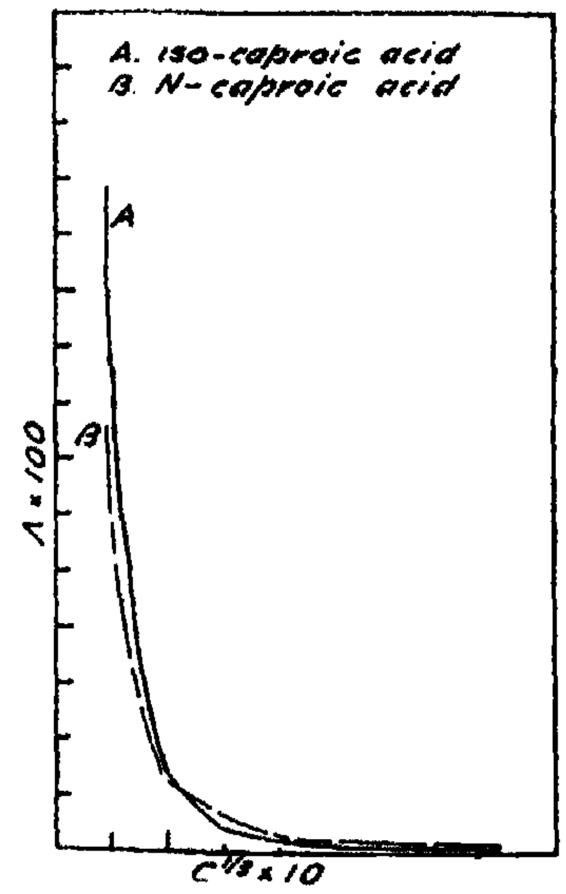


FIG. 3

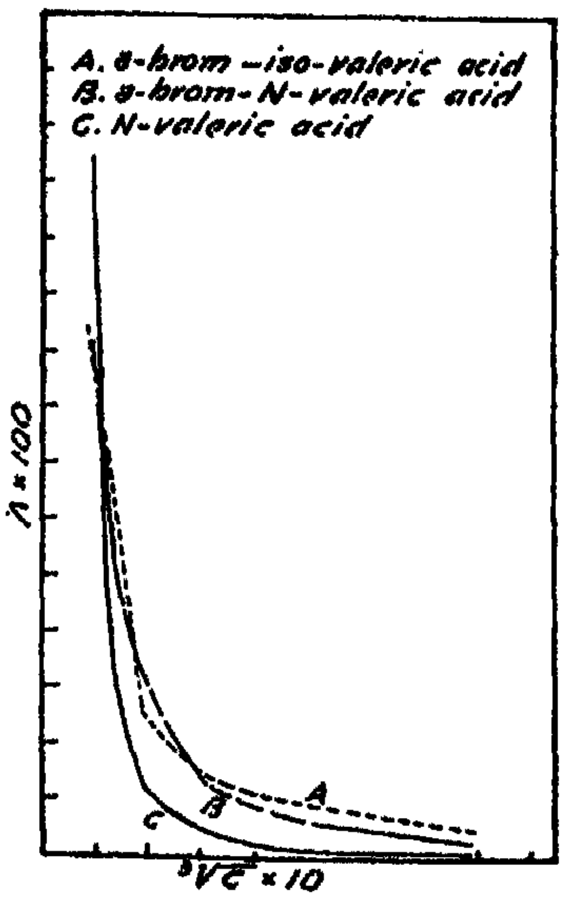


FIG. 4

In alcoholic solutions the iso-acids have a lower conductance than the corresponding normal acids, but in water iso-butyric has a lower molecular conductance than butyric acid, while iso valeric acid has a greater conductivity than valeric acid. Unfortunately, we have only these two pairs of isomers to compare in aqueous solutions.

An increase in the number of chlorine atoms in the molecule of acetic acid causes an increase in the molecular conductivity.

It will be noticed that the CN radical and the OH radical both cause a great increase in conductance. The substitution of oxygen for the two hydrogens on the alpha-carbon atom of propionic acid increases its conductance many times. The substitution of NH_2 for a hydrogen atom in acetic acid lowers the conductance almost 94%. This can probably be explained on the assumption that part of the hydrogen ions which are formed by the ionization of the carboxyl radical unite with the basic NH_2 radical. If such is the case, only after equilibrium has been reached in this system will we have the acid liberating hydrogen ions.

Table IX may be looked upon as a series of radicals or groups in the order of their electronegativities. The order, of course, can be looked upon as correct, only in so far as conductivity data alone can be taken as a measure of the strengths of the acids and the case with which electronic bonds between hydrogen and oxygen in the carboxyl group may be broken.

The Stark-Lewis hypothesis assumes that the degree of ionization of an acid is dependent upon the strength of the bonds between the oxygen and the hydrogen in the carboxyl group. Furthermore, we would expect from this hypothesis that the more electronegative the substituent the more highly ionized the acid. Other factors being equal the acid containing the more negative substituent group should have the greater conductance, provided conductance depends only upon the dissociation of the acid by breaking the oxygen-hydrogen bond in the carboxyl group. For example, chloracetic acid should be stronger than iodoacetic acid and therefore have a greater conductance. We would expect the two acids to have a structure somewhat as follows, since we know that chlorine is more negative than iodine.

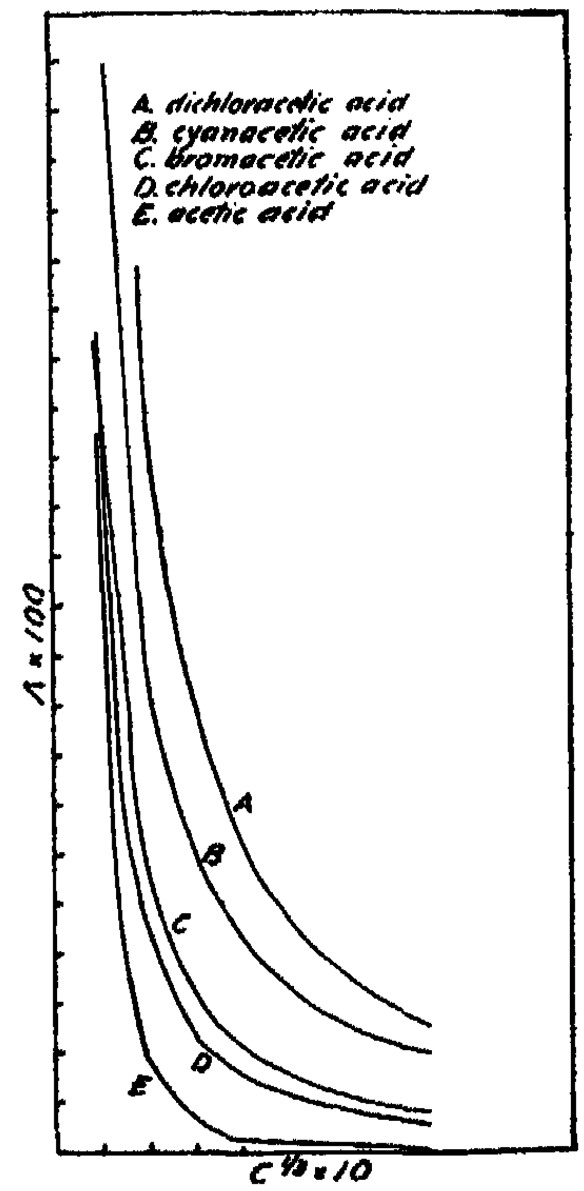


FIG. 5

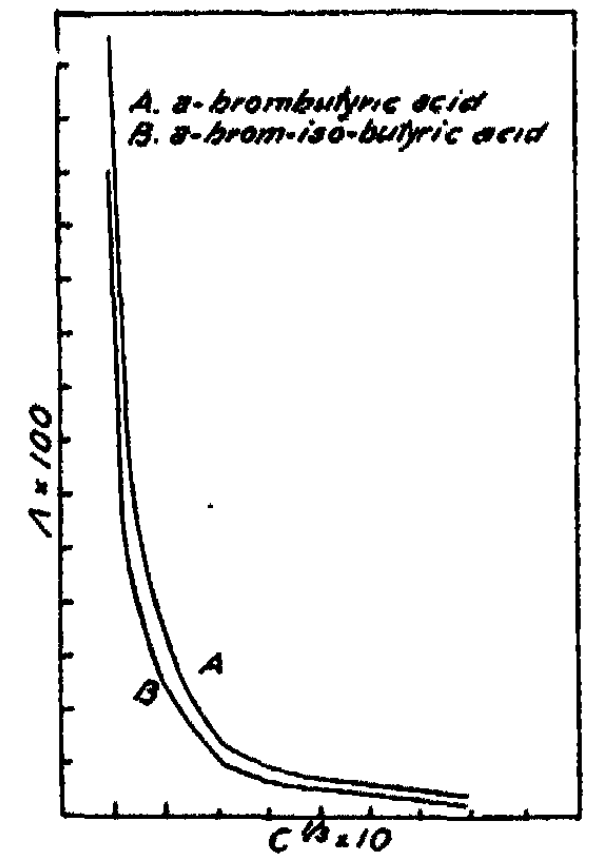
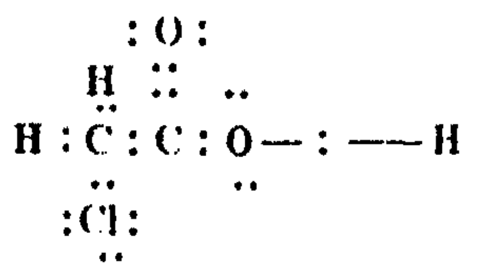
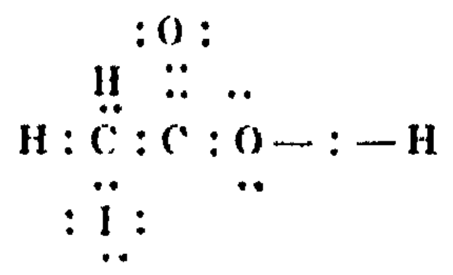


FIG. 6



$$\begin{array}{cccccccc} & & :O: & & & & & \\ & H & :: & \cdot\cdot & & & & \\ H: & \ddot{C} & :C: & O & - & : & -- & H \\ & \cdot\cdot & & \cdot\cdot & & & & \\ & :\underset{\cdot\cdot}{Cl}: & & & & & & \end{array}$$



$$\begin{array}{cccccccc} & & :O: & & & & & \\ & H & :: & \cdot\cdot & & & & \\ H: & \ddot{C} & :C: & O & - & : & - & H \\ & \cdot\cdot & & \cdot\cdot & & & & \\ & :\underset{\cdot\cdot}{I}: & & & & & & \end{array}$$

In the acetic acid molecule the electron pair between oxygen and hydrogen lies somewhat nearer the oxygen atom than the hydrogen. When chlorine replaces one hydrogen in the methyl group, the electron pair between chlorine and carbon is pulled away from the carbon and toward the chlorine atom. This causes a rearrangement of the other electron pairs about the carbon atom, which in turn, causes a shift in the position of the electrons about the carbon and oxygen atoms of the carboxyl group. This shift is toward the part of the molecule into which chlorine is introduced. In the case of the oxygen-hydrogen linkage of the carboxyl group, the electron pair is drawn closer to the oxygen and farther away from hydrogen. This amounts to a decrease in the strength of this bond, and an increase in the extent to which the acid may be expected to dissociate. Since chlorine is more electro-negative than iodine, it should have a more pronounced effect when introduced as a substituent. On these assumptions we would expect chloracetic acid to have a greater conductance than bromoacetic acid and it in turn to have a greater conductance than iodoacetic acid. This is true in aqueous solutions, but in alcoholic solutions we find the conductance decreases from bromoacetic to chloracetic to iodoacetic acid.

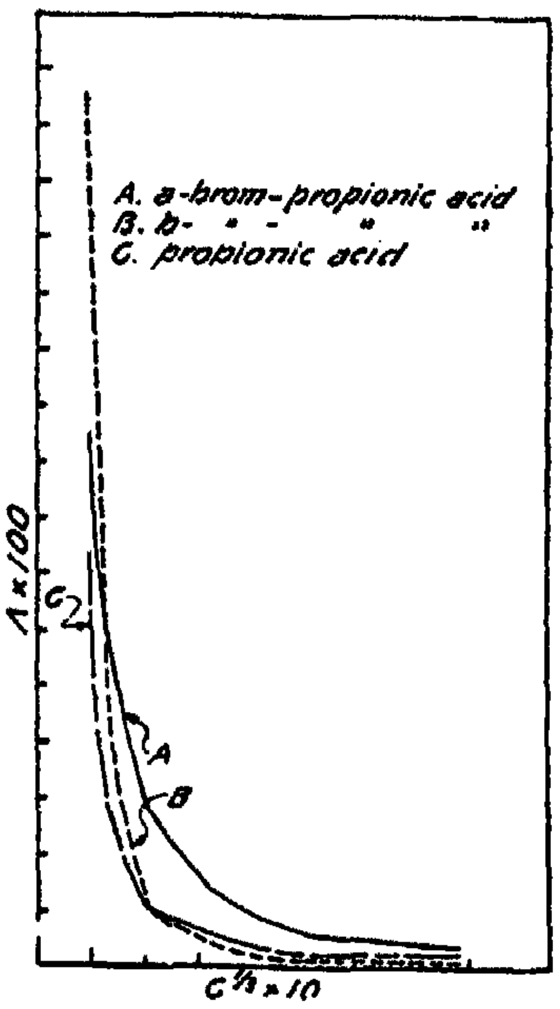


Fig. 7

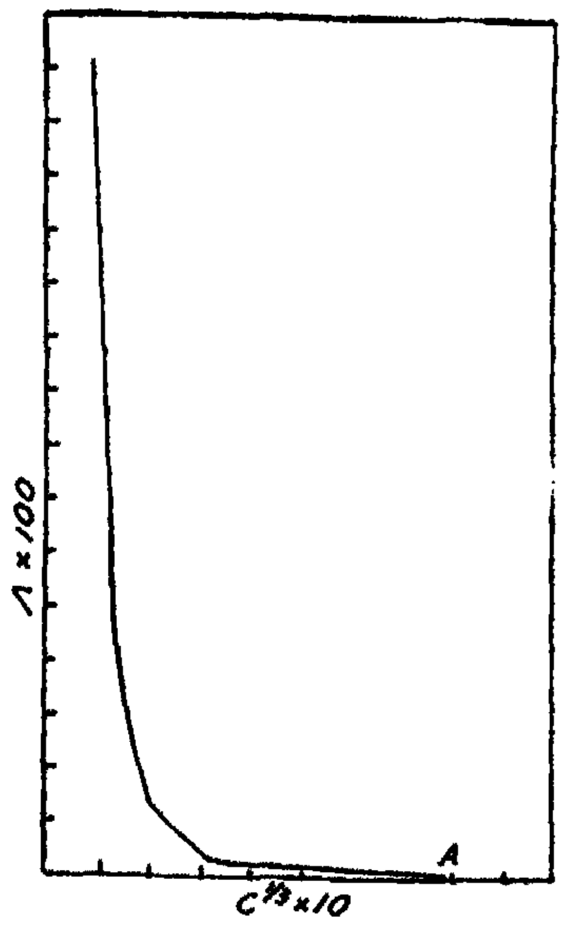


Fig. 8

A. N-butyric acid

It was found that iso-butyric acid fell just a short distance below N-butyric acid, having the same curvature.

Table IX reveals other instances in which conductivity data does not support the theory. It is understood that other factors, such as molecular association, may account for some of these discrepancies.

It is interesting to compare the order of organic radicals in Table IX with Kharasch's table[1] of electronegativities. It is found that the alcoholic series agrees with Kharasch's work but that the water series reveals some differences in position.

Conclusions

1. All the acids studied have a much lower molecular conductance in alcohol than in water.

2. The rate of increase of molecular conductance for the successive dilutions is about twice as great in alcohol as in water.

3. The homologous fatty acids fall in a series with a decreasing molecular conductance as the number of carbon atoms increase. Isovaleric acid in water solutions and the caproic acids in alcohol are exceptions.

4. The data do not consistently confirm Lewis' theory of the effect of substitution of groups possessing different electrical characteristics upon the strength of the acid. This conclusion is true, of course, only in so far as conductivity data can be taken as evidence of the stability of the electronic bond between hydrogen and oxygen in the carboxyl group.

5. The acids do not have the same relative conductivities in alcohol and in water solutions.

6. The substituent radicals have been arranged in the order of their effect upon the conductivity of the acid molecule in both water and alcohol.

7. The log-volume conductance curves show agreement with the mass action law at high dilutions.

8. Simple and efficient means for preparing conductivity alcohol have been given.

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[1] Kharasch: J. Chem. Ed., 5, 404 (1928).

ELECTRICAL CONDUCTION IN TEXTILES. II

Alternating Current Conduction in Cotton and Silk

BY E. J. MURPHY

The first paper[1] of this series described an investigation of the dependence of the resistivity of certain textiles on relative humidity and moisture content. The present paper will give the results of a similar investigation of alternating-current conduction. The data show the variation of the equivalent parallel capacity and conductivity of cotton and silk with humidity. The effect of electrolytic material in the textile on the a.c. capacity, the a.c. conductivity and the d.c. conductivity was also determined; this has proved to be a useful way of investigating the conduction processes. The alternating-current conductances of the samples were also compared with their direct-current conductances over a large range of humidity. Data were obtained on the variation of the equivalent parallel capacity and conductance of cotton samples with frequency in the telephonic range. The main conclusions are that the water paths through which direct current conduction takes place in the textile act as electrolytic cells having a polarization capacity which accounts for most of the capacity of textiles except at low humidities; that the a.c. and d.c. conductivities of cotton are equal within the precision of the measurements at humidities above 80-85% (and dielectric losses therefore practically completely accounted for by the direct-current conductivity in this range of humidity); and that the a.c. conductivity is strongly affected by the electrolytic material in the textile even at humidities where only a small part of it is due to d.c. conductivity.

Alternating-Current Capacity of Cotton and Silk

The alternating-current capacity of textiles and other similar moisture absorbing materials increases with increasing moisture content and decreases with increasing frequency.[2-5] One way of explaining these effects is to regard the water as one component of a non-homogeneous dielectric to which Maxwell's theory of absorption as extended to alternating electric fields is applicable. U. Meyer[6] has concluded that the effect of absorbed moisture on the capacity and loss angle of certain dielectrics is in agreement with the consequences of this theory where the water is regarded as one layer of a three-layer dielectric. In this theory the capacity depends both on the dielectric constant and the conductivity of the absorbed water. DuBois[7] has sug-

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[1] J. Phys. Chem., **32**, 1761 (1928).

[2] H. Jordan: Elektrotech. Z., **32**, 262 (1911).

[3] K. W. Wagner: Archiv Elektrotech., **3**, 67 (1914).

[4] Fleming and Dyke: J. Inst. El. Eng., **49**, 323 (1912).

[5] C. Lubben: Archiv Elektrotech., **10**, 282 (1921).

[6] U. Meyer: Verh. deutsch. physik. Ges., **19**, 139 (1917).

[7] D. DuBois: J. Am. Inst. El. Eng., **41**, 688 (1922).

gested another type of explanation in which the water appears to be regarded as essentially a conductor. He considers that some of the absorbed moisture is distributed as droplets and filaments which reduce the effective separation of the electrodes and thereby increase the capacity. A somewhat similar explanation has been proposed by Setoh and Toriyama,[8] who consider that the absorbed moisture forms conducting paths, some of which bridge the electrodes and some of which only extend part of the way between them: the latter they consider to be equivalent to a capacity in series with a resistance and the former to a shunting resistance. In these two theories the increase in capacity appears to be regarded as due to water which is distributed through the dielectric as droplets or short filaments or in some other way such that it is more or less insulated from one or both of the electrodes. However, there is no experimental evidence that any of the absorbed moisture in textiles is necessarily insulated from the electrodes and takes no part in direct-current conduction. In the explanation of the capacity of cotton which will be described below, most of the capacity is attributed to effects of water which forms continuous filaments connecting the electrodes and providing a path for direct-current conduction.

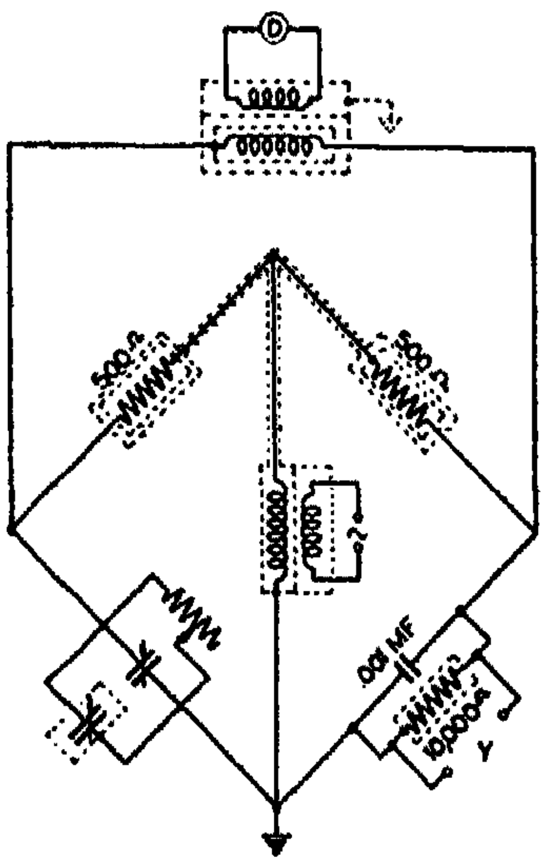

FIG. 1
Conductance and Capacity Bridge
Y represents the admittance of the sample to be measured. It is not shown, but would be connected to the terminals shown in the diagram.

The direct-current conductivity of a textile is practically entirely due to the absorbed moisture and the electrolytic material which it dissolves from the natural constituents of the textile.[1] This indicates the presence of continuous water paths connecting the two electrodes. These water paths form with the electrodes a kind of electrolytic cell which would be expected to have a polarization capacity like an ordinary electrolytic cell. The properties of the polarization capacity of electrolytic cells will be compared below with the properties of the capacity of cotton and silk.

The samples used in this investigation have been described in detail in a previous paper.[1] They were of two kinds: "Threads," which consist essentially of cotton threads attached to two brass electrodes 1.3 cm apart, and "Twisted Pairs" made by twisting two cotton insulated wires together for a length of about 5 cm. Some of these samples were tested in their normal condition while others were washed to reduce the amount of electrolytic material in them.

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[8] Setoh and Toriyama: Inst. Phys. Chem. Res. (Tokyo), Sci. Papers, 3, 483 (1926).

A diagram of the bridge used is shown in Fig. 1. The shielding is also shown. Since the ratio arms give a 1:1 ratio, the condition for balance is that the admittances of the third and fourth arms be equal. If C_1 and C_2 are the

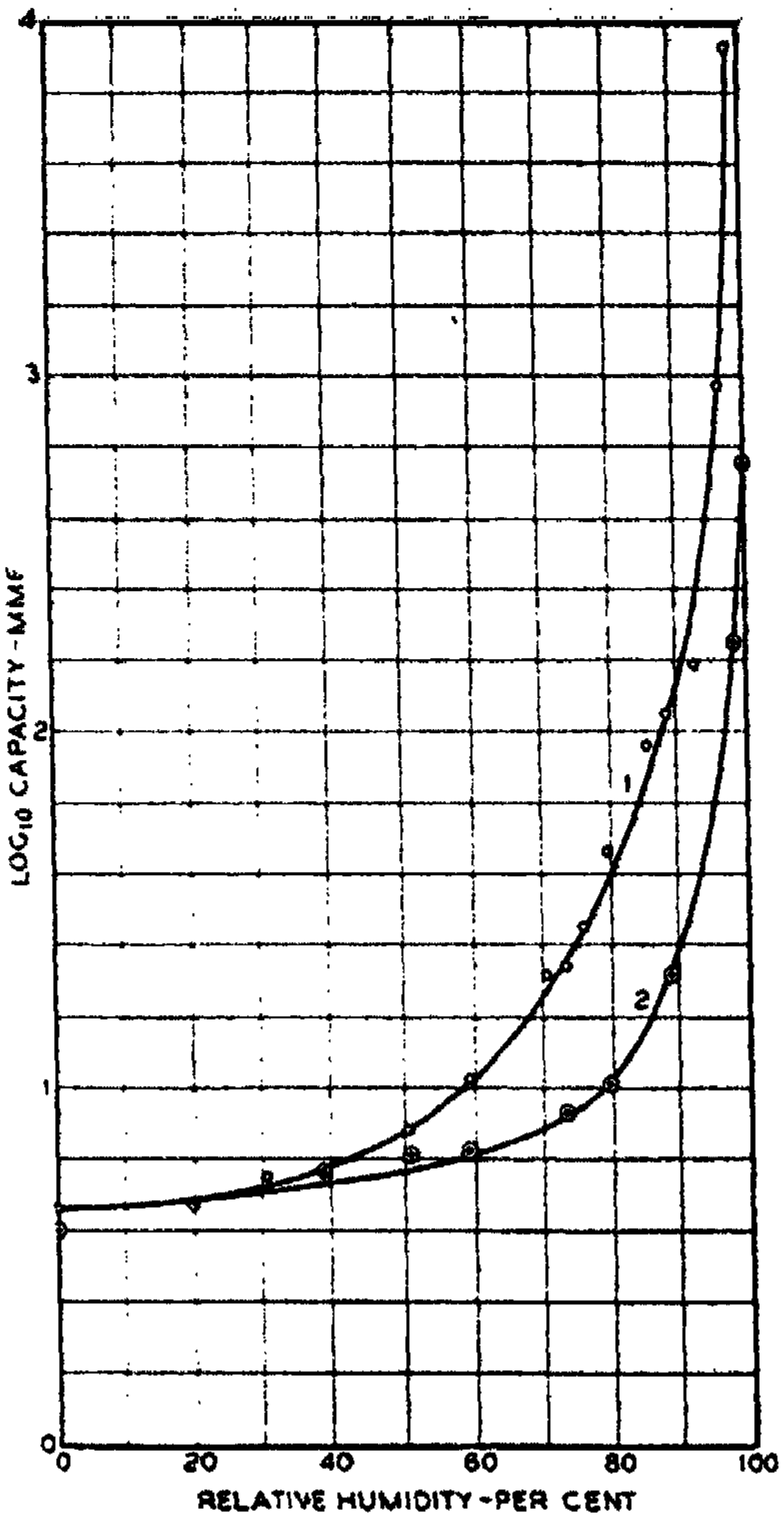

Fig. 2

Equivalent Parallel Capacity of Cotton as a Function of Humidity

1. Twisted Pairs I (normal electrolyte content).
2. Twisted Pairs II (low electrolyte content).

Frequency—1000 cycles per second

readings of the standard condenser when the sample is connected in the fourth arm and when it is disconnected, respectively, and R_1 and R_2 the corresponding readings of the standard resistance, then C_1-C_2 is the equivalent parallel capacity, and $1/R_1 - 1/R_2$ the equivalent parallel conductance of the sample (the conductance of the mica condenser being added when it is used).

The data in Table I and the curves in Fig. 2 show that the capacity of cotton increases very rapidly with increasing humidity and that it also depends to a very large extent on the amount of electrolytic material contained in the textile. For example, the capacity of Twisted Pairs I is 1880 times as great at 98.6% humidity as at approximately 0%; and at 98.6% humidity the capacity of Twisted Pairs II, which contains considerably less than the normal amount of electrolytic material, is only about 1/48th as great as that of Twisted Pairs I, which contains the normal amount. Table II shows that the capacity decreases with increasing frequency with greater rapidity the higher the humidity.

The fact that at high humidities the capacity is strongly affected by the amount of electrolytic material in the cotton indicates that it is of such a nature as to be sensitive to changes in the conductivity of the absorbed moisture, for the dielectric constant of aqueous solutions of electrolytes is only slightly affected by changes in concentration, and for small concentrations

TABLE I

Equivalent Parallel Capacity of Cotton Threads and Twisted Pairs at 1000 cycles/sec. as a Function of Humidity and Electrolyte Content.
Temperature 25°C. Capacities in mmf.

Electrolyte Content:	Normal	Low	Normal	Low
Relative Humidity Percent	Twisted Pairs I	Twisted Pairs II	Cotton Threads I	Cotton Threads II
0.	4.6	4.0	6.3×10^{-3}	5.6×10^{-3}
6.0	—	—	—	5.6
19.5	4.8	—	—	—
30.0	5.7	5.7	—	—
38.8	—	5.9	6.4	4.2
50.5	7.7	6.4	6.8	10.0
59.0	10.7	6.7	7.4	9.9
70.8	20.9	—	8.2	—
73.0	22.1	8.4	13.1	10.2
75.5	28.7	—	13.5	—
79.1	46.8	10.2	13.5	—
85.2	93.0	—	12.5	—
88.4	114.5	20.8	16.0	12.1
92.0	155.6	—	45.5	—
96.3	947.0	—	108.0	—
98.6	8700.0	179.2	268.0	10.4
99.9	—	580.0	—	—

These are the capacities of a single Twisted Pair or Thread sample plus the capcity of the mounting, which was small.

TABLE II

Equivalent Parallel Capacity and Conductance of Cotton as a Function of Frequency and Humidity.
Temperature 25°C

	Relative Humidity Percent	Capacity mmf. Frequency: 500	1000	2000	Conductance mmho. Frequency: 500	1000	2000
Twisted Pairs I	50.5	9.4	9.4	6.5	1.0×10^{-2}	1.4×10^{-2}	1.8×10^{-2}
	59.0	14.0	12.3	10.6	3.1×10^{-2}	3.9×10^{-2}	5.2×10^{-2}
	73.0	24.6	20.5	15.4	1.8×10^{-1}	1.9×10^{-1}	2.3×10^{-1}
Twisted Pairs II	38.8	6.37	6.28	6.22	0.72×10^{-3}	1.20×10^{-3}	1.80×10^{-3}
	50.5	6.23	6.24	6.90	2.26×10^{-3}	3.07×10^{-3}	4.54×10^{-3}
	59.0	8.20	7.82	7.47	5.40×10^{-3}	7.25×10^{-3}	10.1×10^{-3}
	73.0	12.0	—	9.7	2.53×10^{-2}	—	4.14×10^{-2}
	79.1	22.3	19.9	12.5	6.32×10^{-2}	7.52×10^{-2}	9.50×10^{-2}
	88.4	19.8	19.1	15.5	2.22×10^{-1}	2.34×10^{-1}	2.64×10^{-1}
	98.6	263.0	146.0	76.6	1.28×10	1.31×10	1.29×10
	99.9	847.	384.	154.	3.14×10	3.02×10	—
Cotton Threads II	50.5	—	10.0	9.9	—	1.2×10^{-6}	3.1×10^{-6}
	73.0	—	10.3	10.2	—	5.0×10^{-6}	5.6×10^{-6}
	88.4	—	11.9	11.4	—	8.1×10^{-5}	8.3×10^{-5}
	98.6	15.6×10^{-3}	10.5	10.4	1.84×10^{-3}	1.85×10^{-3}	1.85×10^{-3}

The data refer to a single Twisted Pair or Thread Sample plus the mounting.

decreases with increasing concentration.[9] Polarization capacity is a kind of capacity which depends on the conductivity of the solution rather than on its dielectric constant.

There is good qualitative agreement between the characteristics of the polarization capacity of electrolytic cells[10-13] and the alternating current capacity of cotton and silk. Both are very large; both increase with increase in the concentration of the electrolyte[10] (the concentration of the electrolyte in a textile being measured by its ash content); and both decrease with increasing frequency. An exact quantitative comparison between them cannot be made with the available data because polarization capacity depends on a number of factors such as electrode material, nature of the electrolyte, and current, but the order of magnitude of polarization capacities and of their rate of change with electrolyte concentration and frequency appears to be about the same as that of the corresponding quantities for cotton and silk at high humidities.

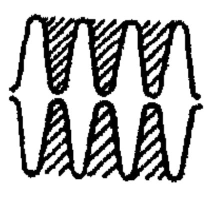

FIG. 3

The moisture which forms continuous conducting paths between the electrodes may contribute to the total capacity also in another way, besides in having a polarization capacity. One of the simplest ways of explaining a number of the facts regarding conduction in textiles is to assume that the resistivity of the water-paths depends more on their form than on the total amount of absorbed moisture or its specific conductance, and there is some basis for considering that the conducting water-paths in a textile form a regular space-pattern or network composed of similar elements possibly corresponding to some structural unit in the interior of the textile material.[1] It is possible that the elements of this network are formed in such a way that a cross-section parallel to the direction of current flow through one of the filaments would in effect have a form something like the sketch in Fig. 3; the unshaded area is water. If the thickness of the constricted sections of the water-paths increases rapidly with moisture content, the rapid change of the resistivity of the textile with moisture content would be explained. Each similar element of such a network would have a geometric capacity to its neighbors and the d.c. conduction paths could therefore be regarded as having a regularly distributed capacity essentially very similar to the distributed capacity of a resistance coil. The impedance of such a network to alternating current might be appreciably less than its d.c. resistance.

These considerations indicate that the total capacity C of a textile sample may be regarded as composed of the following components:

$$C = C_1 + C_2 + C_3 + C_4 \ldots,$$

where C_1 is the polarization capacity of the continuous water-paths connecting the electrodes, C_2 the regularly distributed capacity of these water-paths,

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[9] R. Pechhold: Ann. Physik, (4) 83, 427 (1927).

[10] C. B. Jolliffe: Phys. Rev., (2) 22, 293 (1923).

[11] I. Wolff: Phys. Rev., (2) 27, 755 (1926).

[12] R. T. Lattey: Phil. Mag., (6) 50, 444 (1925) (contains bibliography).

[13] B. B. Banerji: Trans. Faraday Soc., 22, 111 (1926).

and C_3, C_4 . . . are contributions to the total capacity from other sources, such as the solid dielectric, all of these quantities being equivalent parallel capacities. The present results suggest that C_1 predominates at humidities above 30–40%.

The several components of the total equivalent parallel capacity of a textile would be expected to vary differently with frequency. The part due to polarization capacity should follow the same law of variation with frequency as the polarization capacity of an electrolytic cell. Banerji[13] has found that when the capacity of an electrolytic cell is plotted against the square of the frequency an hyperbola is obtained. In the small range of frequency for which data on cotton are available this relationship can also be expressed approximately by $C = C_0f^{-n}$, a relationship which has been found also by some other observers.[14] The most favorable condition for comparing cotton with an electrolytic cell is the highest humidity at which accurate measurements can be made. The data for the capacity of cotton at 98.6% humidity satisfy this equation approximately, the value of n being 0.9. The value of n for an electrolytic cell varies with electrode material, electrolyte concentration, etc., but lies in general between about .3 and 1.[12,13] These values are of the same order of magnitude as the value of n for cotton at high humidities. Banerji has found that the relationship between the capacity of an electrolytic cell and the frequency would be accounted for by the presence at each electrode of a small capacity shunted by a low resistance and in series with a large capacity shunted by a high resistance. The small capacity is regarded as due to the Helmholtz double layer and the larger one to concentration changes in the electrolyte produced by the current. The polarization capacity of a textile should consist of a similar network.

If the water-paths are formed as suggested above, their distributed capacity should also vary with frequency. The elements of the network may be regarded as composed of similar elements consisting of a high resistance in parallel with a large capacity (the narrow sections of the water filaments) and in series with a low resistance which is in parallel with a small capacity (the thickened sections of the filament). Such a network is essentially the same as a Maxwell dielectric of two layers, whose variation with frequency is given by Meyer.[6] It is also the same type of network as found by Banerji for electrolytic cells. The cause of the variation of equivalent parallel capacity with frequency is therefore essentially the same in the three cases, polarization capacity, non-homogeneity of the dielectric, or a regularly distributed capacity of the water-paths; namely, that the method of measurement consists in balancing a capacity shunted by a resistance against a more complex network containing capacities which are in series with resistances.[15] Con-

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[14] See tabulation of relationships found by different observers in ref. 12.

[15] The equivalent parallel capacity C_p of a simple network consisting of a resistance in series with a capacity varies with frequency according to $C_p = \frac{{}_sC}{1 + (R_sC_s\omega)^2}$, where C_s and R_s are the capacity and resistance which are in series and ω is 2π × frequency. The capacity of more complex networks is also a similar type of function of the frequency.

sequently, it seems probable that the various components of the capacity of a textile vary with frequency according to similar laws, but at different rates (i.e., have different values of n) and that the relative prominence of the different components depends on the humidity. Table II shows that the rate of change of capacity with frequency decreases as the humidity decreases.

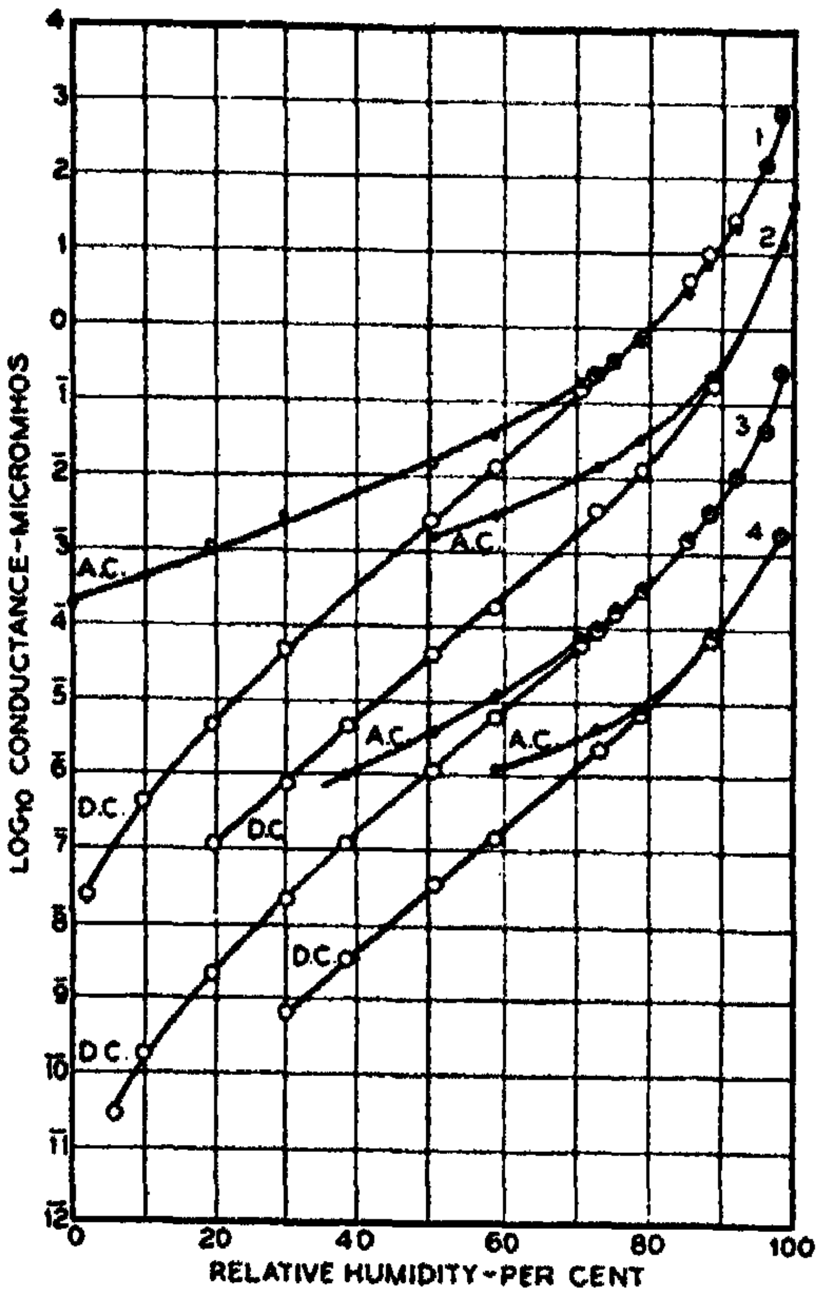

FIG. 4
The A. C. and D. C. Conductivities of Cotton as Functions of Humidity.
The curves show the relationship between a.c. and d.c. conductivity and the effect upon them of differences in the electrolyte content of the samples.

o D.C. Conductances • A.C. Conductances
1. Twisted Pairs I (normal electrolyte content)
2. Twisted Pairs II (low electrolyte content)
3. Cotton Threads I (normal electrolyte content)
4. Cotton Threads II (low electrolyte content)

The conductances are for a single Twisted Pair, or Thread sample. The curves were plotted from Table III.

Alternating-Current Conductivity and Dielectric Loss

The alternating-current conductivity of moisture absorbing, and other dielectrics is in general much greater than their direct current conductivity, and the energy losses in a dielectric are therefore considerably greater for alternating than for direct current. Many theories have been proposed to

TABLE III

The A.C. Conductivity of Cotton as a Function of Humidity and Electrolyte Content and its Relation to the D.C. Conductivity. This table gives the equivalent conductance at 1000 cycles, and the d.c. conductance at 100 volts. The data are for a single Thread or Twisted Pair sample. Temperature 25°C.

Sample:	Cotton Threads I		Cotton Threads II		Twisted Pairs I		Twisted Pairs II	
Electrolyte Content:	Normal		Low		Normal		Low	
Rel. Humidity Percent	D.C. mmho.	A.C. mmho.	D.C. mmho.	A.C. mmho.	D.C. mmho.	A.C. mmho.	D.C. mmho.	A.C. mmho.
0. (ca.)	—	—	—	—	7.70×10^{-9}	1.94×10^{-4}	—	—
2.	—	—	—	—	2.46×10^{-8}	—	—	—
6.	3.05×10^{-11}	—	—	—	—	—	—	—
10.	1.76×10^{-10}	—	—	—	4.55×10^{-7}	—	—	—
19.5	2.24×10^{-9}	—	—	—	4.90×10^{-6}	1.14×10^{-3}	1.18×10^{-7}	—
30.0	2.11×10^{-8}	—	7.17×10^{-10}	—	4.77×10^{-5}	2.76×10^{-3}	7.94×10^{-7}	—
38.8	1.24×10^{-7}	1.00×10^{-6}	3.54×10^{-9}	—	—	—	4.33×10^{-6}	—
50.5	1.16×10^{-6}	3.50×10^{-6}	3.28×10^{-8}	—	2.63×10^{-3}	1.42×10^{-2}	4.08×10^{-5}	1.47×10^{-3}
59.0	6.17×10^{-6}	1.10×10^{-5}	1.49×10^{-7}	1.25×10^{-6}	1.32×10^{-2}	3.52×10^{-2}	1.74×10^{-4}	2.93×10^{-3}
70.8	5.82×10^{-5}	7.52×10^{-5}	—	—	1.56×10^{-1}	1.91×10^{-1}	—	—
73.0	8.70×10^{-5}	9.60×10^{-5}	2.28×10^{-6}	5.00×10^{-6}	2.38×10^{-1}	2.15×10^{-1}	3.50×10^{-3}	1.36×10^{-2}
75.5	1.49×10^{-4}	1.80×10^{-4}	—	—	3.54×10^{-1}	3.60×10^{-1}	—	—
79.1	3.05×10^{-4}	3.34×10^{-4}	7.25×10^{-6}	8.75×10^{-6}	7.88×10^{-1}	6.58×10^{-1}	1.26×10^{-2}	2.95×10^{-2}
85.2	1.56×10^{-3}	1.67×10^{-3}	—	—	4.10	2.94	—	—
88.4	3.62×10^{-3}	3.88×10^{-3}	—	—	9.80	6.42	—	—
89.0	—	—	7.30×10^{-5}	8.15×10^{-3}	—	—	1.63×10^{-1}	2.26×10^{-1}
92.0	1.01×10^{-2}	1.02×10^{-2}	—	—	2.84×10^{1}	2.19×10^{1}	—	—
96.3	4.35×10^{-2}	4.47×10^{-2}	—	—	1.57×10^{2}	1.40×10^{2}	—	—
98.6	2.54×10^{-1}	2.57×10^{-1}	1.83×10^{-3}	1.90×10^{-3}	6.58×10^{2}	6.54×10^{2}	—	1.56×10^{1}
99.9	—	—	—	—	—	—	—	4.24×10^{1}

account for dielectric losses with alternating current.[16] The principles involved in these theories are usually based on inhomogeneity of the dielectric, on inelastic dielectric polarization, or on anomalous ionic conduction. The results of a number of recent investigations appear to favor a theory based on ionic conduction involving the formation of a back-e.m.f. of polarization by the current.[17,18,19] Meyer[6] has concluded that for materials containing moisture Maxwell's theory of non-homogeneous dielectrics as applied to alternating current is able to account for the order of magnitude of the experimentally observed dielectric losses (loss angle) in certain materials. DuBois,[7] and Setoh and Toriyama[8] explain dielectric loss in textiles by conduction in water-paths, some of which bridge the electrodes and some of which only extend part of the way between them.

The results of the present investigation show the relation between the a.c. and d.c. conductivities of cotton and silk as a function of humidity. They also show the effect of electrolytic material in the textile on the a.c. and d.c. conductivity and on their relation to each other. The measurements were made with the bridge shown in Fig. 1 upon the same samples and at the same time as the capacity measurements described earlier in this paper. The direct-current resistivity (insulation resistance) measurements were made immediately before or after the alternating current measurements. Where there was a possibility of the resistance of the sample being changed by the direct current measurement, the a.c. measurement was made first.

The relation between the d.c. and a.c. conductivities of cotton is shown by Fig. 4 and by Table III from which it is plotted. It is evident that at humidities above 80–85% the a.c. and d.c. conductivities are equal within the accuracy of the measurements.[20] Below 80–85% humidity the a.c. conductivity is appreciably higher than the d.c. conductivity, and the discrepancy between them increases as the humidity is reduced; the d.c. conductivity forms less than 1% of the a.c. conductivity at humidities below about 25% for samples of normal electrolyte content, and at humidities below about 45% for samples of low electrolyte content.[21] Since dielectric losses are proportional to the a.c. conductivity, these results show that at humidities greater than 80–85% dielectric losses in cotton and silk are practically com-

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[16] Reviews of these theories with bibliographies are given by E. R. v. Schweidler: Ann. Physik, (4) **24**, 711 (1907); F. Tank: **48**, 307 (1914); U. Meyer, loc. cit., L. Hartshorn: J. Inst. El. Eng., **64**, 1152 (1926); and J. B. Whitehead: J. Am. Inst. El. Eng., (1926).

[17] A. Joffé: Ann. Physik, **72**, 461 (1923).

[18] H. Schiller: Ann. Physik, **81**, 32 (1926); Z. Physik, **42**, 246 (1927).

[19] Sinjelnikoff and Walther: Z. Physik, **40**, 786 (1927).

[20] The coincidence of the a.c. and d.c. conductivity curves is only obtained when the d.c. measurements are made with a period of electrification short enough to avoid the error due to "polarization" (increase of resistance with time of application of the measuring voltage).

[21] Sinjelnikoff and Walther[19] have stated that the true d.c. conductivity of dielectrics is equal to their a.c. conductivity, the apparent discrepancy being due to error in the d.c. measurements caused by a back-e.m.f. of polarization which makes the apparent resistance much larger than the true resistance. However, a number of considerations regarding the present results lead to the conclusion that the wide discrepancy between the a.c. and d.c. conductivities of cotton at humidities below about 80% is established with as much certainty as their equality at humidities above this.

pletely accounted for by the direct-current conductivity, while at humidities lower than this a large part of the total dielectric loss is due to some cause other than the d.c. conductivity.

Comparison of the a.c. conductivity curves for samples of different electrolyte content, but otherwise similar, shows the significant fact that, even at humidities where only a negligible part of the a.c. conductivity is due to d.c. conductivity, the a.c. conductivity of samples of normal electrolyte content is much higher than that of samples of low electrolyte content (compare curve 1 with curve 2 and curve 3 with curve 4 in Fig. 4). This indicates that the part of the a.c. conductivity of cotton which is not due to d.c. conductivity is of such a nature that it is strongly affected by the conductivity of the aqueous solutions present in the textile.

There are several factors which tend to make the a.c. conductivity of a textile greater than its d.c. conductivity. The preceding discussion of capacity indicated that the d.c. conduction paths act as an electrolytic cell having a large polarization capacity. Associated with the polarization capacity of an electrolytic cell is an energy loss which can be represented by an equivalent series or parallel resistance. This loss increases with the concentration of the electrolyte.[10] The equivalent parallel conductance associated with the polarization capacity is therefore able to make a contribution to the total equivalent parallel conductance of a cotton sample which satisfies the requirement of dependence on electrolyte content mentioned in the preceding paragraph. Further, if the direct-current conduction paths have a regularly distributed geometric capacity (Fig. 3) as suggested in the discussion of capacity, there will be an energy loss associated with the charging currents necessary to charge this distributed capacity: this can also be represented by an equivalent parallel conductance. The equivalent parallel conductance of a textile sample may therefore be considered as given by

$$G = G_1 + G_2 + G_3 + G_4,$$

where G_1 is the direct-current conductance, and G_2, G_3 and G_4 the equivalent parallel conductance corresponding respectively to the energy losses associated with the polarization capacity of the water-paths through which the direct-current conduction takes place, with the distributed geometric capacity of these water-paths, and with dielectric absorption due to inhomogeneity of the dielectric or to inelastic dielectric polarization. G_1 predominates in cotton at humidities above 70-80%, G_2 and G_3 may be the largest factors at intermediate humidities, and G_4 may be the most important factor at very low humidities. Dielectric losses are given by

$$E^2 G = E^2 (G_1 + G_2 + G_3 + G_4),$$

where E is the effective value of the alternating voltage.

Several properties of the curves in Fig. 4 can be explained on the basis of the above division of the a.c. conductivity into components which depend to different extents on the moisture and electrolyte content of the textile. It would be expected that the a.c. conductivity of samples of different electrolyte content, but otherwise similar, would converge toward practically the same value at 0% humidity; and it is evident that in Fig. 4, curve 1 approaches curve 2, and curve 3 approaches curve 4 with decreasing humidity. The minimum value of the a.c. conductivity should occur at 0% humidity and the maximum at 100%; the maximum should be higher the greater the electrolyte content of the textile. Consequently, the average slope of the a.c. conductance curve for a sample of normal electrolyte content should be greater than that for a sample of low electrolyte content. This explains the fact that the a.c. conductivity curves for samples of different electrolyte content are not parallel, though those of samples of the same electrolyte content are parallel, even when of very different form (in Fig. 4 the a.c. conductivity curves for Twisted Pairs I and Threads I are parallel, but diverge from those for Twisted Pairs II and Threads II). The fact that the a.c. and d.c. conductivity curves commence to diverge at a higher humidity for samples of low electrolyte content than for those of normal electrolyte content is probably due to the a.c. conductivity of a sample of low electrolyte content containing a smaller d.c. conductivity component than the a.c. conductivity of a sample of normal electrolyte content.

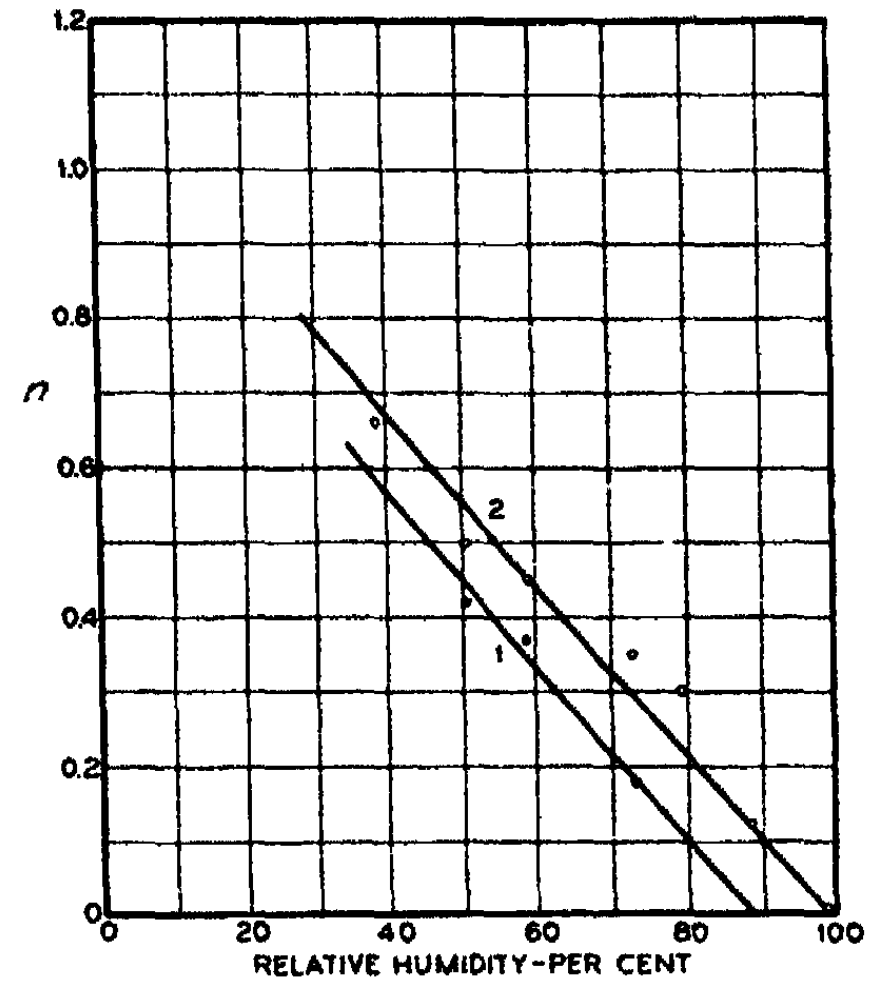

FIG. 5

Effect of Humidity on the Rate of Variation of the A.C. Conductivity (and Dielectric Loss) of Cotton with Frequency. ($G = G_0 f^n$).

1. Samples of normal electrolyte content.
2. Samples of low electrolyte content.

Plotted from Table IV

Table II shows that the equivalent parallel conductance of cotton increases with frequency, but at a decreasing rate as the humidity is increased, becoming independent of frequency at very high humidities as would be expected from the fact that the a.c. conductivity is then practically all d.c. conductivity. The results of some theoretical and experimental investigations indicate that the variation of the a.c. conductivity of a dielectric with frequency is given by

$$G = G_0 f^n,$$

where G_0 and n are constants and f is the frequency.[22] The values of n for cotton as calculated from the data in Table II are shown in Table IV and Fig. 5. It is evident that n is an approximately linear function of the humidity in the range for which data are available. The variation of n with humidity is largely due to the fact that the a.c. conductivity contains a d.c. conductivity component which is independent of frequency. Table II shows that at 73% humidity n is smaller for samples of normal electrolyte content than for those of low electrolyte content. This is due to the fact that the d.c. conductivity forms a larger part of the total a.c. conductivity for the former.

TABLE IV

A.C. Conductivity and Dielectric Loss as a Function of Frequency and Humidity: $G = G_0 f^n$.

Sample	Relative Humidity Percent	n		
		500–2000 cycles/sec.	500–1000 cycles/sec.	1000–2000 cycles/sec.
Twisted Pairs I (Normal Electrolyte Content)	50.5	.42	.48	.36
	59.0	.37	.33	.41
	73.0	.18	.08	.28
Twisted Pairs II (Low Electrolyte Content)	38.8	.66	.74	.58
	50.5	.50	.44	.56
	59.0	.45	.42	.48
	73.0	.35	—	—
	79.1	.30	.25	.35
	88.4	.12	.08	.17
	98.6	.01	.03	—
Cotton Threads II (Low Electrolyte Content)	50.5	—	—	1.37
	73.0	—	—	0.16
	88.4	—	—	0.04
	98.6	0.0	—	—

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[22] The logarithmic plot of the present data for the variation of equivalent parallel capacity and conductance with frequency indicates that for the limited range of frequency investigated the capacity is given approximately by $C = C_2 f^{-n}$ and the conductance by $G = G_2 f^n$. However, the measurements were not made at a sufficient number of different frequencies to regard them as a confirmation of these relationships, and the data are intended to show chiefly the effect of humidity and electrolyte content on the rate of change of capacity and conductance with frequency.

One of the reasons for the variation of the equivalent parallel conductance of a textile sample with frequency is the fact that the equivalent parallel conductance of an electrolytic cell increases with increasing frequency.[10] Other components of the total a.c. conductivity also vary with frequency. In most cases the same cause, in principle, is responsible for their variation with frequency, namely, that the method of measurement consists in balancing a capacity shunted by a resistance against a sample which consists of a more complex network which has capacities in series with resistances.[23] Though the components of the a.c. conductivity may follow a similar law of variation with frequency they probably vary at different rates. The relative prominence of each component should depend on the humidity. The variation of dielectric loss with frequency is given by

$$W = W_0 f^n,$$

where W_0 is a constant and n has the same value as in the preceding equation.

Table V shows that similar relations apply to the a.c. and d.c. conductivity of silk as have already been discussed for cotton. These relationships are also probably applicable in a general way to other textiles and moisture absorbing materials.

TABLE V

The A.C. Conductivity of Silk as a Function of Humidity and Electrolyte Content and its Relation to the D.C. Conductivity

The data are equivalent parallel conductances at 1000 cycles/sec. and the d.c. conductance at 100 volts. They are for a single thread sample. Conductances are in micromhos. Temperature 25°C.

Relative Humidity	Silk Threads I (High Electrolyte Content)		Silk Threads II (Low Electrolyte Content)	
	D. C.	A. C.	D. C.	A. C.
70.8	4.31×10^{-6}	—	3.5×10^{-8}	—
73.0	7.25×10^{-6}	—	5.1×10^{-8}	—
75.5	1.13×10^{-5}	2.54×10^{-5}	7.2×10^{-8}	—
79.1	1.17×10^{-4}	2.03×10^{-4}	6.1×10^{-7}	—
85.2	1.79×10^{-3}	2.98×10^{-3}	9.9×10^{-6}	2.92×10^{-5}
88.4	5.92×10^{-3}	7.47×10^{-3}	2.86×10^{-5}	5.00×10^{-5}
92.0	1.42×10^{-2}	2.94×10^{-2}	1.52×10^{-4}	1.84×10^{-4}
96.3	1.24×10^{-1}	1.57×10^{-1}	1.53×10^{-3}	1.83×10^{-3}
98.6	a) 4.2×10^{-1}	3.83×10^{-1}	b) 4.63×10^{-3}	5.32×10^{-3}

a) Too large on account of Evershed effect or experimental error.
b) Too small due to polarization error.

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[23] The equivalent parallel conductance of a simple network consisting of a resistance in series with a capacity varies with frequency according to

$$G = \frac{R_s (C_s\omega)^2}{1 + (R_s C_s\omega)^2},$$

where C_s and R_s are the capacity and resistance which are in series.

This investigation has led to the following view of the essential nature of conduction in textiles: it was shown in the preceding paper[1] that the direct-current conductivity of cotton is apparently completely determined by three factors, the amount of absorbed water, its specific conductance (as determined by the amount of electrolytic material present in the textile), and its distribution. These facts are consistent with the view that in direct-current conduction a textile such as cotton acts essentially as an electrolytic cell and that the only way in which the cotton itself enters into the direct-current conduction process is in acting as a container which determines the volume, geometric form, and specific conductance of the electrolyte which connects the two electrodes. It would be expected that in alternating-current conduction the dielectric material (regarding the water for the present as a conductor) should play a larger part. But the present results indicate that at very high humidities the function of the textile itself is essentially the same as in direct-current conduction, i.e., the greater part of both the capacity and conductance are properties of the electrolytic cell formed by the absorbed moisture and the electrodes, the textile itself acting only as a container for the electrolyte. At lower humidities, however, the displacement current through the dielectric material becomes an appreciable part of the total current, and the textile acts as a dielectric in parallel with an electrolytic cell.

Summary

The equivalent parallel capacity and conductivity of cotton and silk were determined as functions of humidity, amount of electrolytic material in the samples, and frequency (in the telephonic range) The a.c. capacity of cotton increases very rapidly with increasing humidity, particularly at high humidities. A decrease in the amount of electrolytic material in the cotton causes a very large reduction in the capacity at high humidities. Consideration of such facts as these has led to the conclusion that the capacity of cotton at high humidities is chiefly due to the electrolytic polarization capacity of the water paths through which direct current conduction takes place, these paths forming with the electrodes a kind of electrolytic cell. The direct current conduction paths may also contribute to the total capacity by having a regularly distributed geometric capacity due to regular variations in their thickness, as suggested by other facts.

The a.c. and d.c. conductivities of cotton approach each other as the humidity is increased and become practically equal at humidities above 80–85%. At humidities lower than this the a.c. conductivity is appreciably greater than the d.c. conductivity, the d.c. conductivity forming less than 1% of the a.c. conductivity at humidities below about 25% for samples of normal electrolyte content and at humidities below about 45% for samples of low electrolyte content. The part of the a.c. conductivity which is not due to d.c. conductivity is almost as strongly affected by the amount of electrolytic material in the textile as is the d.c. conductivity, except at very low humidities. This would be explained if an appreciable part of the equivalent parallel conductance of a textile is due to the equivalent parallel conductance asso-

ciated with the polarization capacity of the direct current conduction paths, and possibly also with a regularly distributed geometric capacity of these paths. The rate of increase of the a.c. conductivity of cotton with frequency becomes smaller the higher the humidity, being practically independent of frequency at very high humidities. This is a consequence of the fact that the d.c. conductivity forms a larger part of the a.c. conductivity the higher the humidity. (The conclusions regarding a.c. conductivity are also applicable to dielectric loss to which it is proportional). The above conclusions are also applicable in a general way to silk and other moisture absorbing materials which behave similarly.

In alternating-current conduction a textile acts as an electrolytic cell in parallel with a dielectric, the conducting water-paths forming the electrolyte of the cell. At high humidities the alternating current capacity and conductivity of a textile (and their variation with frequency and electrolyte content) are chiefly due to the electrolytic cell component, while at very low humidities they are chiefly due to the dielectric, and at intermediate humidities to a combination of both.

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Bell Telephone Laboratories,
New York

STUDIES IN ADSORPTION. XXII

The Adsorption of Alkali and of Cupric Salts in the Precipitation of Cupric Hydroxide

BY M. R. MEHROTRA AND N. R. DHAR

It is well known that usually the weight of copper oxide obtained from a certain amount of copper sulphate by precipitation with sodium or potassium hydroxide exceeds the theoretical quantity although the precipitated hydroxide is washed free from alkali and sulphate. The reason for this is not clearly understood and the available literature on the subject does not contribute to any extent to a quantitative explanation. It is generally believed, however, that it is difficult to wash off the adsorbed alkali and by implication it could be interpreted as a probable cause of the increment observed. The present work was undertaken with the object of determining the factors responsible for this increase and to investigate the most suitable conditions under which copper could be estimated accurately by this method. The precipitation has been studied both with copper chloride and sulphate using sodium and potassium hydroxides as precipitants.

Experimental

Seminormal solution of copper chloride was prepared by diluting strong solutions standardised against thiosulphate while that of copper sulphate was prepared by weighing out required quantity of Kahlbaum's pure material. Solutions of the alkalies were also prepared from Kahlbaum's pure materials and standardised against hydrochloric acid.

TABLE I

Adsorption of NaOH by Cupric Hydroxide

Amount of CuO = 0.4885 grm. from Cupric Chloride
" " " = 0.4899 grm. from Cupric Sulphate
Total volume = 100 cc.

Original conc. of NaOH in grams	Amount of adsorption			
	$CuCl_2 + NaOH$		$CuSO_4 + NaOH$	
	End concentration in grams	Amount of adsorption in grams	End concentration in grams	Amount of adsorption in grams
0.43214	0.35501	0.07713	0.36086	0.07128
0.34572	0.26859	0.07713	0.27307	0.07265
0.25929	0.18229	0.07700	0.18527	0.07402
0.17285	0.09673	0.07612	0.10193	0.07092
0.08643	0.01042	0.07601	0.01488	0.07155
0.06482	0.00198	0.06294	0.00280	0.06202
0.04321	0.00159	0.04162	0.00240	0.04081
0.02161	0.00159	0.02002	0.00198	0.01963

The adsorption of alkali by copper hydroxide during the course of its precipitation was determined as follows:— 25 cc. of N/2 solutions of either copper chloride or copper sulphate was taken in 100 cc. measuring flasks to which distilled water was added in calculated amounts to bring the total volume to 100 cc. on adding definite and measured quantities of alkalies in greater amounts than equivalent. The flasks were corked and well shaken and were kept for twenty-four hours undisturbed, after which the end concentration was determined by titrating the clear supernatant liquid against standard hydrochloric acid. As it was observed that quantities of alkalies slightly less than the equivalent amount were sufficient to precipitate the whole of copper from a definite volume of a solution of cupric chloride or cupric sulphate, the adsorption of alkali was studied in such cases as well. The results obtained are presented below in Tables I and II and have been plotted in Fig. 1

TABLE II

Adsorption of KOH by Cupric Hydroxide

Amount of CuO = 0.4885 grm. from Cupric Chloride
" " " = 0.4899 grm. from Curpic Sulphate
Total volume = 100 cc.

	Amount of Adsorption			
	$CuCl_2$ + KOH		$CuSO_4$ + KOH	
Original conc. of KOH in grams	End concentration in grams	Amount of adsorption	End concentration in grams	Amount of adsorption in grams
0.60490	0.50659	0.09831	0.51658	0.08832
0.48376	0.39160	0.09216	0.39660	0.08716
0.36294	0.26162	0.10132	0.26996	0.09298
0.24196	0.13998	0.10198	0.14831	0.09365
0.12098	0.02500	0.09598	0.03166	0.08932
0.09074	0.00277	0.08797	0.00448	0.08626
0.06049	0.00167	0.05882	0.00277	0.05772
0.03025	0.00167	0.02858	0.00277	0.02748

From Tables I and II it will be observed that considerable amounts of both sodium and potassium hydroxide are adsorbed by copper oxide obtained either from chloride or sulphate. It will be further noticed that the hydroxide obtained from chloride is a better adsorbent than that obtained from sulphate. This is due to the smaller size of particles of the hydroxide when produced from chloride than that which is produced from sulphate. This view will be further supported by experiments to be described later on. It may be pointed out, however, that sodium hydroxide is adsorbed more than potassium hydroxide although the tables and the graph suggest the contrary. In the tables and the graphs the amounts have been shown in grams of hydroxide adsorbed but if the result be represented in equivalents the greater adsorbability of sodium hydroxide will be clear. It may also be remarked that the adsorption of hydroxide in all the cases investigated soon reaches a saturation limit.

Gravimetric Estimation of Copper

It is clear from the adsorption experiments that alkali is largely adsorbed by copper hydroxide during the course of its precipitation. But, to show that this was really responsible for the discrepancy between the observed and calculated values referred to in the introduction, it was essential to estimate copper gravimetrically in presence of an excess of alkali.

It was observed early in these experiments that the supernatant liquid exhibited alkalinity to litmus and phenolphthalein even before the equivalent amount of alkali had been added to the copper salt solution. The procedure adopted was briefly as follows:—

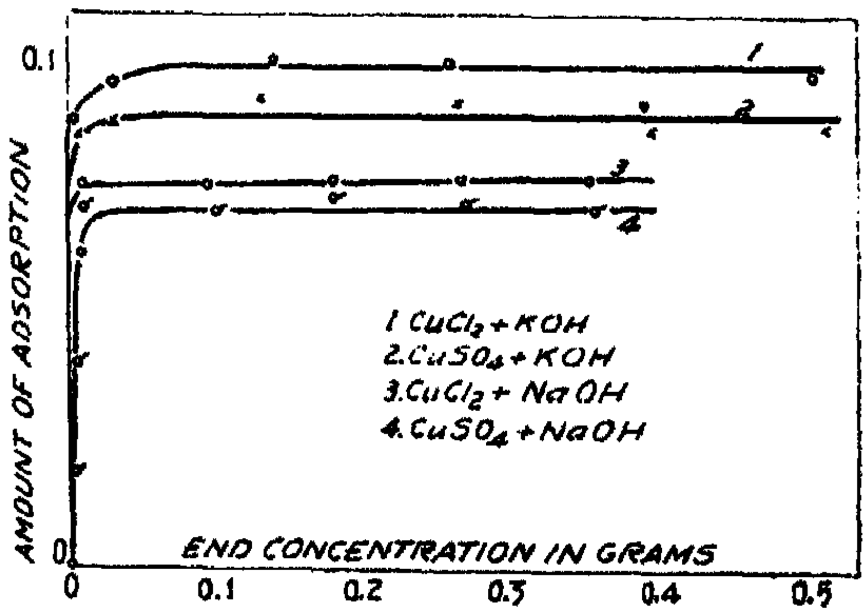

Fig. 1

25 cc. of the copper salt solution was taken in a beaker to which calculated amounts of distilled water were added to bring up the final volume to 100 cc. The mixture was warmed and then the hydroxide was precipitated by adding measured quantities of alkali, the mixture was well shaken and allowed to settle and then washed free from alkali and sulphate or chloride, ignited and weighed. The results obtained are shown below in Tables III and IV.

Table III

Gravimetric estimation of Copper from Cupric Chloride
Amount of CuO (Theoretical) = 0.4885 grams
Total volume = 100 cc.

	Amount of copper taken in gr. equivalents	Amount of alkali necessary for complete precipitation in gr. equivalents	Amount of alkali added in gr. equivalents	Weight of copper oxide obtained in grams
		NaOH	NaOH	
1.	0.0125	0.0125	0.01134	0.4572
2.	0.0125	0.0125	0.01166	0.4686
3.	0.0125	0.0125	0.02157	0.4042
		KOH	KOH	
1	0.0125	0.0125	0.01130	0.4566
2.	0.0125	0.0125	0.01220	0.4790
3.	0.0125	0.0125	0.0216	0.4028

TABLE IV

Gravimetric estimation of copper as hydroxide from cupric sulphate
Amount of CuO (Theoretical) = 0.4899 gram.
Total volume = 100 cc.

Amount of copper taken in gram equivalents	Amount of alkali necessary for precipitation in equivalents	Amount of alkali added in equivalents	Amount of copper oxide obtained in grams
	NaOH	NaOH	
1. 0.0125	0.0125	0.01099	0.5524
			0.5524
2. 0.0125	0.0125	0.01246	0.4987
			0.4982
3. 0.0125	0.0125	0.01513	0.4943
			0.4945
4. 0.0125	0.0125	0.02157	0.4926
			0.4926
	KOH	HOH	
1. 0.0125	0.0125	0.0113	0.5220
2. 0.0125	0.0125	0.0122	0.5014
3. 0.0125	0.0125	0.0216	0.4930

It has to be added that with the chloride in the cases of both NaOH and KOH in experiments Nos. 1 and 2 the precipitate was fluffy and crept up to the edges of the crucible while the oxide was being ignited, displaying green flame on the edges of the crucible and white fumes were seen escaping, presumably of cupric chloride. This loss of cupric chloride is probably the cause of the low weight of copper oxide in the first two cases in Table III. But in the case of sulphate no such phenomena were observable. Instead, it was noticed that when an amount less than the equivalent amount of alkali was used the resulting oxide after ignition exhibited a whitish appearance but the whiteness decreased in intensity with increasing quantities of alkali. Another remarkable difference was noticed in the fact that in the case of the chloride with lesser quantities of alkali the supernatant liquid after 4 or 5 decantations turned turbid due to the formation of a sol, filtered slowly, and gave a milky filtrate which turned brownish on keeping and produced a brown precipitate with K_2SO_4 and Na_2HPO_4. These observations indicate that the sulphate ion exerts a greater cohesive force and produces larger particles than the chloride can do. This difference of size of the particles in the two cases is responsible for the adsorbing powers of the copper hydroxide obtained from chloride and sulphate of copper.

A perusal of the tables shows clearly that instead of obtaining a gradual increase in the weight of the final product (copper oxide) formed from sulphate with increasing quantities of alkali as was suspected, the opposite result is obtained. This unexpected result, together with the observations recorded in the paragraph just preceding, when studied in the light of the fact that quantities of alkali even less than the equivalent are sufficient to precipitate the whole of the copper from a given volume of its salts tends to show that the cause of the increase under question is to be looked elsewhere than in the adsorption of alkali by copper hydroxide. Consequently, the quantitative investigation of the removal of the ions of the copper salt by copper hydroxide was taken up. The effect of the excess of alkali on the removal of sulphate ion from solution has also been studied. The results are tabulated below:—

Procedure—Different amounts of copper sulphate solution were measured out in four 100 cc. flasks. Alkali was added to precipitate in all cases the same amount of copper hydroxide thus leaving an excess of the sulphate in an increasing order in the series of flasks and the copper was estimated volumetrically and sulphate gravimetrically.

TABLE V

Adsorption of SO_4'' ions by cupric hydroxide

Amount of CuO = 0.4899 gram.

Total volume = 100 cc.

Original concentration of SO_4'' in grams	Amount of Adsorption			
	$CuSO_4$ + NaOH		$CuSO_4$ + KOH	
	End concentration in grams	Amount of adsorption in grams	End concentration in grams	Amount of adsorption in grams
0.70752	0.60708	0.10044	0.59639	0.1113
0.82544	0.62230	0.20314	0.62230	0.20314
0.94336	0.75268	0.19068	0.73623	0.20713
1.06128	0.86784	0.19344		

TABLE VI

Adsorption of copper ion by cupric hydroxide

Amount of CuO = 0.4899 gram.

Total volume = 100 cc.

Amount of copper in grams original concentration	Amount of Adsorption			
	$CuSO_4$ + NaOH		$CuSO_4$ + KOH	
	End concentration in grams	Amount of adsorption in grams	End concentration in grams	Amount of adsorption in grams
0.07185	0	0.07185	0	0.07185
0.14995	0.02066	0.12929	0.01590	0.13405
0.22806	0.09219	0.13587	0.09060	0.13746
0.30617	0.15895	0.14722	0.15895	0.14722

The adsorption of copper and chloride from solutions of copper chloride could not be determined as the solution remained clear in only one case; while, in others with increasing amounts of copper chloride the supernatant liquid became turbid exhibiting a milky appearance with a greenish tinge. This was due to copper oxide having been peptised to a positively charged sol which could be precipitated into a green mass with K_2SO_4 and Na_2HPO_4.

TABLE VII

Adsorption of SO_4'' ion in presence of excess of alkali

Amount of CuO = 0.4899 grams.
Total volume = 100 cc.

		Amount of Adsorption			
		$CuSO_4$ + NaOH		$CuSO_4$ + KOH	
Amount of alkali in excess of gr. equivalent	Original concentration of SO_4'' in grams	End concentration in grams	Amount of adsorption in grams	End concentration in grams	Amount of adsorption in grams
−0.00108	0.58960	0.48566	0.10394	—	—
0	0.58960	0.55262	0.03698	0.56233	0.02727
+0.00115	0.58960	0.56825	0.02135	—	—
+0.00337	0.58960	0.57286	0.01674	0.57911	0.01049
+0.00559	0.58960	0.58322	0.00638	—	—

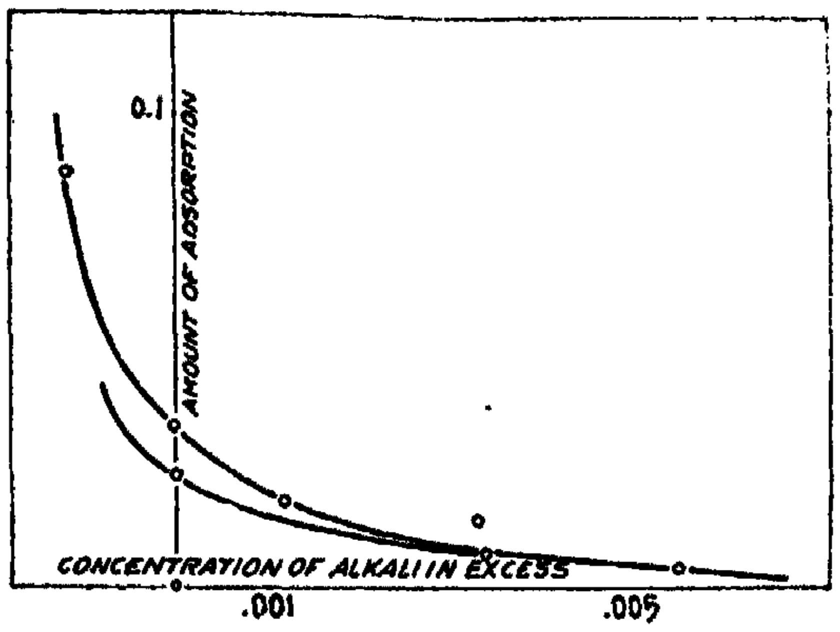

FIG. 2

Table VII contains the results of the amount of SO_4'' ion removed in presence of an excess of alkali. It will be noticed that even at the point where equivalent amount of alkali is added the quantity of sulphate adsorbed is sufficient to vitiate the final weight of copper oxide produced on ignition. In order to present the results more effectively they have been plotted in Fig. 2.

Incidentally we have investigated the amount of adsorption of alkali by different amounts of copper hydroxide. Our experimental results tabulated below show that the greater the amount of hydroxide the greater is the adsorption.

Our experimental results given in Table IV show that the weight of copper oxide obtained when the amount of alkali added is less than the equivalent weight is much higher than the calculated amount of copper oxide. These results are due to the adsorption of copper sulphate by the freshly precipitated cupric hydroxide. Now, on increasing the amount of alkali the amount of cupric oxide obtained goes on decreasing and approaches more and more

TABLE VIII

Adsorption of alkali by different amounts of cupric hydroxide
Total volume = 100 cc.

$CuCl_2 + NaOH$

Amount of copper oxide in grams	Original concentration of alkali in grams	End concentration of alkali in grams	Amount of adsorption in grams	$\frac{x}{m}$
0.29310	0.43214	0.37947	0.05267	0.179
0.4885	0.43214	0.35491	0.07723	0.158
0.6839	0.43214	0.32887	0.10327	0.165
0.8793	0.43214	0.30134	0.13080	0.158
1.0747	0.43214	0.27158	0.16056	0.158

TABLE IX

Adsorption of alkali by different amounts of cupric hydroxide
Total volume = 100 cc.

Amount of copper oxide in grams	Original concentration of alkali in grams	End concentration of alkali in grams	Amount of adsorption in grams	$\frac{x}{m}$
0.2931	0.43214	0.40000	0.03214	0.109
0.4885	0.43214	0.36086	0.07128	0.146
0.6839	0.43214	0.34598	0.08616	0.127
0.8793	0.43214	0.32619	0.10595	0.120
1.0747	0.43214	0.29523	0.13691	0.127

the theoretical amount. This is probably due to the fact that the concentration of unacted copper sulphate and along with it the amount of adsorption decreases with increasing amounts of alkali though the amount of adsorbent (CuO) goes on increasing. Along with the adsorption of copper sulphate, the adsorption of sodium sulphate or potassium sulphate which is a product of the chemical change also takes place.

From our experimental results given in Tables V and VI, it will be seen that cupric hydroxide in the course of its formation adsorbs appreciable amounts of both copper ions and sulphate ions. Now, if we calculate the formula of the adsorption compound on the basis of our experiments on the adsorption of the sulphate ion we find evidence of the existence of the following two compounds, $6\ Cu(OH)_2, CuSO_4$ and $3\ Cu(OH)_2, CuSO_4$. Both these basic sulphates have been described in the literature on basic copper sulphates. Our results on the adsorption of SO_4'' ion by cupric oxide seem to support the existence of the above two basic sulphates.

In precipitating from boiling solutions with the amount of alkali less than equivalent we have found that the cupric hydroxide formed becomes black. In a previous paper[1] published from these laboratories, it was shown that the cupric hydroxide does not turn black even at the temperature of

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[1] Chatterji and N. R. Dhar: Trans. Faraday Soc., October (1920).

boiling water if there is a trace of cupric ion in solution. Consequently, the fact that the copper hydroxide obtained by an insufficient quantity of alkali turns black on warming shows that all the copper has been precipitated in spite of the fact that the amount of alkali was less than that necessary for complete precipitation of the copper.

From the experiment No. 1 given in Table IV if we calculate the composition of the basic salt, assuming that one is formed, the formula comes out to be 15 $Cu(OH)_2$, $CuSO_4$. Now this substance undergoes hydrolysis in boiling water and is converted into cupric hydroxide which turns black. Consequently we are of opinion that the so-called basic salts containing small quantities of copper sulphate along with large one of cupric hydroxide are really cupric hydroxide stabilised by the adsorption of small amounts of copper sulphate.

It is very difficult to state precisely how many basic cupric sulphates actually exist; an overwhelmingly large number of basic sulphates has been described in the literature.[1] Unfortunately our experimental results are not numerous enough for actually verifying the accuracy of the large number of basic sulphates that are supposed to exist, but from our experiments we are led to conclude that the basic sulphate 3 $Cu(OH)_2$,$CuSO_4$ is stable and is likely to form readily, from solutions containing a large excess of copper sulphate.

A very interesting fact to be noticed is that if we express the amount of adsorption of copper and sulphate in gram equivalents we find that the amount of copper and sulphate adsorbed are equal within the limits of experimental error.

Now, in all these cases the precipitation took place in presence of both cupric sulphate and sodium or potassium sulphate which is a product of the chemical change. It could be argued that sodium or potassium sulphate would also be adsorbed by cupric hydroxide during the course of its precipitation ans if it were so, our experimental results should have shown a greater adsorption of sulphate than that of copper. But as a matter of fact with both NaOH and KOH the amount of adsorption of copper and sulphate expressed in equivalents is practically equal in all cases. This should not be taken as a contradiction to what we have previously said about the probable adsorption of sodium or potassium sulphate, being a product of reaction between copper sulphate and sodium or potassium hydroxide. The present results only lead to the inference that in the presence of a large excess of copper salt it is only the copper ion which is more effective and readily adsorbed, and sodium or potassium ions are not appreciably adsorbed. This is quite natural because, copper being a component of $Cu(OH)_2$ more of cupric ions would be adsorbed than sodium or potassium ions, in accordance with recorded experimental fact that a substance adsorbs preferentially the ions entering into its composition. Consequently from a mixture containing a large excess of copper salt more of cupric ions will be adsorbed than that of sodium or potassium.

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[1] Mellor: "Inorganic and Theoretical Chemistry," 3, 261 (1923).

From our experimental results we conclude that in the estimation of copper from cupric salt solution there is more likelihood of introducing error when the amount of alkali added is less than the theoretical amount rather than when an excess of alkali is used. Of course, a very large excess of alkali will certainly lead to higher results because of its adsorption and rentention by cupric hydroxide.

It may be inferred from results given in Tables I and II and plotted in Fig. 1 that the saturation effect indicates the formation of a compound between cupric oxide and alkali. But our results on the gravimetric estimation of copper as hydroxide in presence of excess of alkali show that the excess of alkali can be washed off. These results thus clearly prove that no stable compound is formed between copper hydroxide and alkali for even if one is formed it is decomposed in boiling solutions by water.

TABLE XI

$K = 400$

Maximum Adsorption = 0.0775 grms. Maximum Adsorption = 0.074 grms.

$CuCl_2 + NaOH$		$CuSO_4 + NaOH$	
Adsorption observed	Adsorption calculated	Adsorption observed	Adsorption calculated
0.07713 grms	0.0770 grms.	0.07128 grms	0.0735 grms.
0.07713 "	0.0768 "	0.07265 "	0.0735 "
0.07700 "	0.0765 "	0.07402 "	0.0730 "
0.07612 "	0.0756 "	0.07092 "	0.0710 "
0.07601 "	0.0725 "	0.07155 "	0.0685 "
0.06294 "	0.0644 "	0.06202 "	0.0595 "
0.04162 "	0.0302 "	0.04081 "	0.0362 "
0.02002 "	0.0302 "	0.01963 "	0.0302 "

TABLE XII

$K = 400$

Maximum Adsorption = 0.099 grms. Maximum Adsorption = 0.094 grms.

$CuCl_2 + KOH$		$CuSO_4 + KOH$	
Adsorption observed	Adsorption calculated	Adsorption observed	Adsorption calcuated
0.09831 grms.	0.0974 grms.	0.08832 grms.	0.0935 grms.
0.9216 "	0.0973 "	0.08716 "	0.0933 "
0.10132 "	0.0970 "	0.09298 "	0.0930 "
0.10198 "	0.0962 "	0.09365 "	0.0925 "
0.09598 "	0.0944 "	0.08932 "	0.0875 "
0.08797 "	0.0885 "	0.08626 "	0.0630 "
0.05882 "	0.0532 "	0.08626 "	0.0696 "
0.02858 "	0.033211 "		

In a recent paper we have deduced an adsorption equation

$$A = A \frac{(KC)^{1/n}}{1 + (KC)^{1/n}}$$

where *a* is the amount of adsorption, A is the maximum adsorption, K is a constant, the latter depends on the electrical nature of the adsorbent and also on the viscosity of the medium, C is the end concentration and *n* the valence of the ion adsorbed. From the equation the adsorption corresponding to any end concentration can be calculated.

We have applied the above equation to our experiments on the adsorption of alkali by copper hydroxide during the course of its precipitation and the results are recorded below in Tables X and XI. It will be observed that our results support the equation.

Summary

1) Experimental results show that the hydroxides of sodium and potassium are highly adsorbed by cupric hydroxide in the course of its precipitation.

2) Cupric hydroxide prepared from cupric chloride is a better adsorbent than the hydroxide obtained from cupric sulphate.

3) Both cupric ions and sulphate ions are adsorbed by cupric hydroxide. The two ions are in equivalent proportion. Cupric chloride is also adsorbed by cupric hydroxide but it volatilises when the hydroxide is ignited.

4) Quantities of alkali slightly less than the equivalent amounts can effect complete precipitation of copper from cupric salts. This is due to the adsorption of cupric salts by cupric hydroxide.

5) The experimental results on the adsorption of cupric sulphate by cupric hydroxide support the existence of the basic salt $3\,Cu(OH)_2CuSO_4$.

6) The adsorption equation

$a = A \frac{(KC)^{1/n}}{1+(KC)^{1/n}}$ when 'a' is the amount of adsorption, A is the maximum adsorption and K is a constant, is applicable to the results obtained in the adsorption of hydroxides of sodium and potassium by cupric hydroxide.

Chemical Laboratory,
Allahabad University,
Allahabad,
India.
August 31, 1927.

THE ABSORPTION OF OXYGEN BY RUBBER

G. T. KOHMAN

It is generally believed that the most important factor in the aging of rubber is the absorption of oxygen from the atmosphere. It is also generally agreed that no entirely satisfactory accelerated aging test for rubber goods is available. Because of the increasing importance of rubber in modern industry it is essential that a knowledge of the mechanism of the absorption of oxygen by rubber be available not only for the development of tests which will accurately foretell the natural life of rubber goods, but also for the development of rubber compounds of superior aging qualities. It is surprising how little such information is available and how many conflicting views concerning the influence of oxygen absorption on the aging of rubber exist.

In view of the very complete survey of the literature dealing with aging prior to 1921 made by Dr. Geer[1] in his paper concerning the well-known aging test developed by Geer and Evans,[2] it seems unnecessary to include a complete review in this paper. Since the work to be reported in this paper was completed, Tener, Smith and Holt[3] have reported on a study of the aging of rubber made at the Bureau of Standards and have included a review of the literature. The earliest paper referred to in these bibliographies is that by Spiller,[4] but reference should also be made to a still earlier paper by Hofman[5] who studied the changes taking place in gutta percha during its natural life. He concluded that gutta percha absorbs oxygen from the air and simultaneously changes into a hard brittle material.

The work reported in this paper deals with the absorption of oxygen by rubber and the physical changes associated therewith, and is therefore rather closely related to that of Peachy[6] and of Peachy and Leon.[7] Since the work here reported was completed Leon and Lister[8] have published an account of a continuation of the earlier work of Peachy and Leon. These investigators had no means for keeping the pressure constant throughout the reaction and their rate curves as a result contain irregularities which cannot be interpreted. Also, in most cases the samples used by them were deposited as films from solution and may not have been in the same physical state as the original material. The method used in the work here reported provides

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[1] India Rubber World, **1921**, 587.

[2] Rubber Age, **11**, 345 (1922).

[3] Technologic Paper of the Bureau of Standards, No. 342.

[4] J. Chem. Soc., **18**, 44 (1865).

[5] J. Chem. Soc., **13**, 87 (1861).

[6] J. Soc. Chem. Ind., 1103 (1912).

[7] J. Soc. Chem. Ind., 37, 55T (1917).

[8] J. Soc. Chem. Ind., **46**, 220T (1927).

for constant conditions of oxygen pressure and of temperature throughout the determination and is described in detail later.

Eaton and Day[9] attempted to study the absorption of oxygen at room temperature by following the change in weight of samples exposed to oxygen, but concluded that the change in weight did not represent the amount of oxygen absorbed because of losses of volatile oxidation products from the samples. Their curves are of interest, however, in that they show that the oxidation of rubber at room temperature is autocatalytic. Jones,[10] Henriques[11] and Ditmar[12] find also that the gain in weight of samples is not proportional to the amount of oxygen absorbed as volatile oxidation products are given off. Ditmar finds that in some cases samples actually lose weight during oxidation.

Bruni[13] studied the absorption of oxygen by sealing samples in glass tubes containing oxygen, but in this case rates have very little significance as the progressively diminishing pressure of oxygen in the tubes was not followed during the reaction. Marzetti[14] studied the absorption of oxygen by sealing samples up in tubes containing known amounts of oxygen and measuring the residual amount of gas left in the tubes after keeping them at high temperature for some time. He finds that the various tendencies for different rubbers to age depend upon the rates with which oxygen is absorbed. Others who consider natural aging as the result of absorption of atmospheric oxygen are Miller,[15] Burghardt,[16], Ahrens[17] and Jones.[10] On the other hand, Parks[18] considers aging a more complex phenomenon. Asano[19] finds that raw rubber exposed to light in the absence of oxygen undergoes a change. Jecusco,[20] however, does not entirely agree with Asano upon the effect of light. Bertrand[21] believes that tackiness may be due to a kind of fermentation caused by an organism. Tener, Smith and Holt[3] believe that internal changes which deteriorate rubber take place in the absence of oxygen. Their results will be discussed later.

The general conclusion of those who have studied the aging of rubber is that the absorption of oxygen, if not the sole cause of natural aging, is the most important factor. The two most widely used accelerated aging tests, the Geer[2] test and the bomb test developed by Bierer and Davis,[22] have been

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[9] J. Soc. Chem. Ind., 38, 3339T (1919).
[10] Ind. Eng. Chem., 17, 871 (1925).
[11] Chem. Ztg., 19, 235 (1895).
[12] Gummi Ztg., 20, 628 (1906).
[13] India Rubber J., 63, 814 (1922).
[14] Giorn. chim. ind. applicata, 5, 122 (1923).
[15] J. Chem. Soc., 18, 273 (1865).
[16] J. Soc. Chem. Ind., 2, 119 (1883).
[17] Kunststoffe, 3, 478 (1914).
[18] Rubber Age, 7, 64 (1926).
[19] India Rubber J., 70, 307 (1925).
[20] Ind. Eng. Chem., 18, 420 (1926).
[21] India Rubber J., 35, 620 (1908).
[22] Ind. Eng. Chem., 16, 711 (1924).

developed on this basis. However, as pointed out by Glancy,[23] Vogt,[24] Park[25] and later by Tener, Smith and Holt,[3] these tests are not entirely satisfactory. The extent of aging in these tests is determined by measuring the deterioration of tensile strength, and it is probable that changes in tensile strength under the conditions of these tests are not always proportional to extent of chemical degradation. Additional curing at the temperatures of the tests is known to result in an increase in tensile strength during the tests even though the samples have absorbed oxygen and aged. Also tensile strength measurements cannot be made highly accurate and are subject to gross error in some cases. Suitable samples are not always available, and since the test destroys the sample repetition of the test at intervals involves the assumption that all of the samples of a series originally have the same tensile strength.

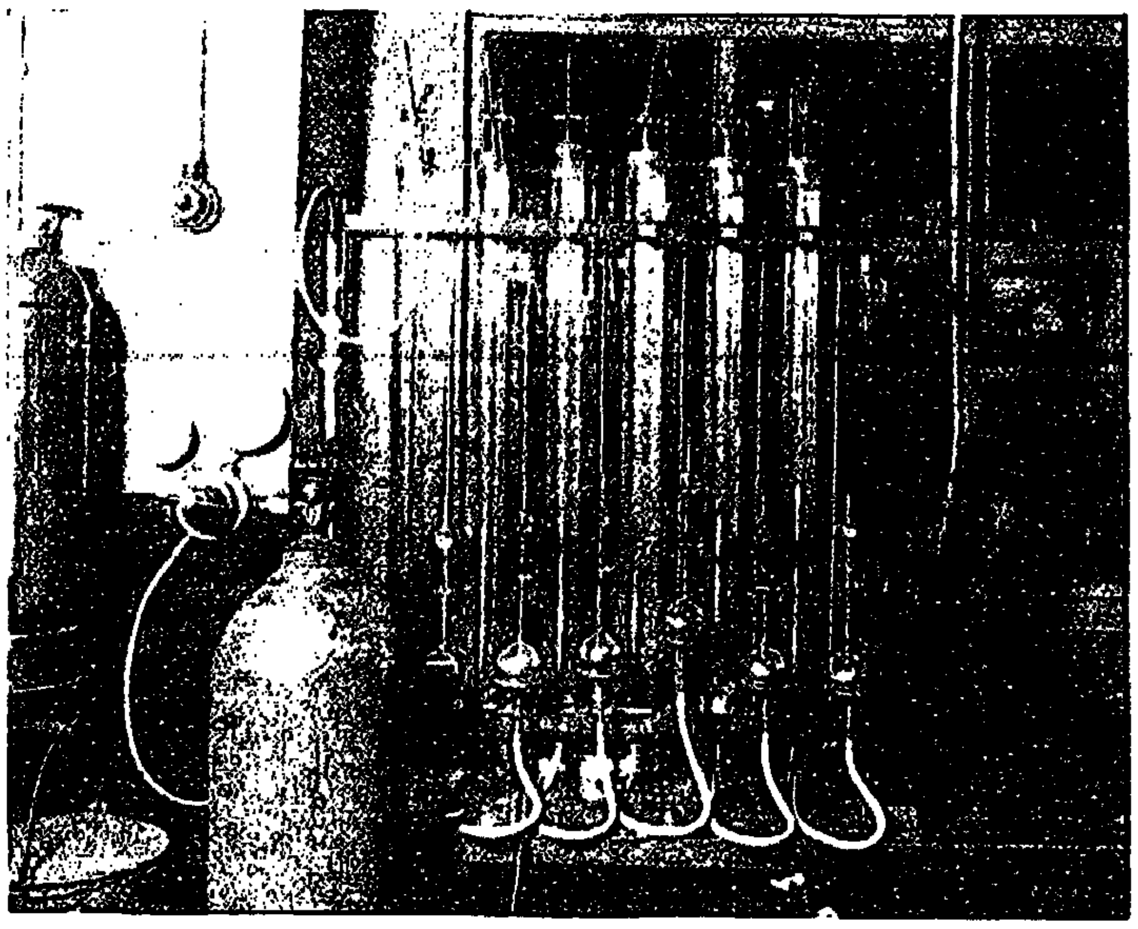

Fig. 1
Photograph of Absorption Apparatus

The work here reported was planned to show the relation between natural aging of rubber and rate of oxygen absorption with the object of developing an accelerated aging test based directly on rates of oxygen absorption. To show this relationship the effect on oxygen absorption of several of those factors which are known to influence the natural aging of rubber have been studied. The results obtained have encouraged us to make a more complete

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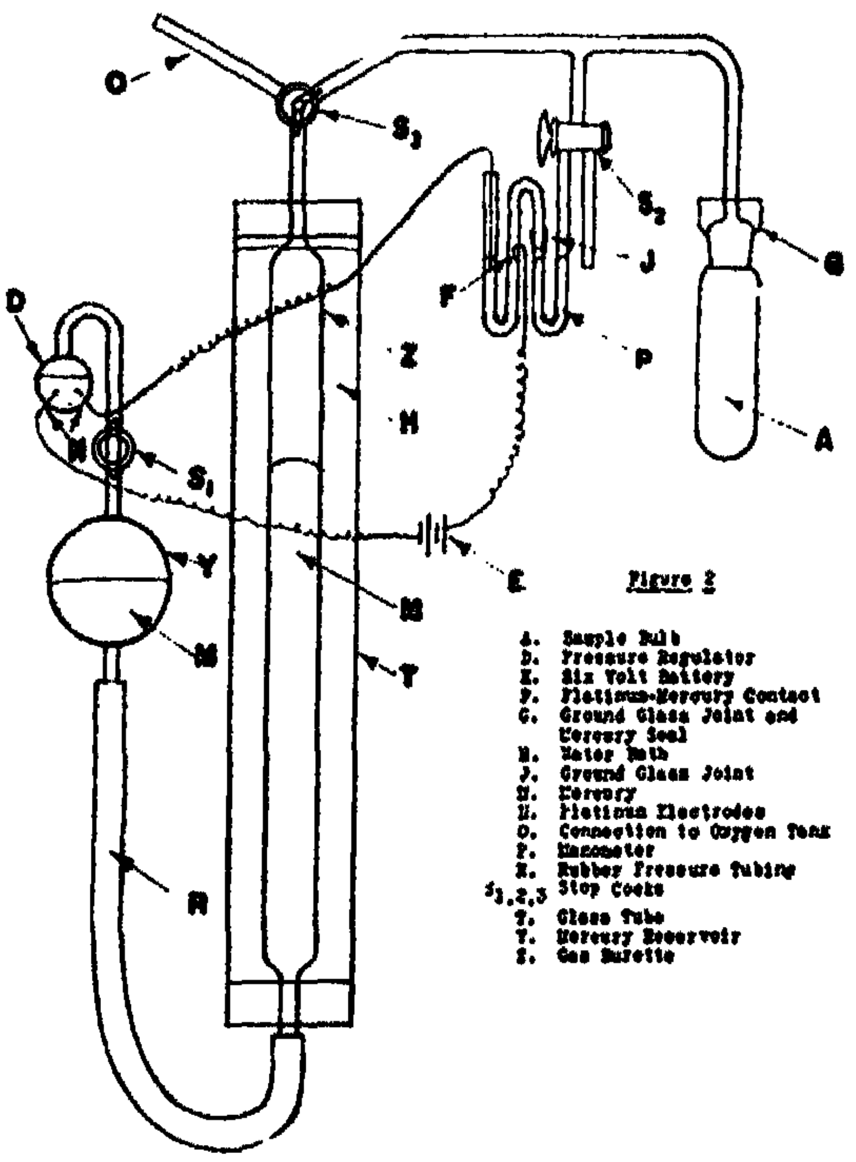
[23] Ind. Eng. Chem., 17, 869 (1925).
[24] Ind. Eng. Chem., 17, 870 (1925).
[25] Rubber Age, 7, 64 (1926).

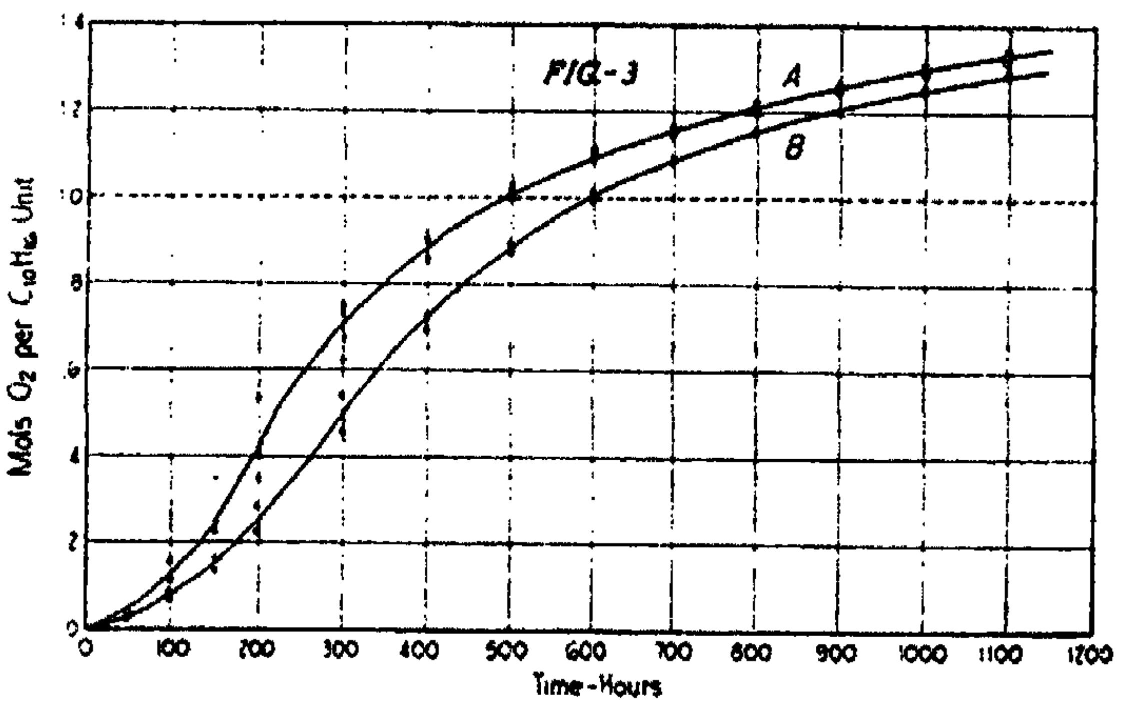
investigation of the mechanism of oxygen absorption. The factors discussed in this paper include the following:

1. Surface Area;
2. Cure;
3. Effect of Milling;
4. Effect of Anti-agers;
5. Effect of Ozonized Oxygen;
6. Effect of Absorbed Oxygen on Tensile Strength;
7. Effect of Heating in Inert Gases on Tensile Strength.



Detailed Sketch of One System of the Apparatus shown in Fig. 1

The apparatus used involves special means for keeping the oxygen pressure surrounding the sample constant as preliminary experiments showed that in a system of constant volume small enough to permit sufficiently accurate measurement of absorbed oxygen the pressure cannot be considered constant during the experiment. The apparatus used is shown in Fig. 1. It consists of six individual systems making it possible for six determinations to be made at one time. The construction of one of the systems is shown in detail in Fig. 2. The sample is placed in bulb A attached to the apparatus by means of the ground-glass joint and mercury seal G. The bulb, when attached to the apparatus, is connected to the gas burette Z through the three-way stopcock S_3, and also to a manometer and vacuum line through the two-way stopcock S_2. The gas burette is surrounded by a water bath H and the sample bulb A immersed in a thermostat for temperature control. In place of the usual mercury reservoir, a reservoir Y, connected to a pressure regulating cell D through the stopcock S_1, is used. This cell consists of a bulb of approximately 20 cc volume into which are sealed two platinum electrodes N, and functions by regulated electrolytic generation of gas within it. A concentrated solution of oxalic acid is used as the electrolyte as it was found that the electrolysis of most inorganic acids and salts results in the liberation of gases which corrode and contaminate the mercury in the reservoir Y and gas burette Z. Sodium hydroxide solutions were tried but it was found that with time the platinum electrodes loosened up in the glass, probably due either to the action of alkali on glass and platinum, or to the alloying of sodium with platinum.



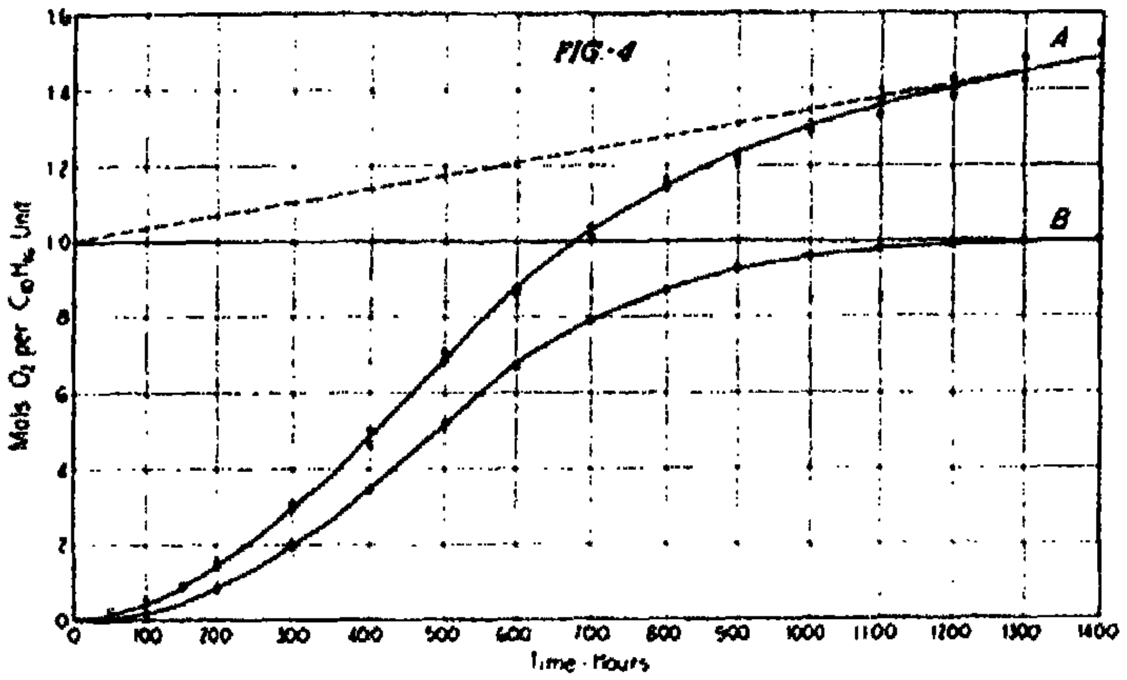
Reproducibility of Results

A. Compound 90C; smoked sheet, 6 hour cure
B. Compound 90C; smoked sheet, 4 hour cure

The manometer P is constructed so as to make possible a making and breaking of an electrical contact at the electrode F when the pressure in the system fluctuates. The double construction avoids the corrosion of contacts which would result if arcing occurred in pure oxygen. The ground-glass joint J also facilitates the adjustment of mercury levels and makes it possible to remove the manometer for cleaning and adjustment without interrupting the experiment.

Experimental Procedure

A determination is begun by pumping out the sample and burette through the stopcock S_2, the position of the mercury reservoir being so adjusted that the atmospheric pressure admitted by removing the core of the stopcock S_1 raises the level of mercury in the burette just to the stopcock S_3. When the sample has been thoroughly pumped out, as determined by noting the constancy of the mercury level in the gas burette with stopcock S_2 closed, oxygen is admitted to the burette and sample bulb through the tube O and the pressure in the system is adjusted by means of the reservoir Y to equal the atmospheric pressure when the gas burette is full. The final pressure adjustment is made by removing the removable half of the manometer and changing the position of the mercury reservoir until the mercury in both limbs of the other half of the manometer is at the same height. The removable portion of the manometer is then attached, the plug of stopcock S_1 inserted and the gas volume, temperature and atmospheric pressure recorded. As the sample absorbs oxygen and the pressure in the system drops, contact will be made at F, closing the circuit consisting of the 6-volt battery E, the pressure controlling cell D and the mercury in the manometer. The gas pressure generated by the electrolysis of the oxalic acid solution forces the mercury up the burette until the pressure in the sample bulb A is atmospheric, when the circuit will be broken. It is possible to recharge the burette with oxygen as often as necessary through the tube O without interrupting the experiment. In case it is desired to determine the amount of oxygen physically absorbed by the sample the gas is first measured in the gas burette before admitting it to the sample bulb. Knowing the total volume of the system makes it possible to calculate the amount of oxygen absorbed.



Reproducibility of Results

90% smoked sheet, 10% sulfur cured 2 hours.
Curve B is curve A corrected for the decomposition reaction.

Experimental Data

General Nature of Results.—Figs. 3 and 4 show the general nature and accuracy of the results obtained. The autocatalytic nature of the reaction is plainly seen, the rate of absorption increasing rapidly during the early stages. These curves appear to be of the same type as those obtained by Eaton and Day[9] for the gain in weight of rubber during natural aging, and this similarity is regarded as evidence that the reactions occurring at 80°C in pure oxygen are the same as those which result in natural aging. The curves as a whole can be reproduced with an accuracy considerably better than 10% as the figures indicate, but occasionally during the part of the reaction where the autocatalytic effect is greatest duplicate samples follow slightly different curves. This is probably due to slight variations in conditions during the first part of the reaction, resulting in slight differences in rates of oxidation which persist and become greatly magnified during the remainder of the autocatalytic portion of the curves. During the later stages of the reaction these differences become smaller.

As a rule the samples absorb more oxygen than the theoretical amount necessary to saturate the double bonds. The curves tend to approach a sloping rather than a horizontal straight line indicating that instead of approaching an equilibrium amount of oxygen absorbed, a constant rate of absorption is approached. This rate has been found to remain practically constant for more than 1000 hours at 80°C. In most cases when the straight line portion of the curve is extrapolated to the time origin it intersects the ordinate at very close to one mol of oxygen per $C_{10}H_{16}$ unit. These facts are taken to indicate that the mechanism of oxygen absorption consists of at least two separate reactions, presumably an addition to the double bonds and a breaking down of the molecule. The latter reaction continues after the first is complete and is indicated by the formation of water during the reaction. During the latter stages of the reaction this water condenses in drops on the cool parts of the apparatus and is strongly acidic. Tests for CO_2 in the system showed not more than a trace.* This is in agreement with the observations of Marzetti, [11] Dawson and Porritt[26] and Thomson.[27] The constant rate of the reaction indicates that the curves represent only the early stages of the decomposition reaction, as it will be referred to in the following discussion, during which concentrations can be considered as remaining constant. If the final oxidation products were assumed to be CO_2 and water, 14 mols of oxygen would be consumed by each $C_{10}H_{16}$ unit. The slope of the latter part of the curves indicates that only $\frac{1}{2}$ mol of oxygen has been consumed by the decomposition reaction during 1100 hours, and since the concentration of oxygen and water in the system has been kept constant the rate of the decomposition reaction can reasonably be regarded as remaining constant throughout the first 1100 hours.

On the basis of this reasoning a curve can be drawn representing the course of the addition reaction alone as has been done in Fig. 4, curve B. Curve A represents both the addition and the decomposition reaction as experimentally determined and the broken line M N′ the decomposition reaction. Curve B was obtained by subtracting from the corresponding

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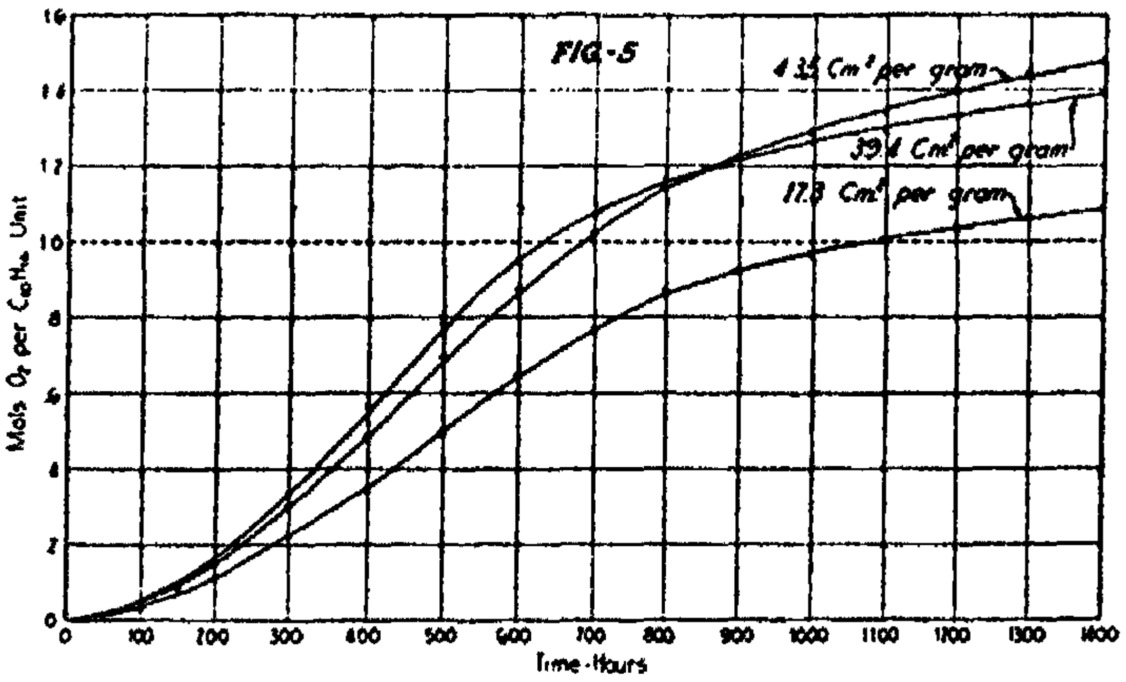
* Since completing the work here reported definite tests for CO_2 have been obtained in certain cases even during the early stages of the oxidation. Correcting for this, however, ordinarily does not greatly affect the absorption curves.

[26] Trans. Inst. R. Ind., 2, 345 (1927).

[27] J. Soc. Chem. Ind., 4, 710 (1885).

ordinates of curve A amounts equal to the vertical elevation of the line M N′ above the horizontal line M N which intersects with M N′ at the axis of zero time. Curve B must, therefore, approach the horizontal line MN asymptotically and as in this case the line represents 1 mol O_2 per $C_{10}H_{16}$ unit, the results indicate that saturation of the double bonds by oxygen occurs in agreement with the observations of Whitby[28] and of Pummerer and Burkard.[29]

During the course of the absorption the rubber first becomes tacky, then the tackiness disappears and it becomes weak and cheesy throughout. Finally it becomes hard and brittle. At 80°C soft rubber compounds of high rubber content were found to become tacky after absorbing from 0.02 to 0.05 mol of oxygen per $C_{10}H_{16}$ unit; the tackiness begins to disappear after approximately 0.5 mol is absorbed and the hard brittle stage is reached after approximately 1.0 mol per $C_{10}H_{16}$ unit is absorbed. At certain stages in the reaction some compounds exhibit the checking phenomenon markedly. It is felt that checking is due to oxidation of the surface to the hard and brittle stage while the inner portion of the rubber is still at an earlier stage of oxidation as suggested by King.[30] On this basis those compounds which react with oxygen very rapidly under the influence of light, and which allow oxygen to diffuse through them very slowly will surface check to the greatest extent. Under these conditions the surface will take up the oxygen before it can reach the inner portions and a hard film of oxidized rubber will form on the surface while the interior remains relatively unchanged.



Effect of Surface Area on Oxygen Absorption Compound, 90% smoked sheet, 10% sulfur cured 2 hours.

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[28] "Plantation Rubber and the Testing of Rubber," (1920).

[29] Ber., 55, 3458 (1922).

[30] Chem. and Met., 25, 1039 (1921).

Surface Area

It was considered advisable to investigate the effect of surface area per unit weight of sample on rates of oxygen absorption to determine whether or not rates of diffusion might be slower than the rate of combination of oxygen and rubber and thus be the controlling factor. A sheet of rubber consisting of 90% smoked sheet and 10% sulphur cured two hours at 40 pounds of steam was cut up into pieces having areas of 17.3, 39.4 and 43.5 square centimeters per gram respectively. The absorption curves determined for these samples at 80°C are shown in Fig. 5. They show that an increase of from 17 to 40 square centimeters per gram does affect the rate of absorption but that small variations in area when it is as large as 40 square centimeters per gram are without great effect in the case studied. It is reasonable to assume that when the area per unit weight reaches a certain magnitude, rates of diffusion will be high enough to keep the rubber particles saturated throughout and will then no longer be a factor in the rate of combination of rubber and oxygen. Therefore, to make the surface area factor relatively small compared with the factors being studied, the area was always made approximately 40 square centimeters per gram.

Effect of Cure

Two important factors in curing rubber with sulphur can be reasonably distinguished; one, the combination of sulphur with rubber, and the other the action of heat apart from a change in combined sulphur content. Although these two factors were not studied separately in the experiments to be reported the results appear to show qualitativley an effect of each on rates of oxygen absorption and will be presented as additonal evidence that natural aging and absorption of oxygen at 80°C are closely related. Many more experiments are required to show definitely the relation of cure to oxygen absorption.

A compound composed of 90% smoked sheet and 10% sulphur was given cures of 2, 4 and 6 hours respectively at 40 pounds steam pressure resulting in sulphur combining to the extent of 1.9, 4.0 and 5.9% respectively. The oxygen absorption curves for these cured compounds and that for raw smoked sheet are shown in Fig. 6, curves B, C, D and E. They show that the higher the degree of cure the more rapid is the rate of absorption of oxygen within the range studied in agreement with the observations of Marzetti,[14] Kirchoff,[31] and Stevens,[32] and also with the order of natural aging of such a series of compounds as determined by general experience. They do not agree, however, with the effect of cure on rates of oxidation as determined by Weber[33] from the acetone extract. It is suggested that the acetone extract may not be a good measure of oxidation in this case as the difficulty of extraction probably increases with the degree of cure. If has been found that samples of vulcanized rubber which have absorbed large amounts of oxygen are only very slightly soluble in acetone.

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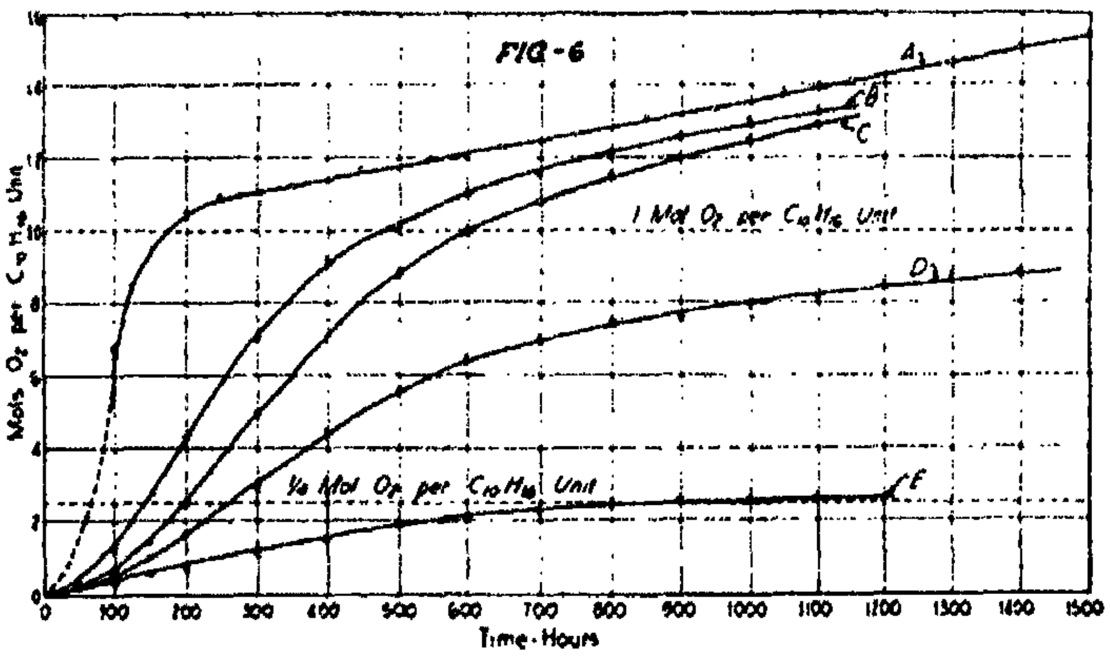
[31] Kolloid-Z., 13, 49 (1913).

[32] J. Soc. Chem. Ind., 40, 269R (1921); 37, 305t, 340t (1918); 38, 193t (1919).

[33] India Rubber J., 25, 639 (1903).

There is also shown in Fig. 6, curve A, representing the absorption of oxygen by a compound consisting of 95% smoked sheet and 5% sulphur which was given a cure of 5.5 hours at 50 pounds steam pressure resulting in a combined sulphur content of 4.0%. This sheet was allowed to age naturally in the laboratory for a period of 18 months before determining its rate of absorption, and because of its overcure it had aged very badly. The purpose of this experiment was first to obtain additional evidence of the relation of natural aging to oxygen absorption at 80°C, and second to determine the effect of overcure other than that due to combined sulphur.



Effect of Cure on Oxygen Absorption

A. 95% smoked sheet, 5% sulfur cured 5.5 hours at 50 #
B. 90% smoked sheet, 10% sulfur cured 6 hours at 40 #
C. 90% smoked sheet, 10% sulfur cured 4 hours at 40 #
D. 90% smoked sheet, 10% sulfur cured 2 hours at 40 #
E. Raw smoked sheet

The experimental origin of curve A is the beginning of the solid line. It was located with respect to the other curves by assuming that they are all members of the same family. Also, as has already been stated, the straight line portion of the curve representing the decomposition reaction usually passes through the ordinate 1.0 mol per $C_{10}H_{16}$ unit, and this straight line portion is ordinarily not reached until more than 1.0 mol per $C_{10}H_{16}$ unit has been absorbed. Since the early portion of the experimental curve lacks the upward inflection which is characteristic of freshly vulcanized rubber, as illustrated by curves B, C and D, it is probable that this had occurred during the natural aging period. The complete curve as drawn represents the absorption which it is assumed would have occurred if an unaged sample had been used, the dotted portion on this basis representing the oxygen absorbed during the 18 months of natural aging.

It is to be regretted that data were not also secured for the rate of oxygen absorption of this sample when in a freshly vulcanized condition, but the apparatus had not yet been developed at that time. We hope to secure such comparative figures in the future.

If our assumptions are correct, the experimental results show that a very close relationship between natural aging and absorption of oxygen at 80°C exists and indicate that the same reactions occur in both cases. The steepness of the early portion of the curve as compared with curve B is in agreement with the bad aging qualities of compound A which, however, has a lower combined sulphur content than B, thus illustrating the importance of overcure aside from its effect upon combined sulphur content.

It appears, as is shown by curve E for raw rubber, that the type of absorption of oxygen in this case is not the same as that for vulcanized rubber. The autocatalytic effect, if present at all, is very slight and instead of taking up one mol of oxygen per $C_{10}H_{16}$ unit only 1/4 mol is consumed. It has been observed by Henriques[34] that raw rubber upon being heated absorbs only traces of oxygen, and deVries,[35] Stevens[32] and Thomson[27] state that raw rubber deteriorates very slowly as compared with vulcanized rubber. Seeligmann, Torrilton and Fauconnet,[36] however, state that raw rubber oxidizes more rapidly than vulcanized rubber and Jones[37] finds that pure rubber oxidizes very rapidly.

Curve D for the vulcanized sample of lowest degree of cure appears to be intermediate between the type for raw rubber and that for fully cured rubber. Since this work was completed a paper by Kirchoff[38] has been published stating that the oxidation products of under-cured and over-cured rubber are not the same chemically or physically. These observations may possibly be interpreted to support the belief of Boggs[39] that there are three rubber-sulphur compounds formed during vulcanization which differ greatly in their stability towards oxygen. Additional support to this theory is that rubber compounds which contain a considerable amount of an anti-ager do not appear to reach the same equilibrium value as those without the anti-ager as will be shown later. Boggs maintains that anti-agers are unnecessary when the vulcanization is carried out so as to prevent the formation of the unstable rubber sulphur compound.

Effect of overworking Rubber before Mastication

The curves of Fig. 7 show the effect of over-working the raw rubber before vulcanization on rates of absorption. The compounds in both cases are 90% smoked sheet and 10% sulphur, but compound A was milled 20 minutes and B one hour before curing. The over-worked sample absorbs oxygen at the fastest rate during the first part of the cure, but crosses curve B before saturation of the double bonds occurs. The reason for this effect is not known, but it suggests absorption of oxygen during the milling process.

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[34] Chem. Ztg., 21, 415 (1897).

[35] India Rubber J., 61, 861 (1921).

[36] "India Rubber and Gutta Percha," (1910).

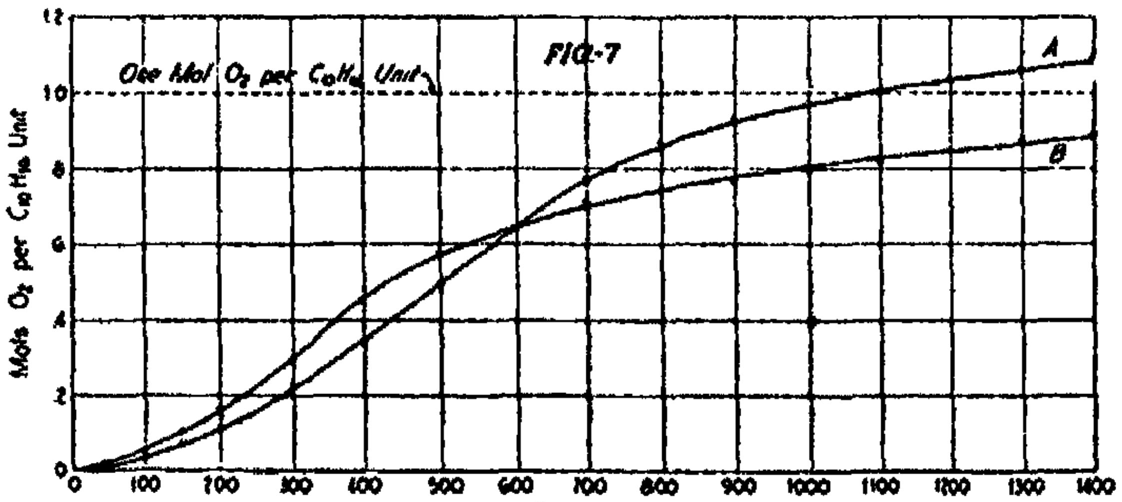
[37] Ind. Eng. Chem., 17, 871 (1925).

[38] Kautschuk, 1927, 239-45, 256-61.

[39] India Rubber World, 76, 79 (1927).

Effect of Anti-Agers

The study of the effect of anti-agers was made for three purposes: first, to determine the mechanism of their action, whether it is a preferential absorption effect as some believe[40] or a negative catalytic effect; second, to obtain additional evidence that rates of oxygen absorption are proportional to rates of natural aging; and third, to determine the relative effectiveness of various anti-agers.



Effect of Milling before Curing on Oxygen Absorption Compound, 90% smoked sheet, 10% sulfur cured 2 hours at 40 #
A. Milled 20 minutes before curing
B. Milled 1 hour before curing

The compound used for this purpose was the following:

First latex crepe	100 parts
Sulphur	2.5 "
Captax	0.5 "
Zinc Oxide	5.0 "
Stearic Acid	1.0 "

To this compound were added 3% and 0.5% of two widely used anti-agers which will be designated as A and B. The absorption curves for these compounds and that for the compound without the addition of anti-agers are shown in Fig. 8. They show plainly that the action of the anti-agers is not preferential absorption but negative catalysis.

It is interesting to note that a small amount (0.5%) of anti-ager A appears to accelerate rather than to retard the rate of absorption. The data indicate that the curves cross at about 300 hours, up to this time the rate being slightly retarded by the anti-ager, but this effect is too small to show on the curves as drawn. The accelerating action of small amounts of this particular anti-ager was at first doubted, but has been confirmed by repeating the experiment. We have been led to surmise that a reaction occurs between the anti-ager and the natural inhibitors of oxidation during the vulcanization process destroying the effectiveness of both. When sufficient anti-

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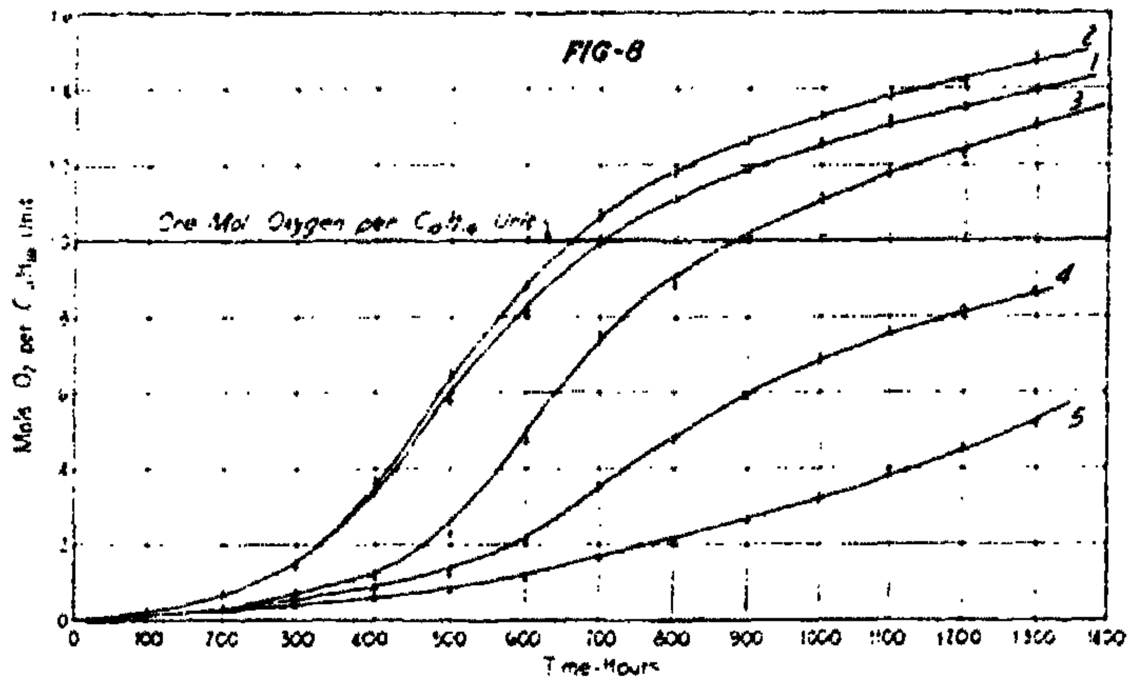
[40] Rubber Age, **20**, 27 (1926).

ager is added to react with all of the natural inhibitors, the effect of the anti-ager becomes apparent. This explanation appears reasonable because during the vulcanization of this particular compound considerable gassing occurs indicating a reaction of some kind. The curves also indicate a considerable difference in the effectiveness of the two anti-agers. This effect of anti-agers of retarding the absorption of oxygen at 80°C is further evidence that rates of oxygen absorption at 80°C are related to rates of natural aging.

Effect of Ozonized Oxygen

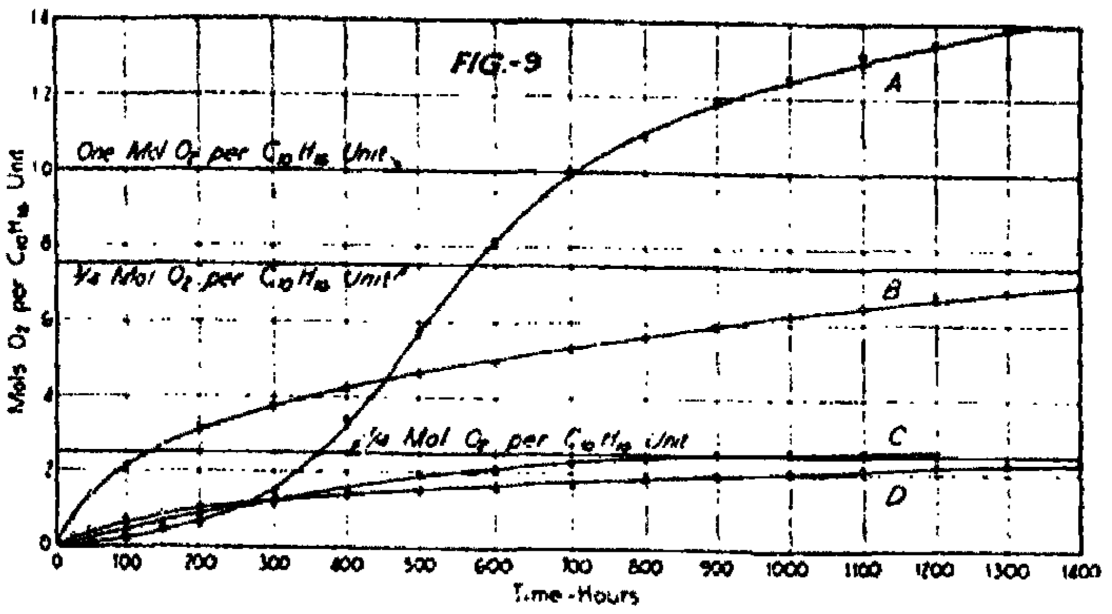
It is well-known that ozonized oxygen causes rubber to deteriorate very rapidly, but no quantitative data on rates of absorption appear to be available. The apparatus used in the previous experiments was modified by sealing in two platinum electrodes with a separation of ½ inch approximately 8 inches above the sample. An electrical discharge in oxygen was generated between these electrodes by means of a Ford spark coil and a six-volt battery thus producing a small concentration of ozone in the system. The sample used was the basic compound used in the investigation of anti-agers. Curve B, Fig. 9, represents the absorption of ozonized oxygen by the compound and curve A the absorption of pure oxygen.



Effect of Anti-agers on Oxygen Absorption

1. 0.0% anti-ager
2. 0.5% anti-ager A
3. 3.0% anti-ager A
4. 0.5% anti-ager B
5. 3.0% anti-ager B

As was expected the rate in the case of ozonized oxygen is very much faster at first, but it rapidly decreases and soon crosses the curve for pure oxygen. There is no evidence that the reaction is autocatalytic and it appears to be of a type different from that of the oxygen reaction, as a different equilibrium value is approached. This value is not three times that for pure oxygen as would be expected if an ozonide were formed instead of an oxide, but even lower than that for pure oxygen. During the later stages of the reaction the ozonized oxygen was replaced by pure oxygen to determine whether or not pure oxygen would be taken up as vulcanized rubber normally does, but no change in rate of absorption was noted. The results indicate that ozone causes a permanen tchange in the rubber, protecting it against the action of oxygen. They also suggest that the action of ozone on rubber prevents the formation or accumulation of the catalyst responsible for the autocatalytic nature of the oxygen reaction. It may even be possible to improve the aging qualities of rubber by giving it an ozone treatment. The action may be similar to that suggested by Ahrens[41] to explain the two percent of oxygen which he claims is usually found in raw rubber. He suggests that a protective coating of oxidized rubber is formed around the latex particle which retards further oxidation. These results are similar to those published in the recent paper by Kirchoff[35] for the absorption of oxygen by rubber under the influence of ultra-violet light and suggest that the action of ultra-violet light is the production of small amounts of ozone which react with the rubber.



Effect of Ozonized Oxygen on Oxygen Absorption Curve

A. Absorption in pure oxygen
B. Absorption in ozonized oxygen
C. Absorption of pure oxygen by raw rubber in ozonized oxygen
D. Curve B replotted dividing the oxygen absorbed by 3

The appearance of the ozone curve, B, suggests a relationship between this curve and that for raw rubber in oxygen shown in Fig. 6 and replotted in Fig. 9 (curve C) as approximately ¼ the amount of oxygen necessary for the formation of an ozonide was consumed and the curves have the same general shape. If the ordinates of curve B be divided by 3 to allow for the difference in the amount of oxygen necessary to form an ozonide and an oxide, curve D is obtained. This is not very different from Curve C.

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[41] Chem. Ztg., 36, 505 (1912).

The Relation between Absorption of Oxygen and Deterioration of Tensile Strength

Before rates of absorption of oxygen can be used as a measure of aging qualities, the relation between the amount of oxygen absorbed and physical deterioration of the rubber must be known. To determine this, tensile strength specimens composed of the basic compound used in the study of anti-agers were placed in the bulbs of the absorption apparatus and allowed to absorb oxygen at 80°C. Periodically, several of the specimens were removed and measurements of tensile strength and elongation made on them. These measured values of tensile strength are shown plotted against the measured amounts of oxygen absorbed by the samples in Fig. 10. Along with these curves are shown curves obtained in a similar manner when the oxygen is replaced by CO_2 and by nitrogen. It was hoped that the complete tensile strength oxygen absorption curve could be determined, but the samples which first became soft and tacky, causing them to settle out of shape in the bulbs later became hard and stiff, making it impossible to remove them from the bulbs and make accurate measurements of tensile strength. Also, when the samples were in the soft and tacky condition they would adhere together and finally form one solid mass of rubber. Rates of diffusion were then no longer fast enough to allow uniform oxidation of all of the samples. As a result the last part of the absorption curve is not the same as that for the same compound cut up into small pieces shown in Fig. 8. However, within the range of practical interest, the two curves are in good agreement. It is believed that if the samples were oxidized further the tensile strength would eventually begin to increase somewhat as shown by the dotted line as the samples undergo changes during oxidation similar to those occurring during vulcanization with sulphur, finally becoming hard and brittle.

The effect of oxygen on tensile strength is very striking, 0.5% by weight, decreasing it by nearly 50%. Heating in CO_2 and nitrogen first results in an increase in tensile strength, probably due to additional vulcanization, and then in a very slow decrease which is insignificant compared with the effect of heating in oxygen. This decrease was greater in carbon dioxide than in nitrogen. It was observed that the samples heated in carbon dioxide changed in color uniformly throughout, from light yellow to black, indicating that carbon dioxide may react in some way with rubber at high temperatures. The results are in agreement with those of Marzetti[11] who found that less than one percent of oxygen produces profound changes in rubber, while heating in inert gases is without appreciable effect. Jones[10] found that samples sealed up in evacuated tubes and placed in the Geer test remain unchanged after 14 days. Gorter[12] observed that rubber in sealed tubes exposed to light remains unchanged when the tubes are filled with H_2 or CO_2. Thomson[27] found that after 2.5 years in vacuum, CO_2 and hydrogen, no deterioration occurred either at room temperature or for shorter periods of time at 100°C.

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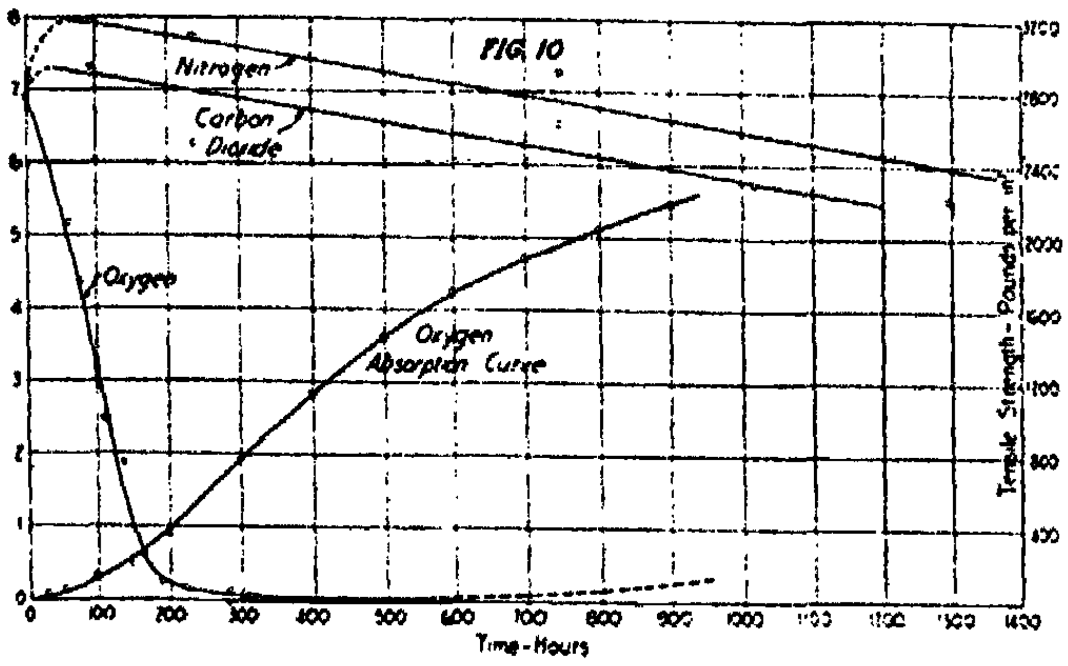
[12] Caout. et G. P., 12, 8724 (1915).

Tener, Smith and Holt[3] claim, however, that very marked changes do take place in rubber when kept in evacuated tubes. It is suggested that in view of the very striking effect of oxygen on tensile strength their results may be accounted for by incomplete protection against oxygen. The tubes in which their samples were kept were closed by rubber caps through which some oxygen might diffuse and the pressure may have been as high as 5 millimeters. Also, to remove free sulphur, it was necessary to open the tubes occasionally, which would allow oxygen to be absorbed by the samples. The effect may also be due in part to further vulcanization because of the large amount of free sulphur in the samples. In the experiments here reported the tubes were evacuated with a two-stage Crowell-McNeill pump to a pressure probably not greater than 0.01 mm for several hours. Then the tubes were closed by means of mercury seals.



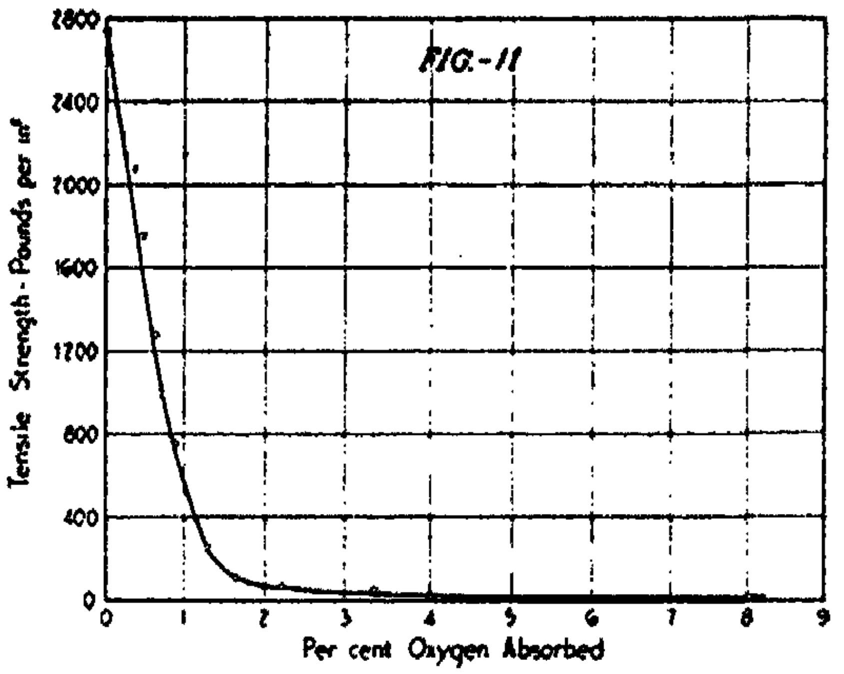
Relation of Absorbed Oxygen on heating in Inert Gases to Deterioration of Tensile Strength

The first attempt to determine the relation of oxygen absorption to change in tensile strength was interrupted by an accident after a period of 30 hours. The samples used in this experiment were somewhat under-cured and the results obtained, though incomplete, are of interest. Only a slight decrease in tensile strength occurred after absorbing oxygen for 30 hours as compared with the decrease represented by the curve of Fig. 10 for fully cured samples, although the rates of absorption were approximately the same in both cases. The decrease in tensile strength due to oxygen absorption was hidden by an increase resulting from further vulcanization as was shown by the large increase in tensile strength which occurred when similar samples were heated in carbon dioxide and nitrogen. This "after vulcanization" of under-cured stock often makes it difficult to interpret the results of any accelerated aging test at high temperature which is based on changes in physical properties of rubber with time. It is believed that measurements of rates of oxygen absorption afford a means of distinguishing between under-cure and good aging qualities.

If the amount of oxygen absorbed as shown in Fig. 10 be plotted against the corresponding tensile strength, Fig. 11 is obtained. This curve indicates first that the decrease in tensile strength of well cured rubber can be considered as being directly proportional to the amount of oxygen absorbed with very little error as long as the rubber possesses sufficient strength to be of practical value: and second, that the absorption curve must be determined very accurately to serve to predict the behavior of rubber over a period corresponding to its natural life.

Summary and Conclusions

In order to determine the relation between natural aging and oxygen absorption at 80°C the effects upon oxygen absorption of a number of factors which are known to affect natural aging have been studied. A piece of apparatus is described with which it is possible to follow the absorption of oxygen at constant pressure, temperature, etc. over long periods of time.



Absorbed Oxygen plotted against Tensile Strength

It has been found that the absorption of oxygen is autocatalytic in nature and appears to consist of at least two separate reactions—a decomposition and an addition reaction.

The rate of absorption of oxygen at 80°C is dependent upon surface area when the area is small, but when it is increased to as large as 40 square centimeters per gram, small variations in surface area are without great effect probably because under these conditions rates of diffusion are high enough to keep the rubber particles practically saturated with oxygen.

As rubber absorbs oxygen it appears to undergo changes similar to those occurring during vulcanization with sulphur. Surface checking is regarded as a preferential surface oxidation.

The mechanism of oxygen absorption appears to be different for raw rubber from that for cured rubber. Curing rubber increases both the rate and amount of oxygen absorption over that for raw rubber, and changes the character of the absorption curve. The rate of absorption increases with the degree of cure.

The action of anti-agers is one of negative catalysis rather than one of preferential absorption. The rate of oxygen absorption may be greatly retarded by their presence and their effectiveness varies with their concentration and constitution.

The type of absorption of ozonized oxygen differs markedly from that for pure oxygen. The former is taken up very much more rapidly at first, but the rate rapidly decreases and less oxygen is finally taken up than in the case of pure oxygen. The action of ozonized oxygen upon rubber appears to protect it from the action of pure oxygen. The reaction between rubber and ozonized oxygen is not autocatalytic.

The relation between absorbed oxygen and deterioration of tensile strength has been determined and it has been found that as long as well cured rubber posseses sufficient strength to be of practical value, the deterioration can be considered directly proportional to the amount of oxygen absorbed. 0.5% of oxygen decreases the tensile strength by nearly 50%.

Heating under-cured compounds in inert gases results in an increase in tensile strength at first due to a curing action, and then in a slow decrease which is insignificant as compared with the effect produced by oxygen.

The results so far obtained indicate that natural aging is essentially the result of absorption of oxygen from the atmosphere. Accordingly, it is felt that information concerning rates of absorption of oxygen will be of value in predicting the natural life of rubber compounds.

The writer takes this opportunity to express appreciation of the helpful suggestions received from Dr. H. H. Lowry who initiated this work, and for the continued interest which he has taken in it; also for valuable advice and assistance received from Mr. A. R. Kemp in choosing the compounds studied and directing their preparation for me.

Bell Telephone Laboratories,
June 23, 1928.

THE EFFECT OF NON-ELECTROLYTES ON THE COAGULATION OF COLLOIDS. PART III

Copper Ferrocyanide Sol.

BY SUBODH GOBINDA CHAUDHURY AND NIRMALA PADA CHATTERJEE

In Parts I and II[1] it has been shown that the effect of a non-electrolyte on the coagulation of colloids by electrolytes depends mainly on a change in two physical factors:

(1) A change in the dielectric constant of the medium, and

(2) A change in the solid-liquid interfacial tension. The effect of the diminution of the dielectric constant is in general to sensitise the sol, whereas the effect of the diminution of surface tension is to stabilise it. On the basis of these considerations we have explained the apparent paradox of higher adsorbability and lower coagulation power.

The considerations hold only for those cases, where there is no chemical interaction when the non-electrolyte is added and also where the presence of the non-electrolyte does not influence the specific adsorbabilities of the ions.

The present work was undertaken with a view to investigate more fully the case of copper ferrocyanide hydrosol[2]. The effect of adding the following substances, methyl alcohol, ethyl alcohol, urea, cane sugar, gelatin, acetic acid on the coagulating concentrations of the electrolytes, hydrochloric acid, sulphuric acid, citric acid, potassium chloride, barium chloride, and aluminium chloride, have been studied.

Experimental

Preparation of the Sol.

The sol was prepared by precipitating copper ferrocyanide by mixing equivalent amounts of $CuSO_4$ and $K_4Fe(CN)_6$ solutions and washing the precipitate till it peptises. The sol, so prepared, was then dialysed till the dialysate gave neither any test for sulphate nor for ferrocyanide. With this sol, equicoagulating concentrations of different electrolytes in presence of non-electrolytes were determined by noting the time, when the light from a filament lamp fed with a constant current just disappears on account of increasing turbidity of the sol. 5 c.c. of the sol were always mixed with 5 c.c. of the electrolyte. The required amount of electrolyte was taken from a burette and the volume was made up to 5 c.c. before mixing it with colloid.

In the following tables the amount of electrolyte just necessary to produce a rate of coagulation such that the turbidity becomes great enough to render the filament invisible to the unaided eye in 3 to 4 minutes, has been expressed in millimoles per litre of the mixture of colloid and electrolyte (i.e. the end concentrations have been given). The limiting concentrations can be determined with a drop, i.e. .05 cc. of electrolyte can be taken:—

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[1] J. Phys. Chem., 32, 1231, 1872 (1928).

[2] Cf. Sen: J. Phys. Chem., 29, 587 (1928).

TABLE I*

Nos. of ccs. of methyl alcohol in 100 cc. of the final vol.	HCl(–)	H_2SO_4(–)	Citric acid (–)	KCl (–)	$BaCl_2$(–)	$AlCl_3$(–)
0	.03872	.08642	2.1619	.07009	.00153	.00072
2.5	.03765	.07901	2.0309	.06338	.00144	.00071
5	.03581	.07037	1.8998	.05965	.00139	.00070
10	.02806	.05679	1.7033	.04772	.00127	.00069
25	.01500	.02457	1.1792	.02535	.00103	.00060

*The sign (+) means Stabilisation.
" " (–) means Sensitisation.
" " (o) means No effect.

TABLE II*

Copper Ferrocyanide sol—Ethyl alcohol

Nos. of c.c.s of ethyl alcohol in 100 c.c. of the final volume	HCl (–)	H_2SO_4 (–)	Citric acid (–)	KCl (–)	$BaCl_2$ (–)	$AlCl_3$ (–)
0	.03872	.08889	2.1946	.06710	.00144	.000708
2.8	.03581	.08520	1.9981	.05806	.00137	.00069
5	.03194	.07901	1.8343	.04687	.00127	.00068
10	.02710	.07160	1.6377	.03355	.00117	.00066
25	.01839	.04938	1.1792	.01342	.00092	.00061

TABLE III*

Copper Ferrocyanide Sol—Urea

Conc. of urea by wt. per 100 c.c. of the final solution	HCl (–)	H_2SO_4 (–)	Citric acid (–)	KCl (+)	$BaCl_2$ (–)	$AlCl_3$ (+)
0	.03872	.08397	2.1618	.06710	.00151	.00064
.15 gms.	.03562	.07284	1.9653	.06710	.00149	.00064
.3 "	.03194	.06271	1.7688	.07158	.00149	.00066
.6 "	.02613	.04938	1.6378	.07381	.00146	.00066
1.5 "	.01819	.03458	1.3102	.07426	.00141	.00068

TABLE IV*

Wt. of sugar added per 100 c.c per the final solution	HCl (o)	H_2SO_4 (–)	Citric acid (o)	KCl (+)	$BaCl_2$ (o)	$AlCl_3$ (o)
0	.04068	.08889	2.2274	.06710	.00144	.00069
.25 gms.	.04068	.09135	2.2274	.06979	.00144	.00069
.5 "	.04068	.09259	2.2274	.07157	.00144	.00069
1 "	.04068	.09382	2.2274	.07381	.00144	.00069
2.5 "	.04068	.09629	2.2274	.07707	.00144	.00069

TABLE V*

Strength of acetic acid added in the final solution in terms of normality	HCl (−)	H_2SO_4	Citric acid (−)	KCl (−)	$BaCl_2$ (−)	$AlCl_3$ (−)
0	.04068	.08642	2.2274	.06934	.00146	.00069
.0029 N	.0405	.08642	2.2274	.06934	.00129	.00040
.0058 N	.0402	.08642	2.1944	.06822	.00127	.00037
.0116 N	.03972	.08642	2.1619	.06710	.00124	.00035
.0348 N	.03972	.08642	2.0636	.06598	.00117	.00034

TABLE VI*

Copper Ferrocyanide Sol—Gelatin

Wt. of gelatin added per 100 c.c. of the final solution	HCl (−)	H_2SO_4 (−)	Citric acid (−)	KCl (−)	$BaCl_2$ (−)	$AlCl_3$ (−)
0	.04068	.8642	2.2274	.06934	.00146	.000708
.00025 gms.	.03875	.08395	1.9653	.0822	.00146	.000708
.0005 "	.03681	.08147	1.9653	.06598	.00151	.000724
.001 "	.03390	.07654	1.8998	.06039	.00161	.000724
.0025 "	.02228	.04938	1.7033	.04921	.00175	.000756

Discussion

Mukherjee, Chowdhury and Mukherjee investigated the effect of adding the following substances: methyl and ethyl alcohols, formic, acetic and oxalic acids on the coagulation of arsenious sulphide sol by the electrolytes hydrochloric acid, sulphuric acid, potassium chloride, lithium chloride, barium chloride, and aluminum chloride. They observed that methyl and ethyl alcohols do not act in the same way for a number of electrolytes. Thus ethyl alcohol stabilises the arsenious sulphide sol against coagulation by potassium chloride, lithium chloride and barium chloride whereas methyl alcohol sensitises it against these electrolytes. Besides, a sensitising effect was observed of both alcohols against hydrochloric acid and aluminium chloride. Sulphuric acid has neither a sensitising nor a stabilising effect. We find on the other hand for copper ferrocyanide sol that both methyl and ethyl alcohols have got uniformly sensitising effect against the electrolytes we have used as has also been found in the case of ferric hydroxide sol (Part II). Obviously the effect varies from sol to sol and the valency of the coagulating ions gives no clue to its behaviour. The behaviour of copper ferrocyanide sol in presence of methyl and ethyl alcohols is simple, as they show uniform sensitising effect.

For other substances the specific nature of the reaction becomes apparent. Urea sensitises copper ferrocyanide sol against the three acids and against barium chloride to a slight extent. It shows stabilisation against potassium chloride. Aluminium chloride has very little stabilising effect. The data with cane sugar again show the specificity of these effects. It stabilises the sol against potassium chloride and sulphuric acid and does not change the coagulating concentration against other electrolytes. The coagulating concentrations of hydrochloric acid and sulphuric acid do not change on addition of acetic acid, a result identical with that observed for arsenious sulphide sol on the addition of acetic and propionic acid. A sensitising effect is observed in all three cases against potassium chloride and alluminium chloride. This regularity breaks down again, if we compare the results when barium chloride is the coagulating agent. A stabilising effect is observed when arsenious sulphide sol is used but with copper ferrocyanide sol, acetic acid sensitises it against coagulation by barium chloride.

Of the above substances all excepting urea and gelatin[1] decrease the dielectric constant. Thus cane sugar also reduces the dielectric constant whereas urea increases it.[2] It is obvious that several factors are at work and that it is a priori difficult to predict what is going to happen in particular case. The specificity of stabilising or sensitising effect is to be attributed to the fact that what we observe is the net result of changes in a large number of variables which affect the coagulating concentrations. The experiments with urea are instructive for we get a sensitising effect against three electrolytes though the dielectric constant is increased by its addition. On comparing the effect of urea with that of ethyl alcohol we find that the sensitising effect of urea against the three acids is equally marked in both cases. On the basis of the views of Weiser[3] one would have expected a stabilising effect of urea, for, in his opinion "the extent of the sensitisation depends on the concentration and adsorbability of the non-electrolyte and its dielectric constant. This effect tends to lower the precipitation value of an electrolyte." Mukherjee, Chowdhury and Mukherjee pointed out the desirability of simultaneously measuring the charge of the colloidal particles under these conditions. Discussions on the amounts of adsorption of the coagulating ion that is necessary at the coagulating concentration are rather wide of the mark, for, the tacit assumption that is always made, namely, that coagulation takes place at a particular critical potential, has no basis on facts (vide Mukherjee and Chowdhury[4], Our knowledge about the mechanism of coagulation of these colloids by simpler inorganic electrolytes is as yet too insufficient to enable us to enter into a reasonable speculation regarding the nature of influences at work in the phenomena dealt with in this paper. Thus it is very difficult to account for the peculiar effects of cane sugar where we find that in four cases there is no change in the coagulating concentration, unless we assume a variation in the coagulation potential. Cane sugar decreases the dielectric constant as does methyl and ethyl alcohols. It also affects the adsorption of coagulating ions[5]

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[1] About gelatin we have no definite data.

[2] Harrington: Phys. Rev. (2), 8, 581 (1926); Lattey: Phil. Mag. (6), 41, 829 (1921).

[3] J. Phys. Chem., 28, 1253 (1924).

[4] See also Mukherjee, Roy Chowdhury and Chowdhury's paper communicated.

[5] Sen: Kolloid-Z., 38, 310 (1926).

and also slightly diminishes the surface tension of the medium at the concentrations used. Cane sugar changes the activity[1] of cations, hydrogen and barium; but it has no effect on the coagulating concentration. What is the probability that a complicated change in all these variables, which together with some others determine the coagulating concentrations, will leave the net effect equal to zero in all these cases? Urea and cane sugar stabilise the sol against the same electrolyte, potassium chloride. It is at present not at all definite that we have even got a clear idea of the relevant physical and chemical properties which determine the coagulating concentration. A change in the surface tension or rather the change in the energy associated with conglomeration of two particles which depends on capillary forces is always kept out of consideration in discussion on coagulations obviously because of the difficulties of experimentally determining them. While measurements of charge carried out in this laboratory are gradually forcing us to the conclusion that the cohesive forces play a very significant part in determining the coagulating concentrations we also feel that, in effect, this statement signifies at the present state of our knowledge that all the difficulties in the way of explaining the facts are being referred to one group of undetermined properties of the system. We could not carry out a sufficient number of charge measurements within the time at our disposal excepting the data given in the tables below. In the following experiments 50 c.c. of the sol were always mixed with 50 c.c. of the non-electrolyte. The required amount of non-electrolyte was taken from a burette and the volume was made up to 50 c.c.

TABLE VII

Cataphoretic experiment

Copper Ferrocyanide Sol—Urea. Temp. 35°

Wt. of urea added per 100 c.c. of the final solution	*V in cm. per sec. per vol. per cm.
0	40.1×10^{-5}
.6 gms.	48.6×10^{-5}
1.5 "	53.4×10^{-5}

* Corrected for viscosity, taking the value for water at this temp. to be unity.

It would appear from the above that not only does urea increase the dielectric constant but it also increases the rate of migration. Assuming that the rate is proportional to the density of the charge we find that the sol ought to be stabilised. The only factor resulting from an increase in the dielectric constant as such, which tends to sensitise the sol is the increased intensity of adsorption of the cation. Sugar on the other hand lowers the dielectric constant and also diminishes the rate of migration though slightly at higher concentration. From the single measurement given in Table No. VIII, we find that the net effect of sugar at the concentrations given is to reduce the

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[1] Anderson (Trans. Faraday Soc., 19, 635 (1923-24)) concluded that as sugar increases the activity of cations this fact explains the lower coagulating concentration of these cations in the presence of sugar (Sen: loc. cit.).

charge considerably but we find instead of a sensitisation a stabilisation in two cases out of six (Table IV) and this is to be attributed to a lowering of the critical potential, consequent on a decrease in the colloid-liquid interfacial tension. With other electrolytes, the sol is neither sensitised nor stabilised, which means the effect of greater adsorbability is just counteracted by lowering in colloid-liquid interfacial tension. Unless we know exactly the dielectric constants and the surface tensions of the mixtures of electrolyte and non-electrolyte, we cannot speak anything more definite.

TABLE VIII
Cataphoretic experiment.
Copper Ferrocyanide Sol—Cane Sugar.

Wt. of sugar added per 100 c.c. of the final solution	*V in cm. per sec. per volt per cm.
0	40.1 × 10^{-5}
.5 gms.	41.6 × 10^{-5}
1 "	40.5 × 10^{-5}
1 gm (in presence of .004 N KCl)	34.7 × 10^{-5}
2.5 gms.	37.5 × 10^{-5}

* Corrected for viscosity taking the value for water at this temperature to be unity.

These measurements amply bear out our contention that it is unjustifiable to discuss the observations on coagulation with mixtures of electrolytes and in the presence of non-electrolytes on the basis of amounts of adsorption of the coagulating ion necessary for coagulation as affected by simple considerations in changes in adsorbability or variation in the original charge. It is not denied that these are factors to be considered but that there are other equally influential factors such as the electrical forces opposing collisions, the electrical adsorbability, the changes in the energy associated with the agglomeration of the particles, and most of all the change in the critical potential of the sol on the addition of a non-electrolyte.

Our best thanks are due to Prof. J. N. Mukherjee D.Sc. for his advice and for facilities for carrying out this work.

Physical Chemistry Laboratory,
University College of Science,
92 Upper Circular Road,
Calcutta.

THE LATTICE ENERGIES AND PHOTOCHEMICAL DECOMPOSITION OF THE SILVER HALIDES*

BY S. E. SHEPPARD AND W. VANSELOW

In a paper[1] by one of the writers and A. P. H. Trivelli the following reaction scheme was proposed to represent the essential photochemical change in the production of the latent image:—

$$\overset{-}{\mathrm{Br}} - \Theta \rightarrow \mathrm{Br} \text{ (bromine atom)}$$

$$\overset{+}{\mathrm{Ag}} + \Theta \rightarrow \mathrm{Ag} \text{ (silver atom)}$$

the bromide ion in light losing an electron, which is then accepted by a silver ion to form a metallic silver atom. The same mechanism was independently postulated about the same time by K. Fajans.[2]

Various subsequent hypotheses on the formation of the latent image have been chiefly concerned with the mechanism of concentration of the product to give developable nuclei[3] rather than with the primary photochemical reaction. However, very important investigations have been made by Eggert and Noddack[4] and by F. Weigert[5] on the application of Einstein's photochemical equivalence principle to silver halides. Eggert and Noddack concluded that the primary reaction agrees with this principle, in the sense that for each quantum of light absorbed, one silver atom is produced.

$$\text{a)}\quad \overset{-}{\mathrm{Br}} + h\nu = \mathrm{Br} + \Theta$$

$$\text{b)}\quad \overset{+}{\mathrm{Ag}} + \Theta = \mathrm{Ag}.$$

Eggert and Noddack's results point to absolute coupling of the reactions (a) and (b). Their experiments were carried out with gelatino-silver bromide plates. In view of the criticisms of Weigert a redetermination of the quantum efficiency with pure silver halides free from binding materials seems very desirable.[6] In the meantime, a discussion of certain of the energy changes in the decomposition of the silver halides in terms of the lattice energies of the crystals appears of interest, because it affords a definite analysis of the steps involved in proceeding from silver and halogen to form silver halide crystals, and conversely from these crystals to metallic silver and free halogen.

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* Communication No. 360 from the Kodak Research Laboratories.

[1] S. E. Sheppard and A. P. H. Trivelli: Phot. J., 61, 403 (1921).

[2] Chem. Ztg., 45, 666 (1921); Z. *Elektrochem.* 28, 499 (1922).

[3] Cf. S. E. Sheppard, A. P. H. Trivelli, and R. Loveland: J. Franklin Inst., 200, 76 (1925).

[4] Sitzungsber. preuss. Akad. Wiss., 1921, 31.

[5] Z. physik. Chem., 99, 499 (1921); also Z. Physik, 18, 232 (1923).

[6] The writers are engaged upon an investigation of the quantum efficiency, using a modification of the method of Hartung in which silver halide is decomposed by light *in vacuo* and the weight loss measured with a very sensitive micro-balance.

Thermochemical Cycle for Calculation of Lattice Energies of Silver Halides

The following reaction cycle for the silver halides is that proposed and used by M. Born[1] and discussed by Foote and Mohler[2] in regard to spectroscopic data. For a given silver halide AgX, where X is a halogen atom, we have the following cycles representing the formation and decomposition of the salt:

$$\begin{tikzcd}
S_{AgX} \arrow[r] & {[AgX]} & Q_{AgX} \arrow[l] & {[Ag]\,1/2(X_2)} \arrow[l] & S_{Ag} + D_x \arrow[l] & (Ag)(X) \arrow[l] \\
(AgX) \arrow[u] & U \arrow[u] & & & & J_{Ag} \arrow[u] \\
J_{AgX} \arrow[u] & (Ag)^+(X)^- \arrow[l] \arrow[u] & & E_x \arrow[ll] & & (X)\ (Ag^+)\ (\Theta) \arrow[ll, dash] \arrow[u]
\end{tikzcd}$$

In the discussion of these cycles, all heat and work units are expressed in kg. cal. The symbols used have the following significance.[3]

[ ] denotes crystalline solid state,
( ) denotes gaseous state,
D = heat of dissociation per gram atom ($\frac{1}{2}$ gm. molecule of X_2),
S = heat of sublimation at absolute zero of 1 gram mol metal or salt,
Q = heat of formation of the salt from the elements in the ordinary state,
J = work in kg. cal. necessary to ionize 1 gram-mol salt or metal,
E_x = electron affinity of 1 gram atom halogen gas, in kg. cal.,
e = 1 gram atom electron gas.

In these cycles, we can obviously start from any state of combination and aggregation of the material, and proceed to any other, evaluating the energy changes. The normal course in the photographic process is from ion pairs Ag^+ and X^- in a dissolved state to the solid crystalline lattice AgX. Making allowance for the hydration of the ions,[4] this will be equivalent to the passage from the gaseous state (Ag^+) (X^-) and correspond to the lattice energy U.

To determine this lattice energy we can proceed either by the left or right cycle indicated, but data for the former are lacking. On the right hand cycle work is counted as *absorbed* by the system for movement against the direction of the arrows, and *afforded* for changes in the opposite direction. Starting from (Ag^+) (X^-) equivalent gram atoms of the ionized gases, the first step is

$$(Ag^+)\ (X^-) \longrightarrow (Ag^+)\ (X)e.$$

This requires energy equal to the electron affinity of the halogen. This might be determined directly from the convergence limit of a spectrum corresponding to the reaction $X + \Theta = X^-$ or by determination of the ionization potential of the atoms.[5] Indirect determination of the electron affinity is possible:—

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[1] Verh. deutsch. physik. Ges., 21, 13, 679 (1919).

[2] "Origin of Spectra," 180 (1922).

[3] Cf. Foote and Mohler: op. cit.

[4] Fajans: Verh. deutsch. physik. Ges., 1, 45 (1920); Grimm and Herzfeld: Z. Physik, 19, 141 (1923).

[5] Cf. Angerer: Z. Physik, 11, 167 (1922); Gerlach and Gromann: 18, 239 (1923); Oldenberg: 25, 136 (1924); 31, 914 (1925); B. Ludlam: Trans. Faraday Soc., 21, 610; J. Franck: 612 (1925-6).

a. By taking Born's values for the lattice energies of the alkali halides, and solving for E_x in the equation for the cycle.

b. Similarly, but using the lattice energies of the alkali halides deduced by Fajans from their heats of solution.

c. By using values for the ionization potentials of the hydrogen halides.

The data may be divided into two groups, corresponding to the direct and indirect methods.

TABLE I

Direct Values of E' in kg. cals.

	Year	Cl	Br	I	Observation
Spectroscopic*	1922	89.3	67.5	59.2	von Angerer: Z. Physik, 19, 149 (1922)
	1925	86.6 89.6	79.1 81.3	71.3	von Angerer and Müller: Physik. Z., 26, 643 (1925)
	1926	89	77	66	Ludlam: Trans. Faraday Soc., 21, 616 (1926).

* The validity of the spectroscopic data as relevant to the electron affinity of the halogens has been questioned by J. Franck: Trans. Faraday Soc., 21, 612 (1925-6)

TABLE II

Indirect Values of E_x in kg. cals.

	Year	Cl	Br	I	Observation
1.	1919	86	86	79	M. Born: Verh. deutsch. physik. Ges., 21, 679; K. Fajans: 714 (1919). Methods (a) and (b)
2.	1920	118.8	88.6	80.7	von Weinberg: Z. Physik, 3, 340 (1920)
3.	1920	119	84	77	M. Born: Die Naturwiss., 8, 373 (1920).
4.	1922	116	87	81	Foote and Mohler: "Origin of Spectra," p. 182.
5.	1923	88	89	82	Grimm and Hertzfeld: Z. Physik, 19, 149 (1923).
6.	1922	81	73	66	von Wartenberg and Henglein: Ber., 55, 1003 (1922).

On considering this last table, it will be seen that the series (2), (3), and (4) all give notably high values for the electron affinity of chlorine. We find that this results from a value for the dissociation heat $Cl_2 \rightarrow 2\ Cl$ having been used in these calculations (see next section) which is probably considerably too great. This value is $Cl_2 \rightarrow 2\ Cl + 2\ D_{Cl} = 113$ kg. cal. due to M. Pier[1] concerning which Lewis and Randall[2] have the following to say: "His data did not give directly either the heat of dissociation or the degree of dissociation; but at each temperature the product of the two was found. Then, employing the thermodynamic requirement for the change of the degree of dissociation with the temperature, he solved simultaneously for both unknowns. Thus he found 0.026 for the degree of dissociation at the highest temperature (2067° K.) and $\Delta H_0 = 113$ kg. cal. for reaction $Cl_2\,(g) = 2\ Cl_{(g)}$. Such a procedure greatly exaggerates the large errors which are inevitable in work of this character."

Using Pier's data, and their own heat capacity and entropy equations, they find for this heat of dissociation $\Delta H_0 = 70$ kg. cals. It will be seen from the spectroscopic data cited in the next section that this value is still somewhat high, but it confirms the conclusion that the values (2), (3), and (4) for the electron affinity of chlorine are too large. If we except these and give the other values cited equal weight, we obtain for the electron affinities of the halogens

	Cl	Br	I
Direct	88.6	76.2	65.5
Indirect	85.0	84.6	77.6

Ionization Work of Silver

The next step required is J_{Ag}, the ionization work of silver. The only datum for this is the determination of first ionization potential of silver vapor by Piccardi.[3] This gave 7.54 volts, equivalent to 174 kg. cals. per gram atom.

Dissociation Heats of Halogens

The term D_x corresponds to the heat of dissociation of the halogen molecules per gram atom

$$Cl_2 \rightarrow 2Cl - 2\ D_{Cl}$$
$$Br_2 \rightarrow 2Br - 2D_{Br}$$
$$I_2 \rightarrow 2I - 2D_I$$

Here again, the values may be determined more or less indirectly from thermodynamical calculations,[4] or more directly spectroscopically from the short wave-length limit of the molecular band spectrum.[5] We have tabulated the significant data as follows:—

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[1] Z. physik. Chem , 62, 385 (1908), quoted by Landolt and Börnstein, p. 906, with the parenthetic comment (Geschätzt!)

[2] "Thermodynamics," p. 490 (1923).

[3] Gazz., 56, 512 (1926).

[4] Cf. Lewis and Randall: op. cit.

[5] Franck: Trans. Faraday Soc., 21, 536 (1925-6).

TABLE III

Dissociation Heats of Halogens in kg. cals. per gram atom

	Year	Cl	Br	I	Observation
1.	1908	56.5			M. Pier: Z. physik. Chem., **26**, 385 (1908)
2.	1910			17.15	Starck and Bodenstein: Z. Elektrochemie, **16**, 961 (1910)
3.	1914			17.8 17.2	O. Stein: Ann. Physik, (4) **44**, 497 (1914)
4.	1919		23 ± 5		K. F. Herzfeld: Ann. Physik, (4) **59**, 635 (1918)
5.	1923	35	20.8	15.8	Lewis and Randall: "Thermodynamics"
6.	1923	27	23	18	Grimm and Herzfeld: Z. Physik, **19**, 149 (1923)
7.	1924	28.5			K. Wohl: Z. Elektrochemie, **30**, 36 (1924)
8.	1924	35	20	17.	R. H. Gerke: J. Am. Chem. Soc., **46**, 953 (1924).
9.	1926			17.25	J. Koenigsberger: Naturwiss., **14**, 779 (1926)
10.	1926	28.5	22.6	17.6	H. Kuhn: Naturwiss., **14**, 600 (1926)

Of these data, the value $D_{Cl} = 56.5$ kg. cal. of Pier has already been discussed and dismissed as too high. The value 35 kg. cal. calculated by Lewis and Randall also appears high according to the spectroscopic data. Gerke's value $D_{Cl} = 35$ (No. 8) appears to be taken from Lewis and Randall. The other values, for Br and I, are consistent enough, so that we may provisionally accept the evaluation of Kuhn, and take

$$D_{Cl} = 28.5,\ D_{Br} = 22.6,\ D_{I} = 17.6.$$

Heat of Sublimation of Silver

For S_{Ag} corresponding to $[Ag] \rightarrow (Ag)$ we have the following:—

H. C. Greenwood	55.8 kg. cal., 1911	Z. physik. Chem., **76**, 484 (1911)
Grimm and Herzfeld	63.3 kg. cal., 1923	Z. Physik, **19**, 149 (1923)
F. Haber	66.0 kg. cal., 1919	Sitzungsber. preuss. Akad. Wiss., **30**, 506 (1919)

The values of Grimm and Herzfeld, and of Haber based on thermodynamics and compressibility are in fairly good agreement, and provisionally the value 65 kg. cal. will be used

Heats of Vaporization of Bromine and of Sublimation of Iodine

In the cases of $1/2\ Br_2 \rightarrow Br$ and $1/2\ I_2 \rightarrow I$ the heat effects of change of state should be included. For the former we have taken 3.70 kg. cal.[1] and for the latter 7.27 kg. cal.[2]

Heats of Formation of Silver Halides

Finally, for the heats of formation of the solid silver halides, according to $Ag\ 1/2\ (X_2) = Ag\ X + Q_{AgX}$ we have the following data:—

Table IV

Heats of Formation of Silver Halides

Year		AgCl	AgBr	AgI	Observation
1914		30.41			Braun and Kauf: Z. angew. Chem., **87**, 186 (1914)
		30.61			L. Wolff: Z. Elektrochemie, **20**, 19 (1914)
1916				15.15 (cryst)	Taylor: J. Am. Chem. Soc., **38**, 2295 (1916)
1925	calc.	28.94	23.52	14.32	B. H. Wilsden: Phil. Mag., **49**, 900 (1925)
	obs.	29.94	23.0	14.0	
			23.81 ±.05	14.97 ±.05	T. J. Wells: J. Phys. Chem., **29**, 816 (1925)

In view of the greater uncertainty in several of the other values involved, it appears sufficient to take the following round number values for our purpose:—

Q_{AgCl} 30.0 kg. cal.
Q_{AgBr} 24.0 kg. cal.
Q_{AgI} 15.0 kg. cal.

For the calculation of the lattice energies we have

$$U = Q - (E - J) + D + S + s.$$

If we take the direct, spectroscopic values for E_X (Table I) this gives

U_{AgCl} 209 kg. cals.
U_{AgBr} 213.1 kg. cals.
U_{AgI} 213.6 kg. cals.

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[1] Andrews: J. Chem. Soc., **1**, 27 (1849) gives 3.65; Lewis and Randall: *op. cit.*, p. 512 give 3.75, Thomsen: Thermochemical Investigations (1905) gives 3.28 kg. cal. (It must be remembered that this will vary with the temperature.) Lewis and Randall find $\Delta H = 10450 - 9.6T$, where T is temperature absolute, for the heat per gram molecule, H which agrees almost precisely with the heat of vaporization determined by Berthelot at 60°, and is a trifle higher than the value obtained by Thomsen.

[2] Baxter, Hickey and Holmes: J. Am. Chem. Soc., **29**, 127 (1907); recalculated by Lewis and Randall: *op. cit.*, p. 522; *cf.* particularly, Lewis and Randall: "Free Energy of Iodine Compounds," J. Am. Chem. Soc., **36**, 2259 (1914). Favre and Silbermann: Comptes rendus, **29**, 450 (1889) gave 6.08 kg. cal.

If we take the indirect values for E_X, then

U_{AgCl} 212 kg. cals.
U_{AgBr} 205 kg. cals.
U_{AgI} 201.5 kg. cals.

The latter values agree better with those of Grimm and Herzfeld.[1]

$U_{AgCl} = 205$ kg. cals.
$U_{AgBr} = 198$ kg. cals.
$U_{AgI} = 192$ kg. cals.

and we might perhaps regard the former somewhat with suspicion, as making the lattice energy of AgI greater than that of AgCl.

There enters here, however, the question as to how far lattice energies computed on the assumption of purely ionic lattices from rigid ions are correct, when there may be deviation from this premise, in the sense of deformation of the ions[2] and approach to less heteropolar, more homopolar lattices. As will be noticed shortly, this tendency increases on passing from AgCl to AgI. Concerning this, Grimm and Herzfeld remark as follows:[3]

"Finally, let us take into consideration the possibility that the assumed crystal lattice of rigid ions is so altered, that the ions are 'deformed,' indeed, that the lattice does not remain an ionic lattice, and that the ionic deformation leads to the 'heteropolar' union passing over into a more or less 'homopolar' union. In this case, which, for example, would present itself in the passage of the salt Xenon chloride XeCl into a compound of the type ICl, we have to consider a 'deformation' energy outside the limits of the theoretical Born lattice theory, the magnitude of which remains unknown to us. *Since, however, the lattice energies of existing compounds used by us later are based on experimental data and not on theoretical values, the deformation energies are already contained in them*, and it only remains questionable, whether the difference of the 'deformation energies,' for example of XeCl and NaCl, or of MgI_2 and AlI_3 can strongly falsify our estimated lattice energies. In the most extreme case, with HCl, the deformation 'energy' amounts to some 100 kg. cal.[4] As, however, with H^+ there is an extreme case, and in our calculations only the *differences* of the deformation energies is important, we conclude, that the deformation will not falsify our results."

The conclusion is somewhat different when, as in the present case, it is the absolute magnitude of the lattice energy which is important.

A principal issue raised in the present communication is the following. In the photodecomposition of the solid silver halides, is the lattice energy something which has to be overcome by radiation? If not, what becomes of this energy? If so, how is it effected, directly or indirectly? Before specifically taking up these questions, we may refer to the direct calculation of the lattice energies in Born's theory, by way of compressibility values.

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[1] Z. Physik, 19, 141 (1923).
[2] See later.
[3] Loc. cit., p. 147.
[4] Cf. Grimm and Herzfeld: Z. Physik, 19, 147 (1923); P. Knipping: Z. Physik, 7, 328 (1921).

Determination of Lattice Energies from Electrostatic Theory[1]

If the ions are assumed to be *infinitely* hard rigid charged spheres, the (attraction) potential for any two according to Coulomb's law is given by $\phi_o = \pm e^2/r$, where e = ionic charge, and r = distance between atomic centers. This picture is inadequate, since the substances formed are not incompressible, and instead there is postulated a force of repulsion which is infinitely small at great distances, but does not increase infinitely rapidly. By analogy with Coulomb's law, the potential energy of this force is given by $\phi = +\beta/r^n$ where β and n are constants. The total potential energy for any two ions is therefore

$$\phi = \pm e^2/r + \beta/r^n.$$

In calculating the potential energy of a whole lattice from the mutual interaction of pairs of ions in different orientations, it is evident that r becomes δ, the lattice constant, *i.e.*, the distance from one ion to the next similar ion on the edge of the unit cube.[2] The solution will be of the form

$$\Phi = -a/\delta + b/\delta^n$$

where a and b are constants obtained by summation over e^2 and β. Calculation of the constant a of the electrostatic term has been facilitated by Madelung.[3] For a lattice of the NaCl type, where Φ is the potential energy for each elementary cube of edge δ, $a = 13.94\ e^2$.

The reaction below δ_o the equilibrium value of the lattice constant and the corresponding energy of unit cube is obtained from the condition that for δ_o the value of $d\phi/d\delta$ is zero. This gives

$$\Phi_o = -a/\delta_o\,(1 - 1/n).^4$$

The lattice constant δ_o for the undeformed crystal can be determined by X-ray spectrographic methods, or can be calculated. If m and m' be the atomic weights of the two ions, then $\frac{m + m'}{N}$ is the weight of one "molecule," AgX, and since in this type of crystal there are four of these in the unit cube, the mass of this is $\frac{4(m + m')}{N} = \rho\Delta^3$, where ρ is the density of the crystal, and $\Delta = \delta_{o/2}$.

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[1] M. Born: "The Constitution of Matter," 50 (1923).

[2] Born: "The Constitution of Matter," 50 (1923).

[3] Physik. Z., 19, 524 (1918).

[4] $\frac{d\Phi}{d\delta} = \frac{-a_2}{\delta} - \frac{nb}{\delta^{n+1}} = 0$ for Φ_o, δ_o.

Hence $\frac{nb}{\delta_o^{n+1}} = \frac{a_2}{\delta_o}$

$$b = \frac{a}{n}\delta_o^{n-1}.$$

Hence $\Phi_o = \frac{-a}{\delta_o} + \frac{a}{n}\frac{\delta_o^{n-1}}{\delta_o^n}$

$$= \frac{-a}{\delta_o}\left(1 - \frac{1}{n}.\right)$$

The exponent n is connected with the slope of the curve relating the repulsive force ϕ with r. Crystal movement from equilibrium involves diminution of the lattice constant, *i.e.*, a compression. The exponent n is closely connected with the compressibility K of the crystal. It is found that

$$K = \frac{9\delta_o^4}{a(n-1)}.$$

If K, the compressibility, is determined experimentally, n can be obtained from this formula. For the alkali-halides of the type NaCl the value $n = 9$ has been found sufficiently accurate. For the calculation of the lattice energy, we have to multiply Φ_o by $-N/4$ because the elementary cube contains 4 ion-pairs. Hence

$$U = \frac{Na}{4\delta_o}\left(1 - \frac{1}{n}\right).$$

Inserting the values for a and δ_o and for N (Avogadro number) we have

$$U = 545\sqrt[3]{\frac{\rho}{m + m'}}\ \text{kg. cals.}$$

For the silver halides the following data were used:

	ρ	m	m′	U	A°.U./δ_o
AgCl	5.570	107.88	35.46	184	5.56
AgBr	6.473	107.88	79.92	178	5.78
(AgI	5.674	107.88	126.92	150)	6.49

The corresponding values of U are given in the last column. The value for AgI is based on the assumption of a cubic lattice, which is correct only above 140°C. But from the lattice constant given for this[1] 6.493-A°.U. the calculated value of U_{AgI} is 130 kg. cals.

These values are low compared with those obtained indirectly from thermochemical considerations. This is possibly due to the value of $n = 9$ being too high. Although deformation of the anion by the cation, such as occurs in silver salts (*vide inf.*), is not assumed to affect the compressibility, it might affect the slope of the compressibility curve.

Relation of Lattice Energy to Photochemical Change

It was stated already that the primary photochemical change in the silver halides has been represented by the equation

$$\overset{-}{X} + h\nu = X + \Theta$$

followed by

$$\overset{+}{Ag} + \Theta = Ag.$$

Now this means, either that we can disregard the lattice energy, and assume that the light acts on the halide ions as if they were independent gaseous ions, or that starting with the system $[\overset{+}{Ag}X]$ solid we pass by the action of

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[1] Cf. R. Wyckoff: "The Structure of Crystals," 319 (1927).

light to the system $\overset{+}{(Ag)}$ $(X)\Theta$. In the latter case, according to the cycle installed, and the values obtained, this would imply that there must be afforded the energies

$$U + E_X.$$

From the values obtained, it will be seen that these quantities would be for the three silver halides of the following order:—

Silver Halide	U + E_X
AgCl	212 + 85 kg. cals.
AgBr	205 + 84.6 kg. cals.
AgI	201.5 + 77.6 kg. cals.

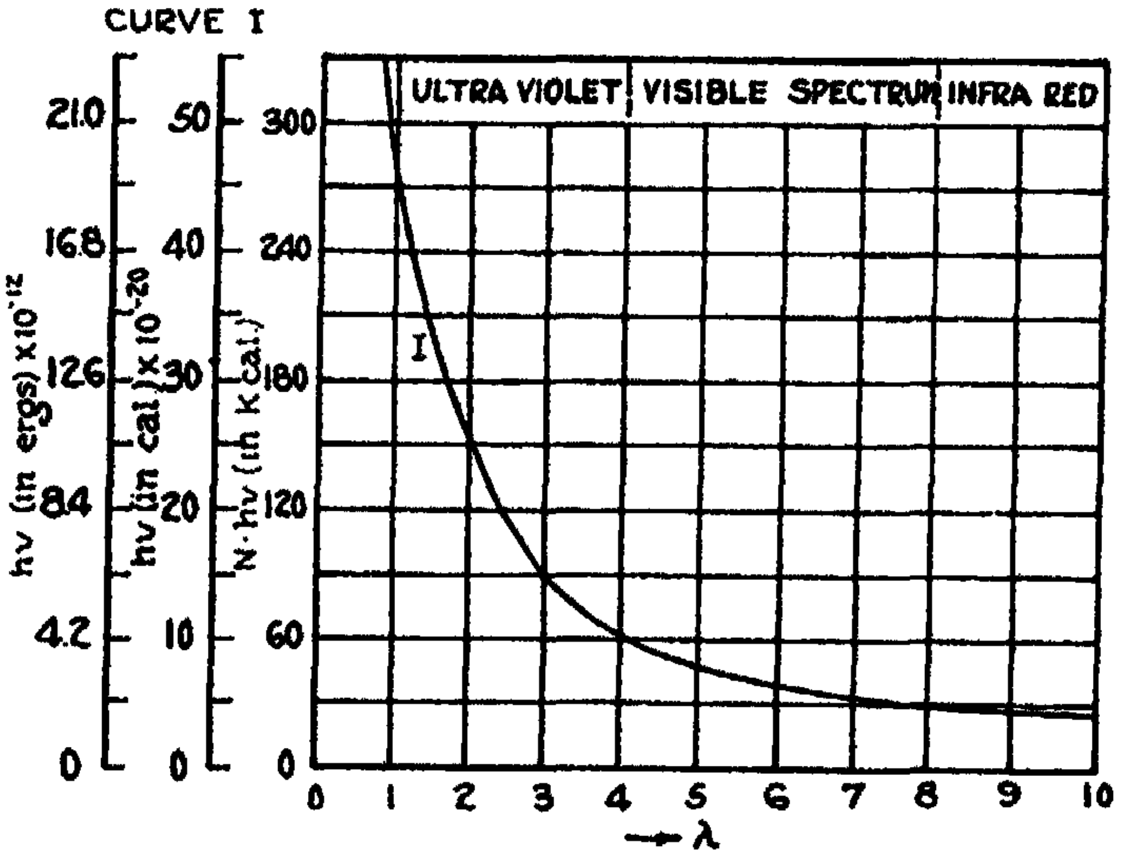

Fig. 1
(Eggert: Lehrbuch physik. Chemie, p. 496 (1926))

Let us suppose that each step requires absorption of an equivalent molar quantum $Nh\nu$ *of radiation. The following graph represents the relation of* wave-lengths to quanta and molar quanta.

A molar quantum $Nh\nu$ = kg. cals. would correspond to a wave-length of about 130 mμ, a molar quantum N $h\nu$ = 86 kg. cals. to a wave-length of about 3200 Å.U.[1] Both these values, notably the first, are far shorter than the wave-lengths active in the photochemical decomposition of the silver halides, which are comprised in the known absorption spectra of these bodies.

The apparent contradiction may be made clearer perhaps by considering a diagram of the energy levels (Fig. 2). The question arises, is this apparent contradiction a real problem? For example, is it necessary to assume the electron separation as the mechanism? If a direct decomposition, corresponding to the heat of formation Q_{AgX} were assumed, (*e.g.*, in homopolar

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[1] Cf. also von Angerer: loc. cit.

molecules) than no contradiction to the wave-length thresholds would exist, since the wave-lengths corresponding to these heats of formation are well in the range of visible and even infra-red radiation (*cf.* Table IV).

But there exists independent evidence that the inner photoelectric effect postulated by Fajans and by Sheppard, actually occurs.

The first piece of evidence is the phenomenon of photo-electric conductivity, particularly of the primary photo-current distinguished by Gudden and Pohl.[1] The correlation of this with the photochemical change is only assumptive and not directly proved. It will be shown that it *might* be possible to regard this effect as *occurring independently of the photochemical change*, and *perhaps as not necessitating any demand by the lattice energy.* But it is evidence of an inner photo-electric effect. The second piece of evidence consists in the production of photo-electric potentials at electrodes of silver: silver halide: electrolyte. The authors will show in another communication that their experimental evidence with this system strongly confirms the simultaneous production of free electrons and atomic halogen, by light acting on the silver halides. We shall assume for the present, therefore, that the assumption of the inner photo-electric effect is justified, and consider the apparent contradiction with lattice energy requirements.

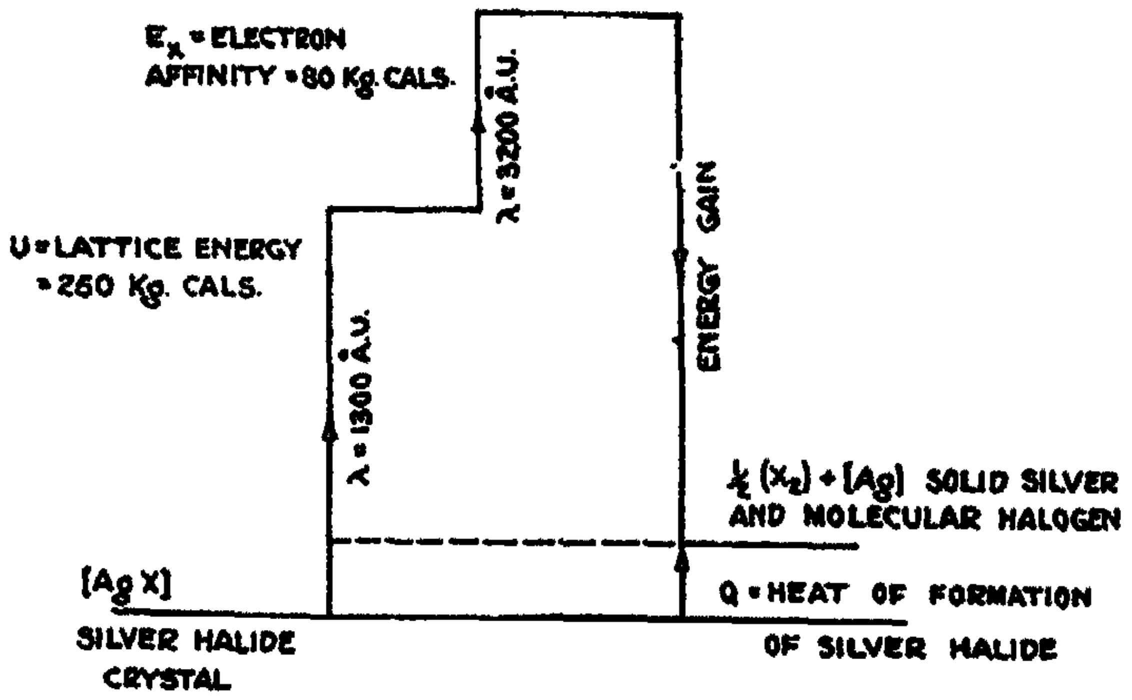

Fig. 2
Energy Level Diagram

One way of meeting the difficulty, which is raised by the quantum theory of energy changes, is suggested by the theory itself. It may not be necessary to supply the full quanta of energy corresponding to U and E$_X$, in view of the free energy liberated in the subsequent stages leading to $1/2(X_2) + [Ag]$. This implies that the electron *is released*, at a cost less than the true electron affinity by an amount corresponding to these subsequent gains. The argument that the free energy of a subsequent reaction phase should be available for an earlier one has usually been rebutted, as teleological. Yet it is

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[1] Z. Physik, 6. 248 (1921).

definitely used in the quantum theory of spectra. For example, Sommerfeld[1] *states: "Consider two atoms, which differ from each other, only in that the* L-shell in the first is present as an L_{11} level, in the second as an L_{12} level. **Should an electron be raised from the K-shell to the surface of the atom,** then the effective nuclear charge of the L-shell is increased by 1; this, therefore, contracts together. *Since in this contraction, energy is set free, the L-shell contributes part of the work for the K-excitation: the excitation-energy is therefore lessened by the presence of the L-shell—and naturally also by the presence of the others."*

It may be objected that there is no way of picturing the over-coming of the lattice energy *U* by a quantum process. The individual ions do not possess lattice energy, as individuals, but only collectively, as a space relation of positive and negative ions. It appears none the less true, that the lattice energy must *ipso facto* exist as a resistance to the freeing of a negative charge. In point of fact, a direct photomechanical action of radiation upon matter has been suggested by one of the writers,[2] and more specifically worked out by F. Weigert for paired systems (atoms or atom groups) of electron donors and electron acceptors.[3] The latter has adduced as further specific evidence for such a process the phenomena of *phototropy* in solids.[4] The latter is shown chiefly by crystal lattices of complex deformable molecules; it is not explicable as an isomeric or tautomeric *molecular* change, but only as an affair of pairs or groups.[5] In view of the problem of disposing of the lattice energy in heteropolar lattices of *relatively* rigid ions, it appears that the evidence for *direct* (primary) *photomechanical* disintegration of the silver halides may have to be reconsidered.[6] Many examples have been cited to demonstrate a direct mechanical disintegration by light acting on solids. Bredig and Pemsel[7] suggested that the developable "latent image" was due to a photomechanical disintegration of the silver halide crystals. Actual disintegration can be observed in the case of silver iodide, as first noticed by C. Schultz-Sellack[8] and studied more fully by H. Scholl.[9] A very thin continuous layer of silver iodide is obtained by exposing a silver mirror to iodine vapor. This becomes turbid and vari-colored by exposure to intense light, and can be shown by rubbing to be actually mechanically disintegrated.

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[1] "Atombau und Spektrallinien." 3rd. Ed., Chap. 8 On Theory of Fine Structures, p. 614 (1924).

[2] S. E. Sheppard: "Photochemistry," 331 (1914).

[3] Verh. deutsch. Physik. Ges., 21, 479, 615, 639 (1919); Z. Physik, 2, 1 (1920); 3, 437 (1920); 5, 410 (1921).

[4] Z. Elektrochemie, 24, 222 (1918).

[5] S. E. Sheppard: Chem. Rev., 4, 319 (1927).

[6] Discussed in a forthcoming article by S. E. Sheppard on "Colloids and Photochemistry" in J. Alexander's "Colloid Chemistry, Theoretical and Applied."

[7] Arch. wiss. Phot., 1, 33 (1899).

[8] Pogg. Ann., 143, 442 (1871).

[9] Ann. Physik, 16, 193, 417 (1905).

Lüppo-Cramer[1] at one time maintained the view that these phenomena, and the "developability" by ammonia induced in silver bromide by light[2] were due to direct photomechanical disintegration.

In 1910–11, The Svedberg[3] observed that a number of metals—mercury, silver, lead, copper, tin—would be disintegrated quite rapidly by ultra-violet light, more slowly by ordinary light. He obtained colloid sols in water or alcohol in this way.

The investigations of Nordenson[4] were held to show that the mechanical disintegration of the metals is a *consequence* of a preliminary photochemical preoxidation, while Lüppo-Cramer also abandoned[5] the view of primary photomechanical disintegration of the silver halides in favor of regarding it as a *consequence* of photochemical liberation of halogen and disruption by halogen pressure.

The importance and magnitude of the lattice energy of silver halide crystals forces a restatement of the question, however. Thermodynamic consideraton of the lattice formation already discussed (p. 200) and the *tensor* character of the radiation in the newer wave-theories[6] suggest that it is neither necessary nor sufficient to regard the mechanical disintegration of the crystal as the *consequence* of a primary photochemical change. It appears that at the least there is an initial synergy of the photomechanical and the photo-electric actions of light. Synergy in the sense that the lattice loosening (Gitter-Auflockerung) and electron liberation and transfer are closely coupled prophases of *any* photochemical change in solids. It is probably much too soon to speak here of one aspect as usually preceding the other.

Lattice Disorientation and Ionic Deformation

We saw that there was another thermodynamic cycle leading from the solid lattice to the gaseous ions, *viz.*, by way of the sublimation heat S_{Ag}; and the work of ionic dissociation J_{AgX}. Hence

$$U = S_{AgX} + J_{AgX}.$$

Is one to suppose that radiation has to furnish two equivalent quanta before valency electrons can be removed from the independent gaseous negative ions by yet a third quantum? This appears even more improbable than a *direct* photomechanical sublimation into gaseous ions.

Moreover, even if we could treat the lattice ions as equivalent to independent gaseous ions, the quantum required to overcome the electron affinity

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[1] Kolloid-Z., 17, 51 (1915);21, 28, 154 (1917).

[2] Cf. "The Silver Bromide Grain of Photographic Emulsions" by A. P. H. Trivelli and S. E. Sheppard. Monographs on the Theory of Photography, No. 1 (1921).

[3] Kolloid-Z., 6, 129 (1910); also M. Kimura: Memoirs Kyoto Coll. Sci. (Japan), 5, 252 (1913).

[4] Kolloidchem Beihefte, I., 91 (1915); *cf.* also The. Svedberg: "The Formation of Colloids," p. 81 (1921).

[5] "Kolloid Chem. Kolloid-Chemie und Photographie," 2d Edit.

[6] Swann: J. Franklin Inst., 205, 323 (1928).

is still much larger than that experimentally found effective. Provisionally, it appears that a way out is to be found in a "loosening" disorientation of the lattice itself—equivalent to a reduction of the lattice energy-correlated with a deformation of the ions, equivalent to a reduction of the electron affinity. Some of the evidence for this will be considered.

Lattice loosening or disorientation has been discussed in relation to diffusion and electrolytic conduction in solid crystals. G. von Hevesy[1] has pointed out that at the melting point the magnitude of the conductance of fused salts changes abruptly. Assuming that the electronic condition does not change at the melting point, the number of free ions must have increased in the melt. Conversely, the fall in conductance on solidification must be due to the immobilization of the ions in the lattice. However, in the neighborhood of the melting point the lattice is relatively loosened or disoriented, so that a notable number of ions can still wander. As a rough measure of this tendency to lattice disorientation he suggests the ratio

$$x = \frac{\text{conductance of liquids}}{\text{conductance of solids}}$$

taken just below and above the melting point. The following table shows how this varies with different salts:

TABLE V

$x = \frac{\text{Conductance of liquids}}{\text{Conductance of solids}}$		$x = \frac{\text{Conductance of liquids}}{\text{Conductance of solids}}$	
	x		x
$NaNO_3$	20000	TlCl	160
KNO_3	20000	TlBr	130
$LiNO_3$	10000	TlJ	100
KCl	9000	AgCl	30
$PbCl_2$	5000	AgBr	5
$SnCl_2$	4000	AgJ	0.9
NaCl	3000		

Of great importance for the present argument is the parallelism indicated by von Hevesy between lattice disorientation, as indicated by this coefficient, and the *inclination of the ions to pass to the neutral state.* According to von Hevesy, *if* $[K^+Cl^-]$ *is to be converted to* $[K] + [Cl]$ *then the electron affinity of Cl must be overcome.*[2] This demands 89 kg. cal. per gram atom, while the ionization work of $K + e \longrightarrow \overset{-}{K}$ which is gained is 99 kg. cal./gram atom, giving the slight excess only of 10 kg. cal. Then in the case of $[Ag^+I^-]$, von Hevesy takes the corresponding values, of $\overset{-}{I} - e \longrightarrow \underset{+}{I}$ as 50 kg. cal./gram

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[1] Über Gitter-Auflockerung," Z. physik. Chem., 101, 337 (1922).

[2] Von Hevesy does not mention the lattice energy itself, nor why the decomposition to $[K] + [Cl]$ (or $1/2(Cl_2)$) might not have proceeded some other way than by that proposed—e.g., by sublimation and dissociation.

atom (which is probably too low, *cf.* Table II) and of Ag + e → Ag as 328 kg. cal./gram mol. Since the halogens were reckoned per gram atom, this should be 164 kg. cals./gram atom,[1] giving an excess of free energy of about 100 kg. cals./gram mol. of halide. Restating von Hevesy's tabulation with the data used in this paper we have:

TABLE VI

	Energy gain on transfer of the ions to neutral state in kg. cal.	x Conductance above M.P. Conductance below M.P.
CsCl	89.8 − 88.8 = 1.0	—
KCl	99.0 − 88.8 = 1.2	9000.00
NaI	118.0 − 66.2 = 41.8	—
TlBr	140.0 − 76.8 = 63.2	130.00
AgCl	174.0 − 88.8 = 85.3	34.00
AgBr	174.0 − 76.8 = 97.2	5.00
AgI	174.0 − 66.2 = 107.8	0.89

The table still supports von Hevesy's contention that "the smaller the work necessary to convert the ions composing the crystal into the uncharged condition, the greater the degree of disorientation of the crystal." Von Hevesy does not indicate definitely the relation of this disorientation to the lattice energy. After referring, however, to Born and Landé's theory of crystal lattices formed by electrostatic equilibrium between rigid ions, he does say however: "If we now assume that *a* K^+ *or a* Cl^- *ion is neutralized at one point or another of the lattice, i.e., is converted to an unchanged state, then that is equivalent to a disturbance of the equilibrium at the corresponding position of the lattice, which must result in a local disorientation.*" He further suggests that such a local disorientation may not require the ions to pass completely to the unchanged state, but that it may suffice for the electrons to be raised to high quantum orbits.

The converse of this argument would seem to be that if reducing electron affinity lowers the lattice energy content, by disorientation, then to reduce the electron affinity must require preliminary work on the lattice, *i.e.*, overcoming of lattice energy.

The "disorientation coefficient" of von Hevesy is discussed by Gudden in relation to conduction in solids.[2] "This conclusion may be so interpreted,

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[1] It appears certain that von Hevesy has taken the value for $\overset{+}{Ag} + e \rightarrow Ag$ at twice the correct value (per gram atom). The energy G for the change $R^+ + e - G = R$ is given by $\frac{e\,V_i\,N}{300\,j.}$ cals. where e = electron charge N = Avogadro's number, j = mechanical equivalent of heat and V_i = ionization potential per atom. Taking von Hevesy's value 99 kg. cals. for K, and taking 4.32 volts per atom as the value of V_i for K, 7.54 volts per atom as the value of V for Ag (Foote and Mohler, *op. cit.* Table X), then the value of G for Ag on von Hevesy's basis for K must be $99 \times \frac{7.54}{4.32} = 170$ kg. cals./gram atom. Evidently he doubled the value for Ag, but not for K.

[2] B. Gudden in "Ergebnisse der exakten Wissenschaften," 3, p. 116.

that in consequence of *heat vibrations*, in the alkali nitrates [equally halides] only an extremely small fraction, but on the other hand in the silver halides a considerable fraction, of the ions are *transiently and oscillatingly* neutralized. Such *neutral atoms* disturb the lattice cohesion and facilitate ionic migration."[1]

There may be distinguished different processes of electric conduction in solids.[2]

$$\text{Dark}\begin{cases}\text{Electronic (metallic)}\\ \text{Electrolytic (unilateral)}\end{cases}$$

$$\text{Light}\begin{cases}\text{Primary (electronic)}\\ \text{Secondary (electrolytic)}\end{cases}$$

It is the photoconductance effect which interests us here. The *primary* photoconductance effect is distinguished, in selected crystals of high refractive index, by production on illumination of a current—on applied p.d.—of finite strength, without inertia. For all applied e.m.f.'s, its strength is proportional to the absorbed light of definite wave-length. This primary current apparently consists of two components, *viz.*, a practically instantaneous wandering of negative charges from the place of light absorption to the anode, and a replacement of these charges from the cathode. There may elapse a considerable interval between the two processes, which can be made practically zero by higher e.m.f., by heating, or by illumination with long wave-length rays.[3]

The primary current is electronic, due to the definite production of electrons, plus their movement under the applied e.m.f. It would appear that the considerations already advanced concerning the liberation of photo-electrons in the silver halides, in respect of lattice energy and electron affinity, should also apply to the process of photoconductance. Here again, as in the photochemical decomposition, the effect is produced at wave-lengths extending into the long wave-length side of the characteristic absorptions. Moreover, in typical cases[4] the Einstein photo-electric equivalence principle is followed, in that one electron is produced for each quantum of radiation absorbed independently of the frequency.

One face of the difficulty of the quantum magnitude for the release of electrons in silver halides by light, *viz.*, that concerning the electron affinity of the halogen, has been definitely recognized by K. Fajans.[5] More than that, his work on ionic deformation is one of the most important recent contributions to the theory of photochemical sensitivity, and furnishes the most promising solution of the electron affinity difficulty as such. Fajans points out that in both [$\overset{+}{\text{Na}}\ \overset{-}{\text{Cl}}$] and [$\overset{+}{\text{Ag}}\ \overset{-}{\text{Cl}}$] *a priori*[6] the energy required to remove

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[1] And also electron movement.

[2] Cf. B. Gudden: loc. cit.

[3] This is attributed to "lattice loosening."

[4] Diamond and ZnS crystals (cf. Gudden: op. cit.). Selenium shows deviation from this, due probably to a secondary interfering factor.

[5] Cf. Fajans and W. Frankenburger: Z. physik. Chem., **105**, 255 (1923).

[6] Or in accordance with the thermodynamic considerations of the Haber-Born cycle.

the valence electron from the Cl ion—i.e., the electron affinity—is the same. "But the energy which becomes free on the attachment of the electron to the cation is different." This greater free energy for silver, or greater electron affinity of silver compared with sodium, might be advanced as an explanation of the greater photochemical sensitivity (in the sense of wave-length threshold) of silver chloride over sodium chloride. On similar lines to those developed by von Hevesy, the energy necessary to decompose the salts may be represented as

$$E_{\mathrm{AgCl}} = \mathrm{Nh}\nu' = x - 173$$
$$E_{\mathrm{NaCl}} = \mathrm{Nh}\nu'' = n - 118$$
$$E_{\mathrm{NaCl}} = E_{\mathrm{AgCl}} = \mathrm{Nh}\nu'' - \nu' = 55 \text{ kg. cal.}$$

"The energy of decomposition into atoms must therefore be 55 kg. cal. greater for NaCl than for AgCl. Introducing the quantum relation this means, however, that a greater frequency ($\nu'' > \nu'$) or shorter wave-length, is necessary for NaCl than AgCl." This is in agreement with the fact that NaCl is colored only by extreme ultra-violet or by X-rays. But he goes on to point out the apparent teleological assumption made in assuming that the "energy requirement for transfer of the electron from the anion to the cation does not depend solely upon the *initial state* (electron affinity of the halogen) but also on the *end state* (attachment to the $\overset{+}{\mathrm{Ag}}$ or $\overset{+}{\mathrm{Na}}$ ions). That is, the electron must know already on its separation whether it is to reach an $\overset{+}{\mathrm{Ag}}$ or an $\overset{+}{\mathrm{Na}}$ ion, and adjust its energy consumption accordingly." He further points out that repugnant as this may be to our causal reasoning, it is the logic inherent in the Bohr theory of spectra. (*Cf.* p. 190). Fajans proceeds, however, to indicate another possibility, *viz.*, that contrary to the tacit assumption so far made, the Cl ion may not be in the same initial state in silver chloride as in sodium chloride. If it were, the quanta necessary to produce photoconductance with NaCl and AgCl, where the electrons are liberated but not accepted by the cations, should be the same. But actually AgCl conducts for λ400 *mμ*. (and beyond), NaCl not even at λ186 *mμ*. This difference he ascribes to the *deformation* of the anion by the cation, which can be represented, first as a polarization, or induced dipole formation, secondly as a distortion of the electron orbits of the anion.

It is to be noted that in crystal lattices of the NaCl (and AgCl) type, this cannot give rise to a one-sided polarization of the whole anion, because of the symmetrical field of the cations surrounding it, but the individual elliptic orbits may be regarded as unilaterally deformed by the cations. This deformation brings about decisive changes in the properties of saline (heteropolar)bodies. It is manifested not only in the molar refraction, but also in the *absorption*. Fajans remarks that "it is of great importance for the photochemical behavior of salts that these deformation phenomena by heavy metal cations often lead to a facilitation of the separation of an electron from an anion." (In this connection he cites Gudden and Pohl's observation[1] that

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[1] Z. Physik, 16, 42 (1923).

the photoconductance of heteropolar compounds proceeds in parallel with the strength of deformation as judged on other grounds.)

Two important conclusions appear to be established by this. Fajans' conception of ionic deformation gives a reasonable explanation of the lowered electron affinity of the halogen and anions due to the influence of the silver cations. In effect, part of the work to be done has already been effected. Since this work is afforded by the cation, the subsequent energy afforded by the binding of the electron to the silver ion must be correspondingly less. Hence, the algebraic sum of the terms $-E_X + I_{Ag}$ can remain the same, leaving the lattice energy calculated by Born's cycle the same.

In that case, while the energy difficulty for the electron affinity of the halogen *qua* free, quasi-gaseous, halide ion, is removed by the deformation principle, the difficulty of the lattice energy itself apparently remains.

Yet von Hevesy's evidence shows that the degree of lattice disorientation, which would indicate local or partial *reduction* of lattice energy, goes parallel with the ionic deformation (cf. Table VI) and this is borne out by Fajans' citation of Gudden and Pohl's observation that the photoconductance of heteropolar compounds proceeds in parallel with the strength of the ionic deformation as judged on other grounds.

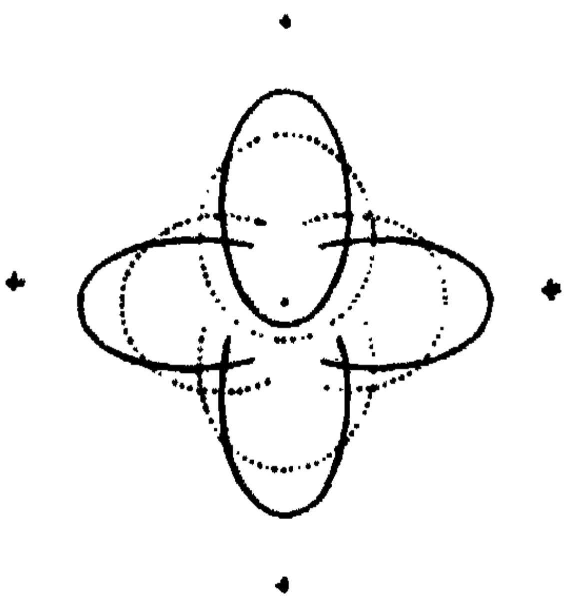

Fig. 3
Lüppo-Cramer: "Die Grundlagen der photographischen Negativverfahren," p. 656 (1927)

Are we then to regard the values of the lattice energies calculated thermodynamically for the silver halides as incorrect? We have seen that the values obtained from the compressibilities were considerably lower, and this might be regarded as supporting this view. However, Heckmann[1] has pointed out that the electric constants involving the compressibility are *not* affected by ionic deformation as such, since these are related to a uniform dilation of the lattice. In any case, the values from the compressibility still require quanta of greater magnitude than those operative either in photochemical action, or in photoconductance.

We are then forced to one of two conclusions. *Either* the lattice energy does not affect the work required to release an electron from a halide ion in silver halides, whether in photochemical or photo-electric effects, *or*, both the photo-electric and the photochemical effects take place primarily in such disoriented parts of the lattice that the initial work can be supplied by the quanta available. The first view is contrary not only to the thermodynamic grounding of the lattice energy, but as will be shown later, is directly in contradiction with the whole electrostatic theory of lattice structure.

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[1] "Die Gittertheorie der festen Körper." In "Ergebnisse der exakten Wissenschaften," 4, (1925).

There remains, therefore, as the more probable conclusion the theory that the light action must be effective in certain portions of the lattice, which are already disoriented parts of the crystal. Now, in the case of photodecomposition, it might seem sufficient to limit this at once to actual surfaces of the crystals. Since the ions in a surface layer are not symmetrically placed in regard to neighboring ions, but unilaterally affected, not only will they have less lattice energy as such, but any ionic deformation will not be spatially symmetrical but will be equivalent to a dipole moment,[1] even *in vacuo*, and apart from the possible effects of adsorbed foreign molecules or ions. The energy of the surface layer is in fact the energy of a half lattice (supposing an infinite lattice cut in two and the two halves infinitely slowly removed from each other) plus the energy of the surface sheet of atoms.[2] It has been shown by Weigle[3] that the potential energy of an electron in the surface of a crystal can be taken on an average as the mean value for all the possible crystal surfaces, and that this mean value equals $1/2\ \phi$, where ϕ is the lattice potential in volts. If we could assume that this held for the liberation of an electron in a silver halide lattice, then without other disorientation effects, the quantum requisite would be brought down to near 400 $m\mu$.

We have only then to suppose a relatively small additional disorientation to have the threshold in the region actually effective in photodecomposition. This may be supplied by the contribution of the ionic deformation to the disorientation in a surface layer of atoms (*cf.* p. 34) or may be supplied by adsorbed gases or vapors, *e.g.*, water. Very careful experiments on superdry[4] silver halides *in vacuo* are required to establish this threshold.

The fact that the photochemical decomposition of the silver halides is not limited to the absolute surface, but can proceed, for thin layers, to nearly 100 per cent decomposition[5] might seem in disagreement with this monatomic view. But actually the photochemical decomposition commences locally on the surface of the crystals[6] and proceeds at the new interfaces thus produced.

Internal Disorientation and Photoconductance

However, the lower lattice energy of surface layers of the crystals does not by itself appear sufficient to account for the photoconductance of single crystals of pure substances, which Gudden and Pohl have shown to be a volume effect. In this case, it appears necessary to assume a certain degree of internal disorientation, which may indeed be limited to individual ions which can react more or less independently of the lattice assemblage. Such ionic "rogues" might be regarded as statistical consequences of the thermal

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[1] Cf. Heckman: loc. cit.

[2] Cf. Born and Stern: Berlin Ber., 1919, p. 901; M. Yamada: Physik. Z., 24, 364 (1923); 25, 52 (1924).

[3] Z. Physik. "Ueber die Gitterenergie und die Ablösearbeit von Elektronen bei Calcium, 40, 539 (1926).

[4] H. B. Baker: J. Chem. Soc., 61, 728 (1892).

[5] Cf. Hartung: J. Chem. Soc., 127, 2691 (1925); 1349 (1926).

[6] S. E. Sheppard and A. P. H. Trivelli: J. Phys. Chem., 29, 1568 (1925).

vibrations of the ions about their main positions, which is in accord with von Hevesy's suggestions on lattice disorientation. As against this, there may be counted the very small temperature coefficients of both the photo-electric conductance and the photo-chemical decomposition.[1] That a temperature influence must begin to appear at higher temperatures seems probable from the phenomena of thermionic emission of heated solids.[2]

There is, however, another aspect of the photoconductance effect which distinguishes it from the case of photochemical decomposition.

Gudden and Pohl have shown that the electrons migrating to the anode are *replaced* by electrons from the cathode. In this case then, the lattice structure need not be broken down, especially if as suggested by Gudden and Pohl, the electronic conduction is not a total migration of free charges, but a handing on of electrons from one excited anion to another. Yet it is significant in this connection that the replacement from the cathode may occurs only after a considerable interval, which may be reduced to practically zero by heating or irradiation with long wave-lengths "which tend to loosen the lattice." The total magnitude of the primary current in these cases does, therefore, depend upon temperature.

The complexity of the influence of wave-length upon the photoconductance has been noticed by von Hevesy also. He states[3] "while crystals with small disorientation tendency first react on exposure to very short wave-length light, it is sufficient to radiate crystals with great disorientation tendency with longer wave-length light to get a notable increase in conductance." He also points out, as observed by Gudden and Pohl, that the primary electronic current gives rise to an extension of the wave-length absorption effective for the replacement current. The degree of internal disorientation cannot be independent of the state of the surfaces of the crystal. When these surfaces are in actual electric contact with other conductors—as in photoconductance experiments, there will be a gradient of unilateral polarization or deformation through the crystal which is simultaneously an ionic deformation and a lattice disorientation. It is pointed out by Heckmann[4] that "increase in electronic binding between cations and anions means a *loosing* of the binding with which a lattice ion is kept in its equilibrium position."

While theoretically the "infinite" ionic lattice has neither a dipole moment nor a quadrupole moment the existence of oppositely charged poles on parallel surfaces will tend to establish a certain degeneration to quadrupole and dipole moments.

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[1] On the small value of the t. c. of photoconductance in Se, see Piersol: Phys. Rev. (2) 30, 664 (1927). More comprehensive studies are required, however, of the t. c. both in photoconductance and photodecomposition, particularly with regard to the wave-length threshold.

[2] *Cf.* O. W. Richardson: "The Emission of Electricity from Hot Bodies," 2nd Ed. (1921).

[3] Loc. cit., p. 349.

[4] Heckman: op. cit.

Energy of Activation and Photochemical Decomposition of Silver Halides

In so far as a preliminary overcoming of lattice energy is necessary before absorbed radiation can loose an electron, it is analogous to the "energy of activation" in chemical reactions.[1] We have suggested that this preliminary work must already be largely accomplished in the case of the silver halides, because the thermodynamic considerations indicate that the quantum required is larger than that afforded. If further it be admitted that the primary liberation of electrons must take place at surfaces and at internally disoriented ions, then since the reaction will be increasing the interface (in the photochemical reaction) it will be autocatalytically supplying the condition for further disorientation. More than this, a certain excess of energy is freed by the combination of the electron with the silver cation (*cf.* p. 253) although this has been drawn on to some extent in the deformation of the anion. Supposing *all* of this to be so absorbed, there remains a considerable excess, together with the energies of dissociation of the halogen, and the heat of sublimation of the silver, as indicated by the equation

$$\phi = U + (E_X - J_{Ag}) - D_X - S_{Ag}.$$

Actually, the silver does not have to be condensed from the gaseous to the solid state, but the silver metal lattice can form *in situ.* This means simply that the relative movement of the electron to the silver cation need be very small, since the silver lattice can be regarded as a silver cation lattice interpenetrated by an electron lattice.

It is concluded from this that the photochemical decomposition of silver halides, and other heteropolar crystals, joins with a number of thermal reactions as a typical case of heterogeneous catalysis at interfaces. The development of this conception in regard to the formation of the latent image is reserved for independent treatment. One corollary with regard to this problem, however, may be mentioned. If a certain quantum of light is required for activation or lattice disorientation independently of the electron liberation from the anion, then some support is found for the suggestion of E. A. Baker[2] with regard to the so-called "reciprocity failure" with photographic plates. It might also be concluded from this that instead of one Ag atom being reduced for each quantum absorbed, as found by Eggert and Noddack[3] it should require *two.* It is in fact notable that Weigert's recalculation[4] of their results indicates a quantum efficiency much nearer 0.5 than 1.0. The possibility of two quanta being required is indicated by Weigert's investigation of the photolysis of *o*-nitro-benzaldehyde. It is too much to say that this supports the view of a preliminary phototropic activation (in the

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[1] Cf. Hinshelwood: Chem. Rev, 3, 227 (1926).

[2] Proc. Roy. Soc. Edin., 47, 34 (1927).

[3] Loc. cit.

[4] Trans. Faraday Soc., 21, 453 (1925-6).

sense of induced dipole movement, corresponding to lattice loosening,[1] preceding or rather synergic with photochemical decomposition in solid crystals. But it suggests the desirability of testing further this hypothesis.

The Photo-Electric Effects

The conclusions reached for photochemical decomposition from consideration of the lattice energy are in good agreement with those reached for the photo-electric effects by Gudden and Pohl.[2] They pointed out that the quantum principle of light absorption yields two consequences for electron emission.

a. The kinetic energy of the electron should vary linearly with the frequency.

b. The number of electrons should increase proportionately to the wave-length.

The first conclusion, expressed by Einstein's equation

$$1/2\ mv^2 = h\nu - p$$

has been very fully confirmed by experiment. The second has had quite other fortune. Two types of dependence of the number of electrons upon the wave-length have been established experimentally. In one, the "normal" effect, the number of electrons increases with the frequency, in the second, the "selective" effect, there is a sharp maximum at a particular wave-length. The latter, although always accompanied by the normal effect can be separated by using polarized light and specular metal surfaces. The "selective" effect is suppressed, when the incident light has no electric vector perpendicular to the metal surface. The "selective" effect also deviates completely from the conclusion (b) while in both cases the "equivalence principle" fails, *i.e.*, there are required many quanta for one electron.

These deviations were attributed to surface factors, because, *e.g.*, the spectral distribution of both the "normal" and the selective effect could be shifted arbitrarily for one and the same metal by alteration of the surface.

For these reasons Gudden and Pohl transferred their attention to the "inner photo-electric effect," or photoconductance, in which the surface is largely eliminated. The principal features they distinguished have been described (p. 034). But it is to be noted that two types of material may be contrasted. In the one, as diamond, or pure zinc sulfide, the absorption is due to the material itself. In the other, as in colored NaCl crystals, it is due to foreign material, in this case dispersed metallic sodium.

The quantum equivalence principle (b) was found to be verified for the first type (proper absorption) on the long wave-length side of the characteristic absorption, but the photoconductance becomes *negligible in the region of higher absorption, i.e.,* on passing to *the short wave-length region of the absorption band.*

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[1] S. E. Sheppard: Chem. Rev., 4, 319 (1927). "Antagonism of Radiations in Photochemical and Photographic Reactions."

[2] Cf. Pohl: Naturw., 14, 214 (1926).

When we reflect that the primary photoconductance effect is obliterated by the production of interfaces and discontinuities, this result is very significant. Because it is the result which would follow if the increasing frequency was approaching a point at which large lattice loosening was effected.

The quantum principle was also verified for one kind of colored NaCl, *viz.*, faintly yellow colored, by X-rays, but not for natural blue and violet rock salt. In this case the verification applied to a selective (resonance) absorption band. It is to be noticed that the blue and violet salts contain ultramicroscopically visible particles, the yellow, amicroscopic. But it was not possible to establish the relation for the typical "selective" photo-electric effect, since it has not been possible to measure the light absorption in the surface layer, which alone is responsible for the "selective" effect. Gudden and Pohl conclude that electrons in crystals exhibit only the quantum absorption and dependence of number upon wave-length in two cases:

(i) In the case of crystals with proper absorption, only in the long wave-length edge of the absorption region. In this region only *such molecules absorb* as are *isolated fom the large mass* by thermal perturbations or other lattice failures.

(ii) In crystals colored by impurities only when these are *molecularly* dispersed. The electron yield is greatly diminished when the metal atoms are packed to even ultramicroscopic particles.

These conclusions are fully in accord with the deduction for photochemical change which we have drawn from consideration of the lattice energy of crystals. This is still more evident in Pohl's final summary, which is, therefore, quoted *in extenso.*

"In both cases the absorbing molecules are separated from their fellows. There can be no mutual action with neighboring, similar absorption centers. This alone appears to be the condition, according to which a quantum $h\nu$ absorbed in a solid body can be retained as kinetic energy of a single electron. Hence an ideal metal lattice should show no surface (external) photo-electric effect. Such can occur only when single molecules are in some way distinguished from the majority, such as by the neighborhood of foreign molecules with quite other proper frequencies."

These single molecules, or rather atom ions, correspond fully to the sublimed or gaseous atomions required by the lattice theory, while the effect of adsorption of foreign bodies in shifting the "selective" photo-electric effect in the spectrum either into the long waves (sensitizing) or into the short waves (desensitizing) finds remarkable parallels in the photographic behavior of the silver halides.

Orientation at Interfaces and the Photo-electric Effect

It is a task for the future to determine how the "activation" producing the responsive isolated ions in photoconductive crystals is brought about. Some of the factors in such lattice loosening have been indicated in this paper. In so far as concerns the photochemical decomposition, the hypothesis of concomitant assymetric lattice distortion and ionic deformation, equivalent to gradients of induced polarity in consequence of adsorbed conductors, has already been indicated by one of the writers in relation to photographic sensitivity.[1] It was then termed the "orientation hypothesis" of sensitivity. It is believed that the considerations advanced here can lead to greater precision of this hypothesis. It is pointed out by Pohl[2] that the influence of the electric light vector in the selective photo-electric effect—which is experimentally measurable chiefly with good specular surfaces—is shown in the production of the effect only when a component vibrating perpendicular to the plane is present. It must, therefore, be concluded that the *adsorbed metal vapor atoms are oriented* relatively to the adsorbing layer, so that there are no electronic orbits (or their equivalents) parallel to the adsorbing layer. Support for this is found in H. E. Ives[3] observations of strong selective photo-electric effects with monatomic layers of sodium metal on glass.

But orientation and increase of electrical moment are synonymous terms. The *dis*orientation of ionic lattices, referred to in the paper, is equivalent to an orientation gradient of the ions concerned giving preferential directions of electron movement and photochemical decomposition.

It may be pointed out further that the conclusions reached, if found valid, establish important connections between photochemical reactions of solids, photochemical reactions of gases, and chemical reactions catalyzed at the surface of solids. *The photochemical reactions of solids are assimilable to photochemical reactions of gases adsorbed to solids.*

Rochester, N. Y.
April 30, 1928.

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[1] S. E. Sheppard: Phot. J., 65, 380 (1925); S. E. Sheppard and A. P. H. Trivelli: J. Phys. Chem., 29, 1568 (1925); S. E. Sheppard: "Colloid Symposium Monograph, 3, 75 (1925).

[2] R. Pohl: loc. cit.

[3] H. E. Ives and A. L. Johnsrud: Astrophys. J., 60, 209, 231 (1924).

THE KINETICS OF THE COAGULATION OF GOLD SOLS

An Investigation of the "Thermo-Senescence Effect" exhibited at Elevated Temperatures*

BY ANN E. DAVIES

Introduction

The present work has been carried out with the object of investigating the change in behaviour as regards rate of coagulation which is exhibited by gold sols as a consequence of the sol having been maintained at a fairly high temperature, namely 80°C, prior to the addition of the coagulating agent. The phenomenon is here termed the "thermo-senescence" or "thermo-ageing" of the sol.

The Smoluchowski equation has been used as a basis throughout the present investigation. Two regions of coagulation have been formulated by Smoluchowski, namely, a region of "rapid coagulation" corresponding to a state of complete electrical discharge of the particles, in which the rate of coagulation is independent of any further increase of electrolyte concentration, and also a region of "slow coagulation" in which the particles are only partially discharged and in which the rate of coagulation is dependent on electrolyte concentration. These terms are used in this sense in the present instance.

The equation obtained by Smoluchowski to give the rate of disappearance of primary particles is

$$\nu_1 = \frac{\nu_0}{(1+\beta t)^2}$$

where ν_0 = no. of primaries at zero time,
ν_1 = " " " " time 't'
β = Smoluchowski's constant.

Smoluchowski has shown that the constant $\beta = 4\pi D\rho\nu_0$

where ρ = radius of sphere of attraction of a primary particle,
D = the diffusion constant as given by Einstein's equation, namely

$$\frac{RT}{N} \cdot \frac{1}{6\pi r\eta}$$

N = the Avogadro constant, r the radius of the particle, and η the viscosity of the medium.

Various investigators have tested this equation for the regions of both slow and rapid coagulation. The general conclusion arrived at is that whilst the Smoluchowski equation holds reasonably well for the region approxi-

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* Communicated by Professor W. C. M. Lewis.

mating to "rapid coagulation," it is inapplicable, in its present form, to the region of "slow coagulation." In this slow region, the equation requires modification to allow for the various electrical influences, but since the exact magnitude and mechanism of these is so far unknown, an adequate quantitative relation for this region has not yet been advanced.

The Problem of Ageing.

The term 'ageing' is usually applied to the changes exhibited by a sol when it is kept at *room-temperature*, but this temperature limitation is purely arbitrary. The ageing process seems to follow no definite law and to differ with the type of colloid. So far, the effect of alteration in temperature on the ageing of sols does not appear to have been investigated systematically. It is possible that maintenance at a high temperature may influence to a noticeable extent one or more of the many possible changes which occur during slow ageing at ordinary temperatures. Physico-chemical changes produced in this manner are denoted by the term "thermo-senescence."

The amount of coagulation experienced by a gold sol when treated with a fixed amount of electrolyte and allowed to coagulate for a definite time interval (coagulation time) at a given temperature, is found to depend on the period during which the sol is maintained at this given temperature before the addition of electrolyte takes place, i.e., prior to the initiation of the actual coagulation process. This period is called here the "Ageing Period" of the sol. A measure of the coagulability of a sol is given by β, the Smoluchowski coefficient.

The present investigation is confined to the region of "slow coagulation," using $BaCl_2$ solution as coagulant.

Experimental

Materials.

In the following investigations, Cox's gelatin, Merck's potassium carbonate, and B.D.H. barium chloride, have been used. The barium chloride was recrystallised from distilled water before use. All solutions were made up with conductivity water. This conductivity water was prepared by the redistillation of ordinary distilled water from a silver-lined copper vessel.

All glass vessels were either Duro or Jena glass. All vessels used for gold sol or electrolyte were thoroughly cleaned before each experiment, with aqua-regia, then alcohol and nitric acid mixture, finally washed well with distilled water and sterilised by steam from redistilled water. The minimum time of steaming was three minutes.

The vessels used for gelatin could not be cleaned in the above manner because acids give an insoluble deposit with the protein. Consequently, these vessels were first treated with strong caustic soda to remove the gelatin and subsequently well washed with soap and water. This was followed by a further thorough washing with distilled water, the vessels finally being steamed.

In the case of the standard Hatschek cells used for the percentage red determinations, the final steaming cannot be carried out as the adhesive used to prepare the cells has a low melting point.

Preparation of Gold Sols.

The following "acetone method" was used:—

To 480 ccs of redistilled conductivity water, 5 ccs of a 1.2 per cent solution of gold chloride were added, together with 14 ccs of a 0.18 N potassium carbonate solution, and 3 ccs of acetone. On warming the solution, a pinkish tinge appears which deepens as the temperature rises. The solution is brought to boiling point and allowed to boil vigorously for about three minutes. A clear ruby-red sol results.

The clear ruby-red sols were dialysed in collodion membranes against distilled water for three days, the water being changed twice a day. The conductivity of the dialysed sols varied from 1–2 × 10^{-5} mhos.

Method of Determination.

Hatschek's[1] colorimetric method was used to determine the degree of coagulation. A stage in the act of coagulation of colloidal gold involves a colour change from red to blue, and this method is based on the assumption that the red colour is due entirely to primaries. The percentage red remaining at any time is proportional to the amount of uncoagulated sol.

The percentage red is measured by means of the "Hatschek wedge" which is fully described in Hatschek's original paper.

Since climatic conditions here prevent the permanent use of "diffuse daylight from a bright sky" (recommended by Hatschek) as a source of light, the source of illumination was an 800 C.P. lamp. The light from this was rendered sufficiently diffuse by reflection from a white surface and passage through a piece of matt glass before reaching the "wedge," an arrangement used by Miss Garner.[2]

Mode of Procedure.

Throughout this investigation, the coagulation reactions have been carried out in flasks immersed in a thermostat at the required temperature. Stirring has been eliminated as far as possible, since, although it is known that this increases the rate of coagulation, the conditions have not been sufficiently worked out to ensure reproducibility and comparability in respect of this variable.

The general mode of procedure was as follows:—

Into two wide-necked chemically-clean flasks were introduced 50 ccs of gold sol and 1 cc of $BaCl_2$ solution respectively. These were corked and fixed, well-immersed, in a thermostat. The flask containing the electrolyte was immersed for about a quarter of an hour before the actual coagulation process began. The flask containing gold sol was immersed for different time intervals, i.e., ageing periods. The gold sol was then poured quickly into the

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[1] Hatschek: Trans. Faraday Soc., **17,** 499 (1921).

[2] Maud Garner: J. Phys. Chem., **30,** 1404 (1926).

electrolyte and the time noted. After a definite period of time, the coagulation was arrested, as recommended by Zsigmondy[1] by pouring the mixture into 10 ccs of a 1 per cent gelatine solution. This mixture (cooled to room temperature) was introduced into the Hatschek apparatus and the percentage red in it determined.

Experimental Error involved.

Different samples of the same batch of sol (the numbers attached to the sols in the tables refer to different batches) have been found to give concordant results to within 1-2 per cent, providing such results refer to the same ageing period. In time measurements, the experimental error is ±½ second.

It must here be emphasized that, owing to the extreme difficulty of manipulation at this high temperature (80°C), it was impossible to keep the flasks *very tightly* corked, and so a slight evaporation effect is inevitable. The influence of this is considered later.

Experimental Results

In all the tables given, the concentration of electrolyte $BaCl_2$ *in the sol* is 0.001068 N.

The choice of coagulation time is purely arbitrary, but 20 seconds gives a suitable degree of coagulation (about 35 per cent to 45 per cent red in most cases.) Readings at the extreme ends of the scale are difficult to determine accurately.

In the tables, the term 'ageing period' refers to the time during which the sol is maintained at the temperature of the thermostat (80°C), prior to the initiation of the actual coagulation process.

The tables given are typical of those obtained during this investigation.

TABLE I. (Sol 11)

Ageing Period	Coagulation time	Per cent red	β
10 mins.	20 secs.	35	2.07
20 "	"	40.625	1.707
27 "	"	48.75	1.296
45 "	"	51.25	1.1895
2 hrs.	"	58.75	0.915
2h. 45m.	"	57.5	0.957

TABLE II (Sol 11b)

Ageing Period	Coagulation Time	Per cent red	β
35 mins.	20 secs.	34.375	2.118
50 "	"	35.0	2.07
1h. 10m.	"	48.75	1.296
2h. 30m.	"	36.875	1.941
3 hrs.	"	36.875	1.941

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[1] Zsigmondy: Z. physik. Chem., 92, 600 (1917).

Table III

Ageing Period	Coagulation Time	Per cent red	β
15 mins.	20 secs.	45.625	1.44
30 "	"	46.875	1.38
1 hr.	"	47.5	1.352
1h. 30m.	"	48.75	1.2975
2 hrs.	"	59.375	0.8925
2h. 50m.	"	58.75	0.915

Table IV. (Sol IV)

Ageing Period	Coagulation Time	Per cent red	β
1h. 30m.	20 secs.	42.5	1.602
2 hrs.	"	44.375	1.503
2h. 30m.	"	49.375	1.269
3 hrs.	"	51.25	1.1895
3h. 30 m.	"	44.375	1.503

Table V

(Sol IV 14 days later, during which time the sol was kept at room-temperature.)

Ageing Period	Coagulation Time	Per cent red	β
1 hr.	20 secs	41.875	1.635
1h. 30m.	"	48.125	1.323
2 hrs.	"	50.625	1.218
2h. 20m.	"	53.125	1.116
2h. 55m.	"	50	1.242
4 h. 40m.	"	50.625	1.218

Measurements similar to those just recorded were also carried out with sols which had been aged for various periods (up to 18 hours) at 25°C. As was to be expected, no detectable thermo-senescence effect manifested itself, the ageing effect at this temperature being immeasurably slow.

Discussion of Results

The results for thermo-senescence at 80°C given in the tables show in general a fall in β followed by a rise as the preliminary ageing period is increased.

All the results point to a minimum value of β corresponding to 2–3 hours ageing period, in most cases. This ageing period corresponding to a minimum value of β is here termed the "critical ageing period," and it appears from the results to be dependent on the properties of the sol itself.

As one would expect, the actual minimum values for β also vary with the sol, though they are sensibly constant for the same sol. In all cases, the minimum for β is followed by a rise, the extent of this rise appearing to differ with the sol, in some cases being only very slight, and in others appreciable. This point is referred to later.

The presence of a maximum or minimum indicates the presence of two opposing effects.

The more important effect is the initial fall of β with increase in the ageing period. This is conveniently termed the "primary effect of thermo-senescence," as opposed to the other effects which may possibly occur during very long ageing periods. The subsequent rise in β following on the minimum has been found to be due to more or less inevitable evaporation effects occurring at the relatively high temperatures employed.

A number of suggestions might be made to account for the metastable condition of the sol, as shown by the initial fall in β. Of these, three may be briefly considered. Thus:

(1) High temperature may cause splitting-up of complexes into primaries, leading to an increase in ν_1.

(2) High temperature may cause a contraction in the surface area of the primaries and hence an increase in the mean charge density on them.

(3) High temperature may cause a decrease in the adsorptive power of the colloid particles for oppositely charged ions, and thus lead to a slower rate of coagulation.

(1) If the first explanation is correct, it would be expected that by a suitable increase in temperature, a completely coagulated blue sol could be converted into a red, or partially red sol. This effect has not, so far, been observed. If, as is generally supposed, uncoagulated red sol contains only primaries, this postulate assumes that the increase in percentage red ν_1) takes place during the actual coagulation process at 80°C and since this is of constant duration in each case, we would hardly expect a previous immersion of the sol to effect it.

(2) A more probable explanation is that in which the meta-stability of the sol during the primary ageing period is assumed to be due to a contraction of the surface area of the particles caused by the increase in temperature. The actual electrical charge on these particles remains the same, but decrease in the surface area would cause an increase in the mean charge density on the particles. Since it is the mean charge density which is important in the coagulation by electrolyte, this would lead to a decrease in β.

Recent work on the structure of gold sols leads us to assume that colloidal gold particles are not solid spheres of gold, but that their structure is very complex, and may be regarded as consisting of a micelle formed of dispersion medium, complex gold ions, possibly some free ions from the dispersion medium, together with an interlacing network of gold,—this forming a kind of mesh. Definite proof of crystalline structure was given by the method of Debye and Scherrer,[1] so that in the micellae of these sols minute crystals of the metal are presumably embedded.

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[1] Debye and Scherrer: Physik. Z., 17, 277 (1916).

Assuming that the colloidal particles in gold sols do possess such a structure as that outlined above, it is then easily seen that during ageing a contraction of the surface area is at least possible. Any particle consisting of such a complex, would be expected at a fairly high temperature to have a tendency to lose some of the dispersion medium contained in the micelle and crystallisation forces could also come into play, both effects leading to a decrease in the surface area of the particle, the particle at the same time becoming more definitely crystalline. Zsigmondy[1] gives evidence to show that the particles in colloidal gold on ageing become more crystalline. It must be emphasized, however, that no definite proof can as yet be advanced for this view of the contraction of the surface of colloidal gold particles by the application of heat and during the process of ageing. The effect attributed to surface contraction might be ascribed to increased ionisation of the sol, in the light of the results obtained by Pennycuick[2] for colloidal platinum.

(3) The third suggestion made to account for the fall in β during thermosenescence, namely, that the adsorptive power of the individual colloid particles for coagulating ion decreases with increase of temperature and with age, is one which has been previously put forward by other investigators as an explanation of results obtained for ageing[3] and for the temperature effect on the rate of coagulation.[4]

It is impossible to distinguish between explanations (2) and (3) on the basis of the experimental work dealt with in the present paper. The point is being investigated further in this Laboratory.

Evaporation as an explanation of the subsequent rise in the value of β.

In order to test the adequacy of evaporation as an explanation of the secondary rise in the co-efficient β shown in the tables, the following experiments were carried out:

Evaporation was reduced to a minimum by the use of narrow-necked flasks of about 50–55 ccs capacity, filled to within 1.5 cm of the top edge. The flasks were stoppered as tightly as was possible under the conditions of experiment. At the same time, experiments were carried out in which evaporation was allowed to occur to an appreciable extent. On graphing the values obtained, it became evident that the rise in β after the minimum has been reached, is considerably lessened by reducing the extent of the evaporation. In those cases where evaporation has been reduced to a minimum, it was found that β reaches a minimum value which is sensibly constant over long ageing periods. Further, the attempt was made to correlate the values for the rise in β with the actual volume change due to evaporation.

The essentially qualitative nature of the results obtainable with colloids only justify a *general* and not a rigid quantitative analysis.

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[1] Zsigmondy: Kolloidchem. Beihefte, 23, 21 (1926).

[2] Pennycuick: J. Chem. Soc., 1927, 2600; Pennycuick and Best: 1928, 551.

[3] Ghosh and Dhar: J. Phys. Chem., 30, 1564 (1926).

[4] Mukherjee: J. Chem. Soc., 117, 350 (1920).

The results are summarized in Table VI, in which the percentage rise in β actually found is compared with the percentage rise in β calculated from the percentage decrease in volume due to evaporation, using the expression

$$\text{per cent increase in } \beta = \frac{100x}{100-x}$$

where x = the per cent decrease in volume.

This relation is easily deduced from Smoluchowski's relation $\beta = 4\pi D\nu_0$ where ν_0 = initial number of particles per unit volume.

TABLE VI

Evaporation effect	Ageing period	Per cent decrease in Vol. (x, found) (mean value)	Per cent rise in β. (found) (mean value)	(calcd.)
Minimum	3-4 hrs.	4.9	4.2	5.15
"	4-5 "	5.25	6.37	5.54
"	5-7 "	7.5	8.1	8.1
Appreciable	2-3 "	10.0	15.2	11.1
"	3-4 "	16.25	26.9	19.4
"	4-6½ "	22.0	38.2	28.2

It can be concluded from the figures contained in the foregoing table that the rise in β is reasonably well accounted for by the effect of evaporation, bearing in mind, of course, the essentially approximate character of the results. We conclude that when evaporation is kept at a minimum, maintenance of the sol at 80°C for at least 3 hours causes β to attain a minimum value which is fairly constant. This means that the sol has reached a state of 'colloid' equilibrium.[1]

The Irreversibility of the Primary Thermo-Senescence Effect

A considerable number of experiments were carried out to determine whether the fall in β due to maintenance of the sol at the elevated temperature was reversible or irreversible. The method employed was to compare the β values obtained with (1) a sol which had been kept at 80° for 3 to 4 hours, and subsequently cooled to 25°C (and maintained for 2 hours at this temperature) prior to addition of the coagulating electrolyte and (2) a sol which had been kept all the time at 25°C. It was found that the β value obtianed in case (1) differed considerably from that in case (2) and further the value of β in (1) was lower than that in (2), in fact about one half of the value of the latter. This is what would be expected on the basis of the irreversibility of the ageing effect.

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[1] This is a vague term which is meant, in this case, to indicate a physico-chemical equilibrium between the electrical, chemical, and other forces which exist in a colloidal system.

Temperature Coefficient of the Rate of Coagulation of Gold Sol

In view of the foregoing results, it may be inferred that it is only legitimate to draw quantitative deductions from measurements obtained with a sol which has reached equilibrium. Since the effect of thermo-senescence is irreversible, it is possible to bring all gold sols to a stable state by merely maintaining them at a high temperature for a suitable period of time, and then, after cooling the sols, to proceed to perform experiments on them, the results of which will be truly comparable. Also, from this standpoint, it is only justifiable to test Smoluchowski's equation with sols which have reached equilibrium. This raises the question of the true temperature coefficient of β.

The following results have been obtained with gold sols working under conditions corresponding to minimum evaporation. The values of β recorded for 25°C refer to sols which have previously been maintained at 80° for the requisite time to ensure colloid equilibrium being attained, the actual coagulation rate being determined at 25°. The values of β for 80° refer to sols which have likewise been maintained at 80° for the necessary time and then coagulated at this temperature. The results are given in Table VII.

TABLE VII

Sol	Coagulation time	β 80°	β 25°	β 80°/25°
XIV	30 secs.	0.596	0.1815	3.283
XIV (1 wk. later)	"	0.53	0.254	2.086
XV	40 secs.	0.269	0.130	2.07
XVI	"	0.289	0.165	1.752
XVI (5 dys. later)	"	0.335	0.217	1.544

Miss Garner[1] has shown that, from theoretical considerations, the temperature effect on β calculated from Smoluchowski's equation is given by

$$\beta_2 = \left(\frac{\eta_1 T_2}{\eta_2 T_1}\right) \beta_1$$

where T_1 and T_2 denote the temperatures (in degrees absolute) at which β_1 and β_2 are measured, and η_1 and η_2 are the viscosities at T_1 and T_2 respectively.

Moreover, since we are dealing with comparatively "dilute" sols, their viscosities are assumed to be that of the medium (water.)

At 25°C., $\eta_{298} = 0.498$[*]

At 80°C., $\eta_{353} = 0.199$

From this follows the relationship:—

$$\beta_{353} = \left(\frac{0.498 \times 353}{0.199 \times 298}\right) \beta_{298}$$

$$\text{or, } \frac{\beta_{353}}{\beta_{298}} = 2.964 \qquad \text{(a)}$$

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[1] Maud Garner: J. Phys. Chem., 30, 1401 (1926).

[*] Specific Viscosities obtained from "Smithsonian Tables," 6th Revised Ed., p. 127 (1914). Values used are those of Hosking: Phil. Mag., 17, 502 (1909).

This relation would be expected to hold if the temperature effect on β is due to the decrease in viscosity *alone*. Therefore, we infer from the results contained in the table that although presumably the temperature effect on viscosity does enter, it is not sufficient to account entirely for the observed temperature effect on β.

The order of magnitude of the observed ratio $\beta_{80°}/_{25°}$, namely between 1.5 and 3, indicates that there is no critical increment involved in the fundamental process of coagulation. This conclusion, though surprising in itself, is the result anticipated from the results of other investigators, notably Freundlich and Basu[1] and Miss Garner[2] working in the region approximating to "rapid coagulation."

It must be emphasised that the results obtained in this investigation refer to the region of "slow coagulation," where there is always the possibility of various electrical influences. Since the result for the temperature effect on β is on the whole less than the value expected from the decrease of viscosity alone, this means that the rate of coagulation at a high temperature is less than we would expect, and there are various possibilities which would account for this, such for example as that of the electric charge being a function of temperature which has already been discussed in another connection.

In the region of "rapid coagulation," corresponding to complete electrical discharge of the particles, we would expect that the temperature effect on β would be wholly accounted for by the decrease in viscosity, since no electrical forces are here involved. This point is under investigation.

Summary

(1) The change in behaviour exhibited by a gold sol as a consequence of it having been maintained at a fairly high temperature (80°C) for a comparatively short period of time (about 4–6 hours) has been investigated. The maintenance of a sol under standard conditions at a given temperature implies ageing, and since in this case the temperature is abnormally high, the term "thermosenescence" or "thermo-ageing" has been coined for the phenomenon.

(2) The effect of thermo-senescence at 80°C is very pronounced and consists of

(a) a primary effect which is a fall in the Smoluchowski coefficient β with increase of the "ageing period" of the sol, until β reaches a minimum, after about three hours;

(b) a secondary effect which is the subsequent rise in β after the minimum has been reached.

(3) Various explanations of the "primary effect" have been suggested.

(4) The "secondary effect" has been shown to be fully accounted for by the influence of evaporation. When evaporation has been reduced to a minimum, then during thermo-senescence over periods up to six hours, β attains

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[1] Freundlich and Basu: Z. physik. Chem., 115, 203 (1925).

[2] Maud Garner: loc. cit.

a minimum value which is fairly constant, after an ageing period of about three hours. This means that the sol has reached a state of "colloid" equilibrium.

(5) The "primary effect" has been shown to be irreversible. This is important in that it enables sols to be brought to an equilibrium state by merely maintaining them at a high temperature for a suitable period of time.

(6) An attempt has been made, in the light of these results to obtain the *true* temperature effect on the rate of slow coagulation. The ratio β_{80}/β_{25} is found to lie between 1.5 and 3.3. for different sols. If the temperature effect on B were due to decrease in viscosity *alone*, then this ratio would equal 2.9 for all sols. The discrepancy is briefly discussed.

The main general significance of this work is the demonstration of the necessity of first eliminating the variability due to thermo-senescence in the case of measurements of any colloid property even when such measurement is carried out at room temperature.

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Muspratt Laboratory of Physical and Electro-Chemistry,
University of Liverpool,
September 29, 1928.

SOLUBILITY OF CALCIUM HYDROXIDE

BY L. B. MILLER AND J. C. WITT

Introduction

The solubility of calcium hydroxide has been repeatedly determined by numerous workers with greatly varying degrees of precision. One of the first facts discovered was that the solubility of this compound decreases with rise in temperature. In summarizing the results of some of the more exact data, Mellor[1] [from the composite results of Dalton[2], Phillips,[3] Wittstein[4] and Bineau[5]] gives the solubility of calcium hydroxide expressed in grams of calcium oxide per 1000 grams of water as approximately 1.18 at 30 degrees C. Seidell,[6] from the average curve obtained by plotting the results of Lamy, Mobeu, Herzfeld and Guthrie, gives a solubility for this substance of 1.16 expressed as grams calcium oxide per 1000 grms of saturated solution at 25°C. A. Lamy[7] found that calcium hydroxide varies in solubility according to the source from which it is obtained. He gives the following values for the solubility expressed as grams calcium oxide per liter of solution at 30 degrees C.

Calcium hydroxide obtained by hydration of calcium oxide from the calcination of calcium nitrate	1.142
Calcium hydroxide obtained by hydration of calcium oxide from the calcination of marble	1.162
Precipitated calcium hydroxide	1.195

With the increased interest in solutions during the last quarter century, the solubility of calcium hydroxide has been redetermined under carefully controlled conditions. Noyes and Chapin[8] obtained a value of 1.13 grams of calcium oxide per liter of saturated solution at 25°C. Bassett and Taylor[9] in their study of the three-component system calcium nitrate-calcium oxide-water, obtained a solubility of 1.150 grams of calcium oxide per 1000 grams of saturated solution at 25°C. They used calcium carbonate precipitated from calcium nitrate by ammonium carbonate as their source of calcium oxide. The solubility of the compound was determined analytically after shaking for six months in cerasin-coated bottles at the indicated temperature. Cameron and Robinson[10] obtained a value for the solubility of 1.18 grams of calcium oxide per 1000 grams of water at 25°C. In their determination calcium oxide was shaken in small glass bottles for ninety days.

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[1] "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 3, 677 (1923).

[2] " A New System of Chemical Philosophy," 2, 331 (1810).

[3] Annals of Philosophy, (2), 17, 107 (1821).

[4] Report. Pharm., 1, 182 (1815).

[5] Ann. Chim. Phys. (3), 51, 290 (1857).

[6] "The Solubilities of Inorganic and Organic Compounds," (1919).

[7] Ann. Chim. Phys. (5), 14, 145 (1875).

[8] Noyes and Chapin: Z. physik. Chem., 28, 518 (1899).

[9] J. Chem. Soc., 105, 1926 (1914).

[10] J. Phys. Chem., 11, 273 (1906).

Purpose of the Investigation

In connection with certain researches upon a related subject, it was found desirable to determine the solubility of calcium hydroxide in water at 30°C. It was of especial interest and value to us to know the solubility exhibited when freshly hydrated calcium oxide is kept in contact with water for a relatively short period of time.

Apparatus and Method of Procedure

The solubility and conductivity of calcium hydroxide in water was determined for a temperature of 30°C. A temperature of 30° ± .005 was obtained with a De Khotinsky constant-temperature water-bath. Conductivity was measured by means of the Leeds and Northrup equipment for precision work. Well-steamed Pyrex bottles of one liter capacity were used as containers. The cell constant was determined at 30°C. with solutions made from conductivity water and three times recrystallized and fused potassium chloride. Calcium oxide was obtained from two sources. Iceland spar was ignited to constant weight in platinum, and constituted the first source. For the other a c.p. grade of precipitated calcium carbonate was dissolved in c.p. nitric acid, and precipitated with a similar grade of ammonium carbonate. The precipitated calcium carbonate was filtered, washed, dried, and ignited to constant weight in platinum. Conductivity water was obtained by distillation from alkaline permanganate solution.

Since, from the nature of the materials the solubility of which was being studied (fine-grained solids), it was difficult to obtain samples of the solution for analysis free from the solid phase, except by allowing the solutions to stand at constant temperature over periods of several hours, the conductivity of the solution was used to indicate when equilibrium had been established. This method has the advantage of being simple and rapid, and of being unaffected by the presence of the undissolved solid materials. Determinations of conductivity may be made after successive small increments of time and the approach to equilibrium may thus be closely followed.

Two complete and separate determinations of the conductivity and solubility of calcium hydroxide were made.

The procedure followed in the first solubility determination was as follows: Two separate portions of Iceland spar were ignited to constant weight in platinum containers. Each of these portions was then divided into fractions A and B. Samples 1-A and 2-A were slaked with a small quantity of conductivity water and allowed to stand over night in stoppered containers. These were then placed in well-steamed one-liter Pyrex flasks containing conductivity water previously brought to temperature, immersed in the water bath at 30°C. and shaken in a mechanical shaker until equilibrium was reached. At the same time samples 1-B and 2-B were placed in one-liter Pyrex bottles nearly filled with conductivity water, allowed to slake, and likewise shaken until equilibrium was reached. In all cases sufficient calcium oxide had been used so that an excess of the solid phase was present. The conductivity of the solutions was determined from time to time until three successive readings at two-hour intervals of shaking showed no further change in conductivity.

By this procedure, solubility equilibrium was approached from both sides. In the case of the samples 1-A and 2-A, which had been previously slaked with water, the conductivity was found to increase with time until a constant value was reached. Sample 1-B and 2-B formed supersaturated solutions of calcium hydroxide, the conductivity first rising to a maximum and then decreasing to a constant value. The solid phase was then allowed to settle and aliquot portions of the supernatant solution drawn off for analysis. The calcium oxide content was determined by precipitation as the oxalate followed by ignition to constant weight. The results are given in Table I.

TABLE I

Sample	Solubility expressed as grams CaO per 1000 cc. of saturated solution at 30°C	Conductivity expressed as mhos × 10^3
1-A	1.195	8.937
1-B	1.200	8.937
2-A	1.198	8.918
2-B	1.202	8.946
Average	1.199	8.933

Before the second series of experiments was made, some time had elapsed. The cell constant was therefore redetermined. Sample 3 was prepared by igniting a sample of Iceland spar to constant weight in platinum. It was then divided into portions 3-A and 3-B. A sample of precipitated calcium carbonate (prepared as previously described) was similarly ignited and divided into portions 4-A and 4-B. Samples 3-A and 4-A were first hydrated in a small quantity of conductivity water for twenty-four hours. They were then placed in one liter quantities of conductivity water at 30°C. and shaken until no further change in conductivity occurred with three readings taken at two hour intervals. At the same time, samples 3-B and 4-B were thrown into one liter quantities of conductivity water brought to a temperature of 30°C. and similarly observed. The solubility was determined as in the previous series. The values obtained are given in Table II. The samples were then shaken for seventy-two hours more, but no further change in conductivity occurred.

TABLE II

Sample	Solubility expressed as grams CaO per 1000 cc. of saturated solution at 30°C	Conductivity expressed as mhos × 10^3
3-A	1.196	8.856
4-A	1.194	8.856
3-B	1.201	8.929
4-B	1.196	8.911
Average	1.197	8.888

In Fig. 1 are plotted the time-conductivity curves for samples 1-A and 1-B. These are typical of the type of curves obtained in this work.

Discussion

A comparison of the values for the solubility of calcium hydroxide obtained in this work with the best values reported in the literature show them to be somewhat higher than those previously obtained. It is a well-known fact that a very finely divided crystalline substance will show a higher solubility than the same substance in a more coarsely crystalline state. The solution of higher solubility will gradually assume the same solubility as that of the more coarsely crystalline substance if the solid phase is left in contact with the solution for a sufficient time. The calcium hydroxide used in this work, prepared by the rapid hydration of calcium oxide, was very finely crystalline as was readily demonstrated with a microscope. It is possible, therefore, that the difference in solubility of calcium hydroxide as determined here and in previous researches, may be accounted for by a difference in the size of particles constituting the solid phases. It must be emphasized, however, that, if such is the case, the true solubility value is represented by an equilibrium which is attained very slowly, since the equilibrium value we obtained was maintained for several days without appreciable change, as was evidence by the constancy of the electrical conductivity. No attempt was made to connect these results with those of previous workers by continuing the solubility experiments over an extended period of time.

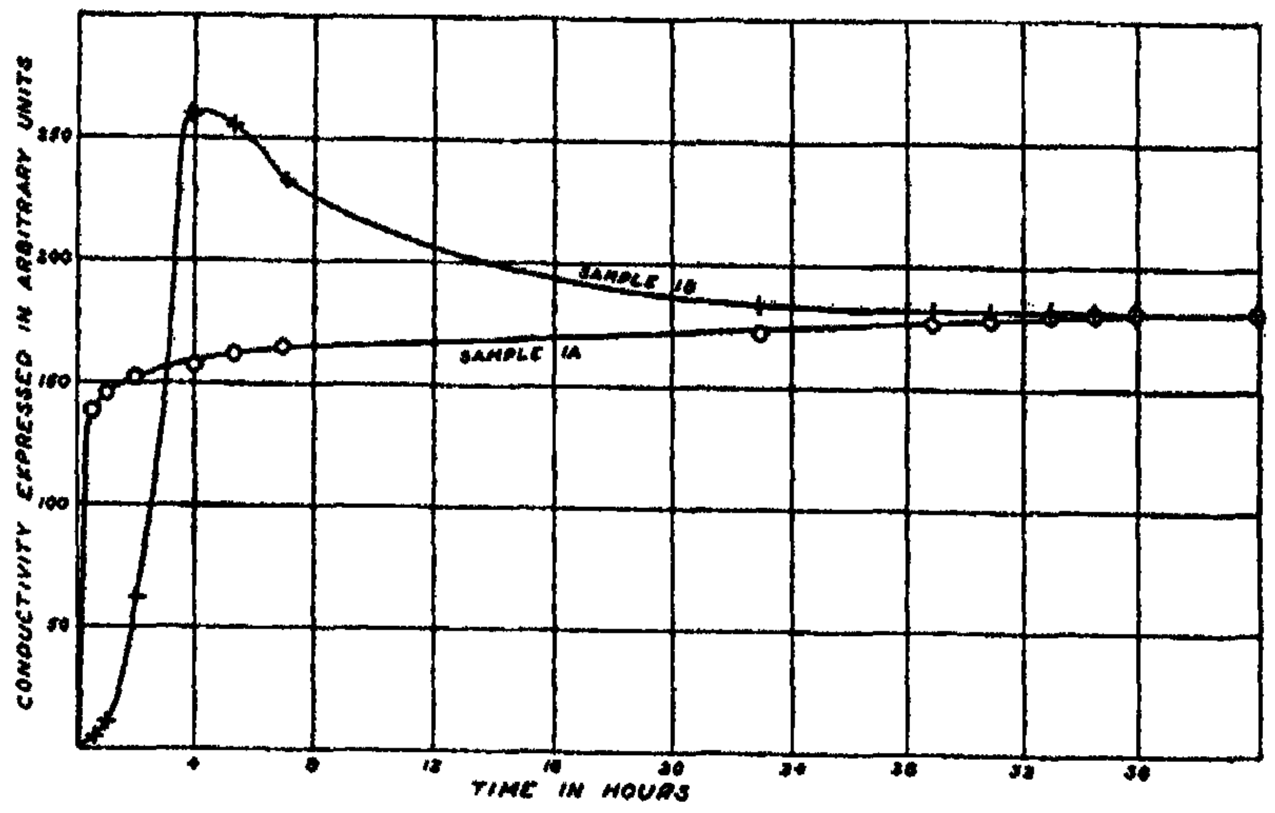

Fig. 1
Rate of Solution of Calcium Hydroxide as indicated by Conductivity.

Summary

1. The solubility of calcium hydroxide in water as exhibited by freshly hydrated calcium oxide has been made the subject of a detailed study.

2. The progress towards equilibrium of the system consisting of an excess of freshly hydrated calcium oxide and water was followed closely by means of the electrical conductivity of the solution.

3. Values for the solubility of calcium hydroxide and for the conductivity of the saturated solution are given.

Chicago, Illinois.

THE PHOTODECOMPOSITION OF ETHYL IODIDE

BY THOMAS IREDALE

It is universally known that the alkyl iodides and many other organic compounds containing iodine are unstable in the presence of light; but few quantitative studies of this phenomenon have ever been made. Burke and Donnan[1] tried to find a relationship between the sensitivity of the alkyl iodides to light and their reactivity with silver nitrate. They considered that the production of iodine through decomposition by light was not a simple process and involved an oxidation of the hydrogen iodide first formed. Stobbe and Schmidt[2] came to a similar conclusion, that oxygen was necessary for the photodecomposition of solutions of the alkyl iodides. Some years later Job and Emschwiller[3] studied the photodecomposition of ethyl iodide and found that oxygen was not necessary for the reaction. According to their results the reaction is rather complicated, the final products being ethylene, ethane and iodine, and small amounts of butane and hydrogen. They argue that the first stage in the photochemical process is the detachment of an iodine atom from the molecule of ethyl iodide as the result of the absorption of a light quantum.

$$C_2H_5I + h\nu \rightarrow (C_2H_5I) \rightarrow C_2H_5 + (I)$$

They consider also, that another light reaction takes place: the decomposition of hydrogen iodide, which results as the consequence of the original I atom acting as acceptor towards one of the hydrogen atoms in the ethyl radical.

$$C_2H_4.H + (I) \rightarrow C_2H_4 + HI.$$

$$HI + h\nu \rightarrow H + (I).$$

It was with a view to settling one or two of the main points in this conflicting evidence that the present research was undertaken. It was considered that a study of the quantum efficiency of the decomposition would settle the question as to the nature of the primary photochemical process. The reaction is interesting in view of its analogy to the decomposition of HI which has usually been investigated in the gaseous state,[4] though recently as a liquid by Bodenstein and Linweig.[5] It was decided, however, in the first part of this investigation to work with *liquid* ethyl iodide as the previous work was carried out on this substance either as a liquid or as a solution in other organic liquids.

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[1] J. Chem. Soc., 85, 574 (1904).

[2] Z. wiss. Phot., 20, 57 (1920).

[3] Compt. rend., 179, 52 (1924).

[4] Bodenstein: Sitz. Akad. Wiss. Berlin, 1918, 300,; Z. physik. Chem., 22, 23 (1897); Trautz and Scheifele: Z. wiss. phot., 24, 177, (1926); Tingey and Gerke: J. Am. Chem. Soc., 48, 1838 (1926); Bonhoeffer and Steiner: Z. physik. Chem., 122, 287, (1926); Lewis: J. Phys. Chem., 32, 270, (1928).

[5] Z. physik. Chem. 119, 123, (1926).

In 1926 the author in conjunction with Mr. W. N. Madgin of Armstrong College, University of Durham, began some experiments to test one of the main points at issue—whether oxygen were necessary for the photodecomposition. Carefully purified ethyl iodide was introduced into an all-glass apparatus and the dissolved gases removed by a process of successive coolings and evacuations with an oil pump. The ethyl iodide was then distilled at room temperature through a layer of purified phosphorus pentoxide into a tube of standard dimensions which was then sealed off. Comparisons were then made with a sample of purified ethyl iodide which had not been treated in this manner in a standard glass tube having access to atmospheric oxygen. Irradiation from a mercury vapour lamp under identical conditions seemed to produce the same effect in the two cases, so far as the production of iodine was concerned. It would seem then that for light of wave lengths extending to about 313$\mu\mu$ in the ultra-violet, oxygen is not necessary for the photodecomposition. This does not rule out the possibility that over a long period of time the oxidation of the HI may play some part in the reaction. But for the purpose of the present investigation this matter is not important.

The initial stage of the decomposition should be a reaction of zero order for absorbed light of constant intensity; but owing to secondary absorption by the iodine accumulated in the system, the rate of reaction begins to deviate from this law. The experiments to be described were therefore never carried beyond the stage where this secondary absorption effect was appreciable.

Experimental

The source of radiation was a quartz mercury vapour lamp run on a 110 volt D.C. circuit with a burner voltage of 80 volts and a current of 2.5 amperes. It was enclosed in a circular metal box, blackened on the outside, and with an aperture 1.8 cms. in diameter in the front arc. When first used the lamp was quite new and gave lines below 220$\mu\mu$. These spectral measurements and others of a more quantitative character were made with a Hilger quartz spectrograph. The magnitude of the adsorption by ethyl iodide in any spectral region could be estimated with fair accuracy by varying the times of exposure on a photographic plate, taking the Schwarzchild constant as unity.[1] Accurate measurements of the absorption and of the radiant energy from the lamp were carried out with a Moll thermopile and galvanometer.

Ethyl iodide in alcohol has an absorption band[2] at about 260$\mu\mu$ and it also absorbs at 365$\mu\mu$ when a column of the liquid several centimetres long is employed. Job and Emschwiller state that it begins to decompose with light of wave length 410$\mu\mu$, but the absorption in this region is very slight, and the decomposition would only be noticeable with a long column of the liquid.

The filter employed for isolating the 365 $\mu\mu$ region was that described by Winther[3] and made by using a 1 cm. thickness of a 0.03% neutral solution

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[1] Baly and Riding: Proc. Roy. Soc., 113A, 709 (1927).

[2] Crymble, Stewart and Wright: Ber., 43, 1183 (1910).

[3] Z. Elektrochemie, 19, 389 (1913).

of diamond fuchsin.[1] The spectral transmission of this filter was tested with the quartz spectrograph. Transmission of the 313μμ and 334μμ lines was negligible, the small amount of 404μμ and red lines were not absorbed appreciably by the ethyl iodide and the infra-red radiation was shut off in the usual way by water screens. By the use of a quartz lens and screen and appropriate apertures in front of the lamp, a nearly parallel beam of light was obtained passing the water screens and the filter.

The radiation from the lamp was carefully measured at different times during the course of a photochemical decomposition. Owing to the narrow dimensions of the light beam attempts were made to measure its average energy by rotating the thermopile to different positions at right angles to the beam. The variations in the galvanometer readings for these different positions were, however, very slight.

The amount of 365μμ light in the beam was found by replacing one of the water screens by Winther's 313μμ filter, a dilute solution of nitrosodimethylaniline and potassium chromate, which absorbs the 365μμ rays.

The thermopile was calibrated in two ways:

(1) with a Hefner lamp. There were several reasons, however, for doubting the accuracy of this particular instrument.

(2) with the radiation from the blackened surface of a tin box—Leslie cube—containing boiling water, using appropriate screens and apertures. 90% of the possible radiation was allowed for in calculating the energy reaching the thermopile, which was covered with a rock-salt plate during these calibration tests, and tested at different distances from the radiating surface. The surface density uf the radiation was calculated with the aid of the usual equation,[2] using the theoretical value for the Stefan-Boltzman constant.[3] For the working distance of galvanometer and scale calibration with the Hefner lamp gave 119 ergs per sq. cm. per sec. for 1 cm. deflection;[4] with the Leslie cube, 112, 114, 112, 113 ergs per sq. cm. per sec. for several distances of the thermopile. The average of these figures, 116 ergs per sq. cm. per sec., was used in all subsequent calculations of radiant energy.

The ethyl iodide was purified by shaking with dilute alkali and successive quantities of water, drying over calcium chloride, and distilling, the fraction boiling at 72°–73°C/760 mm. being collected and preserved in a dark bottle over silver foil. In the experiments the ethyl iodide was contained in a cylindrical cell, 5.45 cms. long, on the ends of which were cemented circular quartz plates. The thermopile was covered with a similar quartz plate, as the correction for surface reflection at the front of the cell would amount to 5%. The amount of light absorption by the ethyl iodide was calculated from the spectrographic figures—about 85% for this particular

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[1] Gray: J. Phys. Chem., 31, 1732 (1927).
[2] Lummer and Pringsheim: Ann. Physik, (3) 63, 399 (1897).
[3] Millikan: "The Electron," 238.
[4] Gerlach: Physik. Z., 14, 577 (1913).

length of reaction cell. It was also estimated from the change in energy of the light beam on passing through the ethyl iodide. Owing to the slightly divergent nature of the beam and the change in refractive index of the medium, measurements were made across a constant area of the beam, and an average figure for the absorption was obtained which agreed very well with that calculated from the percentage of 365$\mu\mu$ light in the beam and the spectrographic data. Very little of the infra-red radiation passing the water screens could therefore have beeen absorbed by the ethyl iodide.

The iodine liberated through the decomposition was estimated by titration with a very dilute solution of sodium thiosulphate. This analytical method was checked with the aid of solutions of known iodine content, and can be made very exact. The rate of reaction[1] of the iodide with the thiosulphate would be negligible in this case. The errors in this analytical method are certainly less than those involved in the measurement of the light absorption. A more accurate spectrophotometric method was not available.[2]

TABLE I

Wave length of light: 365$\mu\mu$

Period of decomposition Hours	No. of quanta absorbed per sec. by C_2H_5I $\times 10^{-14}$	No. of quanta abs. by C_2H_5I during period of decomp. $\times 10^{-18}$		No. of mols. of C_2H_5I decomposed $\times 10^{-18}$	Molecules division Quanta
10.0	1.04		3.74	3.41	0.91
5.0	1.04	1.87	3.55	3.18	0.89
4.0	1.17	1.68			
4.75	1.13	1.93	3.21	3.13	0.98
4.0	0.89	1.28			
4.0	0.70	1.00	3.02	3.28	1.08
1.35	0.90	0.43			
2.65	0.70	0.66			
2.25	1.15	0.93			
2.83	1.13	1.16	2.20	1.94	0.89
3.00	0.96	1.04			
5.62	1.21		2.45	2.46	1.00
4.5	1.06	1.71	3.09	2.60	0.85
1.5	1.06	0.57			
2.5	0.90	0.81			
9.0	1.02		3.41	3.14	0.92
4.0	1.30		1.86	1.91	1.03

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[1] Slator: J. Chem. Soc., 85, 1286 (1904).

[2] Bodenstein and Linweig: Z. physik. Chem., 119, 123 (1926).

The results of measurements of the quantum efficiency are given in Table I. The intensity of the absorbed light was not varied very widely. The magnitude of the variation can be gauged from the second column. No accurate temperature control was attempted. The temperature of the laboratory varied from 18–23°C.

The number of molecules of C_2H_5I decomposed was equated to the number of iodine atoms formed, a quite reasonable procedure in view of the simplicity of the results. Within the limits of experimental error it seems that the quantum mechanism is a very elementary one, Einstein's law of the photochemical equivalence being valid for this special case. The quantum efficiency is slightly higher for ultraviolet light below 365μμ. An average value was obtained for the region 248–365μμ, which was worked out for the quantum corresponding to wave-length 310μμ from the considerations of the data for mercury vapour lamps,[1] the present lamp being 100 hours old when these particular measurements were made. It is obviously an approximation, but adequate means were not available in the laboratory for testing the spectral distribution of energy from the lamp.

It would seem that with the exclusive use of light of the shorter wave lengths, the quantum efficiency would become identical with that of the HI decomposition.

TABLE II

Wave length of light: 248–365μμ
Average quantum corresponding to 310μμ

Period of decomposition Hours	No. of quanta absorbed by $C_2H_5I \times 10^{-18}$	No. of mols. of C_2H_5I decomposed $\times 10^{-18}$	$\frac{\text{Molecules}}{\text{Quanta}}$
2.83	6.43	7.67	1.2
2.75	5.00	5.52	1.1
1.50	1.44	1.90	1.3
2.37	2.37	2.76	1.2
1.66	3.51	4.12	1.2

Discussion of Results

The results seem to show that the photodecomposition of liquid ethyl iodide is a very simple process, one quantum effecting the detachment of an iodine atom from one molecule. This rules out the second postulate of Job and Emschwiller—the formation and decomposition of HI; unless we imagine some collision mechanism whereby the energy furnished by the light in excess of that found from thermal measurements is effective for the decomposition. The heat of dissociation of C_2H_5I is, according to Bowen[2] 40,000 calories, whereas the energy furnished by light of wave-length 365μμ is 72,000 calories per gram-molecule. This leaves 32,000 calories to be accounted for, which is only half the heat of dissociation of HI.

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[1] J. Phys. Chem., 30, 1427 (1926).

[2] Trans. Faraday Soc., 21, 544 (1926).

Comparisons of thermochemical and photochemical data, however, may not always be satisfactory, because the former are based on measurements made on a system of molecules in statistical equilibrium, whereas the latter are calculated from the results of selective light action, and may only apply to molecules in special quantum states.

As in the case of HI the decomposition of C_2H_5I results in the formation of an excited I atom, the excess energy probably being dissipated as kinetic energy through collisions. This analogy is not unreasonable in view of the fact that a non-ion linkage has been attributed to HI.

Studies of the photolysis of these alkyl iodides is being continued.

University of Sydney,
N. S. W., Australia.

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[1] Franck and Kuhn: Z. Physik, **43**, 164 (1927).

SIGNIFICANCE OF THE "PACKING FRACTION"

BY MARCEL FRANÇON

The discovery of the radioactive properties and of the electron, common constituent of all atoms, led to the assumption that the atoms of all elements were formed of protons and electrons. Thus Prout's hypothesis, according to which all the elements would be formed of hydrogen and would have whole numbers for atomic weights, was considered again with great attention. If, indeed, the atomic weights of the elements are not whole numbers, in general, the atomic masses of the different isotopes had been found to be whole numbers, except for hydrogen. Costa,[1] however, began to determine the atomic masses with a greater accuracy than Aston's first apparatus had enabled him to reach. Aston[2] then built an apparatus the resolving power of which was five times greater than that of his first apparatus, and thanks to which he could make measurements with an approximation of 1/10000. The experimental results showed then that as a rule the mass numbers were not whole numbers, in the system O = 16.

Aston[3] had introduced the notion of "packing" in order to describe the compression of the protons and of the electrons in the nucleus of all the atoms except those of hydrogen. He thus explained how hydrogen seemed alone to have an atomic mass which was not a whole number. In 1927, Aston[2] introduced the term of "packing fraction" which is the divergence of the mass number of an atom from a whole number, divided by the mass number. Aston drew a curve representing the variations of the "packing fractions" with the mass numbers. He found that all the atoms, except the light atoms of even number, can be put on the same curve, descending rapidly from hydrogen to reach a minimum in the region of the element bromine (mass number 80); then the curve goes up again and crosses the line of zero packing for mercury. The curve for the atoms of even mass number starts below the first curve, with helium and goes to the minimum much less steeply than the first curve does. Aston points out that the packing fraction is not a periodic property; this shows that the nucleus has a structure very different from the arrangement of the electrons outside the nucleus. Thus the packing fraction would give us information on the structure of the nuclei and, therefore, on the relative stability of the atoms. Cabrera[4] has remarked that the atoms could be put into two classes according to their position at the right or at the left of the minimum of Aston's curve. On one side are the light elements for which the packing fraction is decreasing rapidly, passing from a high positive value for hydrogen to a negative value. On the other side, are the heavy elements

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[1] Costa: Compt. rend., **180**, 1661; Ann. Phys., **4**, 425 (1925).

[2] Aston: Proc. Roy. Soc., **115A**, 187 (1927).

[3] Aston: "Isotropes" (1923).

[4] Cabrera: Compt. rend., **186**, 228, 501 (1928).

for which the packing fraction is changing slowly; between the two classes there is a flat space of the curve where it is difficult to determine exactly the minimum.

In 1913, Langevin,[1] adopting the relativity formula, $m = E/v^2$ showing the relation between the variation of mass, the variation of energy and the light velocity, wrote that the divergences from the whole number rule might be due to the variation of internal energy by emission or absorption of radiation according to the case during the formation of the elements from the elementary constituents. Costa[2] took up this theory[3] again applying it to mass numbers and not to atomic weights as Langevin had done. Costa saw that the value of the "packing fraction" could give us information as to the energy emitted or absorbed during the formation of the elements. If the dissociation of a radio element into helium and a derivative element is exothermic, it means that the sum of the atomic weights of helium and of the derivative element is inferior to the atomic weight of the parent element. If the dissociation had been endothermic, the reverse would be true.

Thus a diminution of mass would correspond to a diminution of energy; the greater the loss of mass would be, the more stable the element would be. If we consider again the two classes of elements of which we spoke above, in one class are the elements which would tend to produce elements with a smaller packing fraction and a greater mass number; in the other class, there would be elements which would tend to produce elements with a smaller packing fraction and a smaller mass number; the elements of each class would tend to produce elements which are placed on the minimum of Aston's curve, since at this minimum the elements have the smallest packing fraction and the greatest stability. These considerations seem to be in accord with the radioactive transformations of the heavy elements on one hand and on the other hand with the building up of heavier atoms with the help of light elements, as the formation of O_{17} with an atom of nitrogen, an alpha particle and a loss of a proton.[4]

Recently Millikan and Cameron[5] have shown that the powerful cosmic rays were formed of bands of definite frequency. The cosmic rays would comprehend four chief radiations which would correspond to the energy liberated during the formation, with the help of protons: (1) of helium atoms; (2) of oxygen and nitrogen; (3) of silicium and magnesium; (4) of iron. Thus the loss of mass corresponding to the formation of helium from hydrogen

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[1] Langevin: J. Phys., 1913, 553.

[2] Compt. rend., 180, 1661; Ann. Phys., 4, 425 (1925).

[3] J. Perrin (Trans. Faraday Soc., 17, 546 (1921-1922)) calculated that the loss of mass corresponding to the transformation of hydrogen into helium was about 3×10^{19} ergs, and thought it possible for iodine and caesium to exhibit a loss of mass. He (Ann. Phys., 10, 90 (1919); Scientia, 30, 335 (1921). *Cf.* also Czeslaw Bealobrzeske: Bull. intern. acad. Polonaise, 1927A, 349-362) explains the radiation from the stars, by the energy evolved during the formation of heavier elements from hydrogen, and can account for the continuous radiation from the sun during the geological times.

[4] *Cf.* "Ejection of Protons from Nitrogen Nuclei, photographed by the Wilson Method." P. M. S. Blackett: Proc. Roy. Soc., 107A, 349 (1925). "Disintegration of Light Elements by Alpha Particles." E. Rutherford and J. Chadwick: Phil. Mag., (6), 44, 417 (1922).

[5] Millikan and Cameron: Science (2), 67, 401 (1928); Phys. Rev. (2), 31, 921 (1928).

(or $-4.002 + 4 \times 1.00778$) would be equivalent to the energy corresponding to the ether wave with the most characteristic frequency among the cosmic rays. Cabrera has tried to calculate the packing fraction with the help of the heat evolved during the transformation of radium into radium C and C′.

Thus it seems that the packing fraction can be calculated in the case of the radioactive decompositions as well as in the case of the building up of atoms.

It seems that the elements tend towards the formation of the elements for which the packing fraction is as small as possible and which correspond to as large a loss of mass as possible or to a maximum loss of energy, the light elements continually forming heavier elements, the heavy elements transforming themselves into lighter ones. The region of greatest stability would correspond to the elements of mass 60 or about, or of atomic number 26 (iron group). Thus would be explained the rarity of the heavy elements and the relatively great amount of iron in the composition of the earth as well as the great proportion of iron and nickel in meteorites.[1] Above iron, the elements are comparatively rare in the earth. Clark[2] points out that in several groups, the greater the atomic weight the rarer the element, it is the case for K, Rb, Cs; S, Se, Te; Cl, Br, I; As, Sb, Bi. This fact could be explained by the position of K at the left of the minimum, rubidium and caesium at the right, rubidium (85.45) being nearer to the minimum than caesium (132.81); in the same way, sulphur at the left, selenium (79.2) and tellurium (127.5) at the right; chlorine at the left, bromine and iodine at the right, while As, Sb, Bi are all at the right, but As (74.95) being nearer to the minimum than both [both] Sb and Bi. For, indeed, if it were admitted that all matter is made up of protons and electrons, it could be conceived that at the beginning the most abundant elements were the simplest and the lightest; then the light elements would evolve towards the elements with the smallest packing fraction, while the heavy elements, which might have been formed in an unknown and transitive way in small quantities, would tend to disintegrate into lighter elements, so that, in fine, the elements on the descending curve and near the minimum packing fraction would be the most abundant of all; and, for the elements of mass number superior to 60, the most abundant would be near the minimum also. Thus, iron might be the ultimate term of the evolution of the elements.

It seems that matter[3] obeys the two principles of thermodynamics: the principle of the conservation of mass being another way of stating the prin-

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[1] F. W. Clarke: "The Data of Geochemistry" (1924).

[2] F. W. Clarke: "The Relative Abundance of the Chemical Elements." Phil. Soc. Washington (1889).

[3] According to O. Stern (Trans. Faraday Soc., 21, 47 (1925-1926)), who adopts the stellar theory of Eddington, a star would lose a considerable portion of its mass during its evolution by radiation; matter would be transformed into radiation and radiation would be transformed into matter. O. Stern tries to calculate the equilibrium between these two processes

P. Jordon, (Z. Physik, 41, 711-7 (1927) studied the probability laws for the transformation of matter into radiation.

ciple of the conservation of energy[1] while the evolution of the elements would obey the second principle of thermodynamics, according to which at constant energy the entropy tends towards a maximum value or, at constant entropy, the internal energy tends toward a minimum value.

The chemical reactions are assumed to be due to the outside electrons, while the radioactive changes would depend on the protons and electrons of the nucleus; but it seems that the chemical reactions and the radioactive changes might both be submitted to the general principles of energetics. If, under certain conditions of temperature, pressure and volume, chemical reactions may take place in a reversible manner and can be affected by varying the conditions, the enormous variations of energy which accompany a radioactive change might make it impossible for us, so far and with our means, to act upon such changes; but it is not illogical to suppose that the radioactive changes might have taken place in a reversible way, under conditions very different from what they are today. The radioactive phenomena obey statistical laws and can very well obey the laws of thermodynamics since this science is nothing after all but statistical mechanics.

Among the elements at the left of the maximum, potassium[2] only is supposed to be radioactive, while all the other radioactive elements are at the right of the maximum. By emission of a beta particle, potassium would produce an isotope of calcium, the evolution being towards the production of elements with greater atomic number, for the light elements, and the reverse for the heavy elements which disintegrate by ejection of alpha particles and beta particles, ultimately to form lead.

The precise determination of the packing fraction is of the utmost importance, since the packing fraction gives us information on the forces which hold the protons and the electrons together in the nucleus and on the relative stability of the different nuclei. The determination of packing fraction is, in general, made with the help of the mass spectrograph; but, for the simple elements, the ordinary physical and chemical methods used for the determination of atomic weights could give the packing fraction with as great a precision as the determinations made with the mass spectrograph.[3]

Theodore W. Richards and Marcel Françon[4] have furnished a confirmation of the atomic weight of caseium determined by Richards and Archibald.[5] If it is assumed that caesium is simple, as Aston[6] claims, the packing

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[1] The doctrine of electrons forces us to admit the variability of mass with velocity and even the electro-magnetic nature of mass.

[2] E. Henriot: Radium, 7, 40-48; N. R. Campbell and A. Wood: Proc. Cambridge Phil. Soc., 14, 15 (1905-1908); M. Levin and R. Ruer: Physik. Z., 10, 576 (1909); Martin Biltz and Hans Ziegert: Physik. Z. 29, 197-200 (1928).

[3] Thus Baxter found for the atomic weight of helium 4.002 which corresponds to the atomic mass found by Aston.

[4] T. W. Richards and Marcel Françon: J. Am. Chem. Soc., 50, 2162 (1928).

[5] T. W. Richards and E. H. Archibald: Proc. Am. Acad. Arts Sci., 38, 443 (1903).

[6] Aston: Phil. Mag. (6), 42, 436 (1921).

fraction of caesium would be about three times as great as Aston's curve would indicate; the last determinations of the atomic weight of titanium[1] would indicate a packing fraction greater than would be expected, but, for titanium, it is quite possible that an isotope may exist. It would be very important to verify the non-existence of an isotope of caesium, for the anomaly of caesium might be of great significance.

In fine, the packing fraction contributes with the atomic number and the mass number to our knowledge of the nucleus: its charge, its mass, the number of electrons in the nucleus and the possible arrangement of protons and electrons in the nucleus. Besides, the packing fraction may be indicative of the evolution of the elements, it helps us to understand the rarity of certain elements and gives us a clue for the radiation emitted by the stars.

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[1] G. P. Baxter and A. Q. Butler: J. Am. Chem. Soc., 50, 408 (1928).

ADSORPTION OF IONS AND THE PHYSICAL CHARACTER OF PRECIPITATES

BY HARRY B. WEISER AND G. E. CUNNINGHAM

The first systematic investigation of the form in which substances precipitate from solution was made by von Weimarn.[1] He calls attention to a number of different factors on which precipitation depends: the solubility of the substance, the latent heat of precipitation, the concentration at which the precipitation takes place, the normal pressure at the surface of the solvent, and the molecular weights of the solvent and solute. He points out the impossibility of taking all these factors into account and simplifies the problem by considering but two of the factors: the solubility of the precipitating substances and the concentration at which the precipitation begins. The process of condensation (precipitation) is considered as taking place in two stages: the first stage, in which the molecules condense to invisible or ultramicroscopic crystals; and the second, which is concerned with the growth of particles as the result of diffusion. The velocity of the condensation at the important first moment of the first stage of the process is formulated thus:

$$W = K\frac{\text{condensation pressure}}{\text{condensation resistance}} = K\frac{Q - L}{L} = K\frac{P}{L} = KU \qquad (1)$$

in which W is the initial rate of precipitation, K a constant, Q the total concentration of the substance that is to precipitate, L the solubility of coarse crystals of the substance, $Q - L = P$ the amount of supersaturation. The ratio $P/L = U$ is the percentage supersaturation at the instant precipitation begins. To take care of other factors which may enter into the process, von Weimarn introduces a "variable multiplier," J, and the equation becomes:

$$W = KJ\frac{Q - L}{L} \qquad (2)$$

The velocity of the second state of the process is given by the Nernst-Noyes equation:

$$V = \frac{D}{S} \cdot O \cdot (C - l) \qquad (3)$$

where D is the diffusion coefficient, S the thickness of the adherent film, O the surface, C the concentration of the surrounding solution and l the solubility of the disperse phase for a given degree of dispersity. $C - l$ may be termed the absolute supersaturation.

By the aid of these equations, several facts are interpreted. It will be seen that the velocity of precipitation depends not alone upon the supersaturation P, but upon the percentage supersaturation P/L. Thus, with a given value of P (say a few grams per 100 cubic centimeters), a very soluble substance,

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[1] Kolloid-Z., 2, 199, 230, 275, 301, 326; Supplement 2, LII; 3, 89, 282 (1908); 4, 27 (1909); "Grundzüge der Dispersoidchemie" (1911); "Zur Lehre von den Zuständen der Materie" (1914).

such as sodium chloride, will deposit nothing at first and finally a few crystals may form; but with the same value of P an almost insoluble substance, such as alumina or silver chloride, will give an immediate gelatinous or curdy precipitate. The difference is, that the velocity of the precipitation is much smaller in the first case than in the second. On the other hand, if sodium chloride is formed by the interaction of sodium ethylate or sodium thiocyanate and hydrochloric acid in a mixture of ether and amyl alcohol, in which sodium chloride is practically insoluble, the precipitate is curdy like that of silver chloride.

Von Weimarn recognized that the velocity W of the first stage of precipitation cannot be measured in actual practice, and that, in many cases especially interesting in the synthesis of colloid systems, the velocity W of the growth of the particles cannot be determined. In due time, therefore, he introduced a specific coefficient called the "precipitate form coefficient" or "dispersity coefficient," N, which is given by the expression:

$$N = \frac{P}{L} \cdot K_{ab} \cdot K_{cd} \cdot K_{bd} \cdot K_{ac} \cdot Z \tag{4}$$

in which P/L is the percentage supersaturation as in the velocity equation, Z the viscosity, and K_{ab}, K_{cd}, etc., represent the "physical and chemical association" of the substances AB, CD, etc., which enter into the reaction: AB (in solution) + CD (in solution) = AC (precipitate) + BD (in solution). The significance of "physical association" is known but it is not clear what von Weimarn means by "chemical association." This is immaterial however, if the several factors are neglected and N is set down equal to P/L, that is,

$$N = \frac{P}{L} \tag{5}$$

or, if the several variables are lumped together and

$$N = J\frac{P}{L} \tag{6}$$

in which J has the same significance as in equation (2).

Now, if N is taken as approximately equal to P/L, as von Weimarn first assumed, then for the different substances x, y, and z,

$$N_x = \frac{P_x}{L_x};\ N_y = \frac{P_y}{L_y};\ \text{and } N_z = \frac{P_z}{L_z}. \tag{7}$$

If the character of the precipitate is to be the same in each case, irrespective of the chemical nature of the salt; in other words, if

$$N_x = N_y = N_z$$

then

$$\frac{P_x}{L_x} = \frac{P_y}{L_y} = \frac{P_z}{L_z} \tag{8}$$

This is the simplest expression for von Weimarn's Law of Corresponding States for the Precipitation Process, which says that under corresponding conditions of precipitation the mean magnitude (expressed in gram molecules) of the crystals of substances capable of precipitation will be the same.

In the form given in equation (8) the so-called law can hardly be regarded as a first approximation, even with substances that are related chemically.[1] A much more generally applicable formulation of the law of corresponding states for the precipitation process is

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

in which J_x, J_y, and J_z are specific variable multipliers, the value for any substance being "the product of all other factors (in addition to P/L) which influence the crystallization process. These values must be expressed by abstract numbers such that the values of P/L are equivalent."[2] In other words, von Weimarn's equation for his so-called law becomes quantitative and generally applicable by putting in "variable multipliers," handy wastebaskets, as it were, into which are thrown all the variable factors, known or unknown, which have not been evaluated.

While facts may be expressed fairly accurately by means of such flexible formulas, it is doubtful whether anything is gained scientifically by regarding formulations of this kind as quantitative representations of natural laws. Von Weimarn evidently thinks so, but his opinion is not shared generally. Thus, Bancroft[3] prefers to discard the formulas altogether and state the whole thing from a different point of view. He points out that the mean size of the crystals is determined by the total amount of material crystallizing and the number of nuclei. The really important thing, therefore, is the number of nuclei which are formed under any given conditions. It is contended, very properly, that factors other than percentage of supersaturation influence the number of nuclei formed. Thus, the specific nature of the substance, stirring, and temperature have a profound effect on nucleus formation, and adsorption exerts a marked influence on the growth of particles.[4] Freundlich[5] likewise does not believe that the separation of a solid phase is generally and uniformly regulated by its solubility and the supersaturation prevailing: "What is known concerning the extraordinary sensitiveness to foreign substances of the velocities of formation of nuclei and crystallization makes it *a priori* improbable, and experience has not confirmed this theory."

The effect of adsorption on the physical character of precipitates is considered in the following way by von Weimarn:[6] At constant $U = P/L$, foreign molecules have the same effect as greatly increasing U. The reason is that, during the growth of grains, the foreign matter keeps the reacting solutions away, so that not far from a given grain a local supersaturation results in the formation of a new grain. This would not happen in the absence of foreign molecules.

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[1] Cf. Buchner and Kalff: Rec. Trav. chim., 39, 135 (1920); Weiser: "The Colloidal Salts," 6, (1928).

[2] Von Weimarn: Kolloidchem. Beihefte, 18, 48 (1923).

[3] J. Phys. Chem., 24, 100 (1920).

[4] Weiser: J. Phys. Chem., 21, 314 (1917).

[5] "Kapillarchemie," 631 (1922).

[6] "Grundzüge der Dispersoidchemie," 97 (1911).

As would be expected, von Weimarn[1] includes the variable adsorption factor in his "variable multiplier:" "According to my theory, the adsorption factor at constant P/L acts in the same way as simply increasing P/L; that is, the precipitate is more highly dispersed. Now I have included the adsorption factor in the variable J of the precipitate form coefficient, $N = J \cdot P/L$. It follows, therefore, that J is increased by adsorption. If, however, P/L remains constant it follows that the value of N must likewise increase. A larger value of N corresponds to a higher degree of dispersion of the precipitate."

This categorical way of disposing of the effect of adsorption on the physical character of precipitates is not helpful. Von Weimarn's view is that the foreign substance always forms a protective film around the particles and thereby prevents their growth. This is apparently what takes place when precipitation occurs in the presence of a strongly adsorbed protective colloid such as gelatin. However, the effect on the physical character of a precipitate, produced by the adsorption of the solvent and of ions of varying charge and degree of hydration, cannot be disposed of so simply as von Weimarn would lead one to expect. Any substance should form a gel provided a suitable amount of highly dispersed substance is precipitated, and provided the particles adsorb the dispersion medium very strongly.[2] The amount of the dispersed phase that must be present in a given volume to form a jelly will depend on the size and orientation of the particles and the extent to which they adsorb the dispersing liquid, water in most cases. Now it is too well known to need comment that some substances adsorb water more strongly (that is, are much more hydrous) than others, so that at the same degree of dispersity some substances will form gels while others will not. This specific capacity of the particles to adsorb the solvent is altogether independent of their size and the rate of precipitation. In many instances, this is of far more importance than the rate of precipitation in determining the form of the precipitate. A notable example is the case of manganese arsenate, which can be made to form a stiff jelly by mixing very dilute solutions of potassium arsenate and manganese sulfate. The value of L for the precipitate is so large that precipitation is slow and quantitative precipitation is impossible. $P/L = N$ is very small, and yet a typical transparent jelly results.[3]

Von Weimarn would take care of the variation in the adsorption of the solvent by the particles by putting it into the J of the expression $N = J \cdot (P/L)$, and so make the calculated values of N fit the facts. There is, of course, no objection to doing this, but it is difficult to see what is gained by such a procedure.

The peptizing action of adsorbed ions may have a marked effect on the physical character of a precipitate. Thus, the analyst knows that barium sulfate, formed in ordinary analytical procedures, comes down very much finer when precipitated with barium chloride in excess than with sulfuric

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[1] Kolloidchem. Beihefte, 18, 68 (1923).

[2] Weiser: "The Hydrous Oxides," 26, 27 (1926).

[3] Weiser and Bloxsom: J. Phys. Chem., 28, 26 (1924).

acid in excess. This happens notwithstanding the fact that barium ion and sulfate ion are adsorbed about equally, and yield positive and negative sols, respectively, when the precipitation is carried out under suitable conditions. Finer crystals are obtained from potassium sulfate solution than from sulfuric acid. The explanation of this behavior is as follows: In addition to adsorbing its own ions strongly, barium sulfate adsorbs hydrogen ion more strongly than most cations. When sulfuric acid is treated with barium chloride in excess, the precipitate tends to come down in a finely divided state because of the peptizing action of the relatively strongly adsorbed barium and hydrogen ions. It would also come down in a finely divided state from a solution containing sulfuric acid in excess were it not that the strongly adsorbed hydrogen ion neutralizes the peptizing action of the sulfate ion. From potassium sulfate solution it comes down finely divided since potassium ion is not strongly adsorbed.[1]

That the effect of foreign material on the physical character of a precipitate may not be due chiefly to increasing the number of points of crystallization, is well illustrated in the case of sulfur, which is thrown down from the sol in a variety of conditions in the presence of different electrolytes. Thus, Stingl and Morawski[2] showed that potassium and barium salts precipitate sulfur in a plastic form, while calcium, magnesium, and sodium salts give flocculent sulfur. Odén[3] states that sulfur is thrown down from the sol as a hard precipitate with potassium salts, fine-grained with copper sulfate, plastic with barium salts, fluid with hydrochloric acid and slimy with other salts. Since the physical character of sulfur thrown down in the presence of different electrolytes shows such marked variations, it seemed to furnish a satisfactory substance for studying the general effect which the adsorption of ions may have on the physical character of precipitates. The results of this study are reported in the next section.

Experimental

Formation of Sulfur Sol. The sols used in this investigation were prepared by an adaptation of the method used by Sobrero and Selmi,[4] namely by passing hydrogen sulfide and sulfur dioxide simultaneously into a saturated solution of sulfur dioxide. By dissolving various amounts of sulfur dioxide in water, and then saturating with hydrogen sulfide, Odén found that a high initial concentration of sulfur dioxide favors the formation of finely divided particles, whereas a low initial concentration of the same gas favors the formation of non-peptizable clumps. Accordingly, in order to obtain large quantities of colloidal sulfur, the water was first saturated with sulfur dioxide and the excess was then maintained throughout the process by passing the theoretical amount of sulfur dioxide for the reaction, $SO_2 + 2H_2S = 2H_2O + 3S$, into the water simultaneously with the hydrogen sulfide. By this method it was possible to carry on the reaction for several hours without chang-

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[1] Weiser: J. Phys. Chem., **21**, 314 (1917).

[2] J. prakt. Chem. (2), **20**, 76 (1879).

[3] "Der kolloide Schwefel," 134, 157 (1912).

[4] Ann. Chim. Phys., (3), **28**, 210 (1850).

ing the reaction medium. After the sol became highly concentrated, sulfur settled out as a yellow mass which was readily peptized by shaking with water. The constancy of the conditions of formation gave particles of a much more uniform degree of dispersion than could be obtained by strict adherence to Odén's method.

The characteristic hydrophilic properties of Odén's sulfur sol are attributed by Freundlich[1] to the presence of pentathionic acid in the micelles. This conclusion is based on the observation that the sols have different properties if obtained under conditions such that the pentathionic acid cannot form. There seems to be no good reason for believing that the only thionic acid present in the micelles is the pentathionic, since Debus[2] showed that the mixture formed by the interaction of sulfur dioxide and hydrogen sulfide contains, in addition to colloidal sulfur and pentathionic acid, di-, tri-, tetra-, and probably hexa-thionic acids.

For the preliminary macro-observations on the physical character of the precipitated sulfur, the sol prepared as described above was purified by finally saturating the reaction liquid with hydrogen sulfide and then boiling out the excess gas. Any non-peptizable sulfur was removed by filtering through a fine filter paper. The sol obtained in this way contained nothing except the products of the reaction by which it was formed, and required no dialyzing. Moreover, it was quite stable, a part of the colloidal particles remaining suspended for more than two years. On the other hand, due to the decrease in the concentration of sulfur dioxide at the end of the reaction, the particles showed considerable variation in size, and for the microscopic and submicroscopic investigations, sols having particles of approximately uniform size were preferable.

The preparation of such monodisperse sols was readily accomplished, since the sol thrown down by sodium chloride is repeptized by washing with water, and since the smaller particles are more stable and require a higher concentration of salt to cause coagulation. The method employed was the same as used by Odén.[3] After fractionation, the sols were dialyzed for two or three weeks, until the dialysate showed no residue on evaporation and gave no test for chlorides. The first dialyses were done with parchment membranes, which gave trouble because of the tendency of the particles to diffuse through. A similar difficulty was reported by Nevinny.[4] Later dialyses were made with "cellophane" membranes, which proved to be entirely satisfactory.

Coagulation of Sulfur Sol by Electrolytes, and the Form of the Precipitate. The precipitation values of the sol for a series of electrolytes were determined using a mixing apparatus consisting of a small test tube sealed inside a larger one.[5] Ten cubic centimeters of sol was placed in the inner compartment of

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[1] Kolloidchem. Beihefte, 16, 234 (1912); "Colloid and Capillary Chemistry," 618 (1927).

[2] Chem. News, 57, 87 (1888).

[3] Z. physik. Chem., 78, 682 (1911).

[4] Berl. klin. Wochenschr., 45, 1833 (1908).

[5] Weiser and Middleton: J. Phys. Chem., 24, 48 (1920).

the apparatus, and a measured amount of standard electrolyte, diluted to 10 cc., in the outer compartment. The stopper was inserted in the mixer which was shaken vigorously, thus ensuring rapid and uniform mixing. The mixture was then poured into a Pyrex test tube and allowed to stand for 15 minutes, at the end of which time it was centrifuged for 3 minutes at 2000 r.p.m. By trial, the concentration of electrolyte was determined which was just sufficient to leave a clear supernatant liquid. At the same time, an amount of electrolyte slightly in excess of the precipitation concentration was added to the sol, and the nature and physical character of the precipitate was observed* after allowing the mixture to stand 15 minutes and then shaking. The results are given in Table I.

TABLE I

Coagulation of Sulfur Sol by Electrolytes and the Physical Character of the Coagulum.

Electrolyte	Precipitation Concentration, Milliequivalents per cc.	Physical Character of the Precipitate
HCl	0.5	Slimy; reversible
LiCl	0.55	Gelatinous; reversible
NaCl	0.25	Gelatinous; reversible
KCl	0.12	Plastic flocks; irreversible
CsCl	0.12	Plastic flocks; irreversible
$CuCl_2$	0.012	Gelatinous; reversible on repeated washing
$MgCl_2$	0.015	Granular; reversible on repeated washing
$ZnCl_2$	0.015	Granular; reversible on repeated washing
$CaCl_2$	0.008	Granular; partly reversible
$SrCl_2$	0.006	Curdy; irreversible
$BaCl_2$	0.0076	Plastic; irreversible
$FeCl_3$	0.00045	Curdy; almost entirely reversible
$AlCl_3$	0.00035	Curdy; almost entirely reversible
H_2S	(Saturated)	Only a small amount of slimy precipitate formed in 4 hours; almost entirely reversible
NaOH	0.15	Curdy to plastic; slightly reversible

That the character of the precipitate is not determined by the rate of precipitation was shown in the following way: Ten cubic centimeters of sol was placed in a test tube, and 10 cubic centimeters of electrolyte solution containing enough NaCl or $BaCl_2$ for exact precipitation was poured into a cellophane cup partly immersed in the sol. After about one hour precipitation was complete, and the nature of the precipitates formed was as indicated for the same salts in Table I.

As a further experiment, precipitates were formed by passing the sol-forming gases into dilute solutions of LiCl, NaCl, and KCl previously saturated with sulfur dioxide. After the concentration of the salt had been reduced below the precipitation value through adsorption by the precipitate, a sol

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* For some representative photographs of the precipitate see Colloid Symposium Monograph, 6, 329 (1928).

was obtained in each case. However, the precipitate first formed was identical in character with that obtained by adding the electrolyte to the sol. It is therefore evident that, in this case, the nature of the precipitate is not determined by the degree of dispersity and percentage supersaturation at the beginning of the precipitation.

Ultramicroscopic Observations

Since the form of the precipitate is apparently due in the last analysis to the manner in which the individual colloidal particles come together after neutralization by the several electrolytes, attempts were made to view the process microscopically. As might be expected, this was unsuccessful, since the colloidal particles are invisible in the ordinary microscope. Attempts were then made to view the coagulation process in the presence of electrolytes by means of the Jentzsch (Leitz) and the Siedentopf cardioid[1] (Zeiss) ultramicroscopes. The results were not satisfactory with either apparatus. On account of the depth of the Jentzsch cell, the precipitated clumps settled out of the range of the objective as they formed and therefore could not be kept in focus. On the other hand, the cardioid cell is too shallow (depth of liquid under observation, 0.002 mm.) to allow the clumps to form, the individual neutralized particles merely settling out after the Brownian movement had ceased.

Since the process of clump formation was not readily followed, observations were made, by means of the cardioid ultramicroscope, of the nature and behavior of previously formed clumps. These observations were accomplished in the following way: About 1 cc of sulfur sol was mixed with slightly more of the electrolyte than the amount necessary for complete precipitation and the mixture was allowed to stand for several minutes, after which a drop of the liquid containing a considerable amount of precipitates was placed in the ultramicroscope cell and examined. Differences in the ultimate structures of the precipitates are brought out in a striking way by a comparison of typical photographs which have been reproduced elsewhere.[2] In the precipitate obtained with lithium chloride or sodium chloride, focussed at different levels in the clump, the individual particles are clearly discernible, separated by a film of water. On the other hand, ultramicroscopic observations on the clump formed with potassium or barium chloride show distinctly that the individual particles have coalesced into a more or less uniform anhydrous clump of plastic sulfur. The edges of the clumps are smooth as a result of the coalescence of the particles and the surface tension of the plastic mass.

Still more illuminating is the behavior of a hydrous clump formed in the presence of lithium or sodium ion, when treated with a solution containing the more readily adsorbed and less hydrated potassium, caesium or barium ion. The observations were made, as before, with the cardioid ultramicroscope. In this apparatus the container for the sol is a quartz disc with a

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[1] For a theoretical discussion of the cardioid condenser, see Siedentopf: Kolloidchem. Beihefte, 23, 218 (1926).

[2] Colloid Symposium Monograph, 6, 319 (1928).

central depression 0.002 mm deep and about 12 mm in diameter, surrounded by a circular moat about 2 mm deep and 5 mm wide, into which any excess liquid is expelled when the quartz cover glass is put on. Two holes were bored on opposite sides of this cover glass in the same position as the moat, so that the latter could be cleaned out and refilled with any solution desired. The removal of liquid from the moat was accomplished by means of a narrow strip of filter paper rolled into a pointed rod, which was inserted into a hole in the cover glass and served as a wick. The moat was refilled by means of a medicine dropper drawn out to a capillary.

To make the observations, the cardioid cell was filled with a suspension of sulfur neutralized with lithium or sodium chloride. The moat was cleaned out and a satisfactory clump was brought into the field of view. The moat was then filled with a second solution containing the more strongly absorbed potassium, caesium, or barium ion, which diffused into the liquid bathing the precipitate and gradually, with repeated changing of the liquid in the moat, displaced the more weakly adsorbed sodium or lithium ion. This was accompanied by a marked change in the physical character of the clump, which change was followed photographically by means of an Ernemann motion picture camera especially constructed for microscopic work. The microscope used a glycerine-immersion objective of 3 mm focal length (N. A. 0.85), and the ocular employed had a magnifying power of 20 diameters. The magnification is roughly estimated at 1,500 diameters. The light for the microscope was supplied by a 17.5-ampere carbon arc, a single quartz lens placed near the arc serving as a collimator. The beam of light was passed through a 2-inch thickness of 5 per cent copper sulfate solution and a 12-inch thickness of water in order to cool it. For the purpose of minimizing vibration it was found necessary to mount the camera and microscope on separate bases.

The motion pictures of the changes taking place in the precipitates were made by taking one exposure every two seconds. To show the exact nature of the change photographs reproduced elsewhere[1] were made from sections of the motion picture negative taken at suitable intervals. The phenomena observed under different conditions will be considered in order:

Dehydration and Coalescence of Particles. Experiment I. The first observations were made on a clump thrown down by sodium chloride, in which the individual colloidal particles were rather widely scattered but were imbedded in a sheath of adsorbed water. When the adsorbed sodium ion was replaced by barium ion in the manner described above, the excess water flowed out of the clump, leaving the colloidal particles stranded in approximately their original positions. At the same time there was an apparent contraction in the volume of the ultramicrons. A photograph of the original clump shows the individual particles, but the voluminous hydrous character of the clump gives it a somewhat hazy appearance since all portions could not be brought into focus at the same time. A photograph of the same clump after the excess water had flowed out shows the individual particles in sharp outline.

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[1] Colloid Symposium Monograph, 6, 334 (1928).

Experiment 2. Since in the first experiment the particles were too widely scattered to come in contact after the excess adsorbed water was removed, attention was directed to a more compact clump obtained with sodium chloride, in which the ultramicrons were somewhat unevenly distributed. In this case, replacing the sodium ion with barium ion produced the same phenomena described in Experiment 1: but, in addition, the particles in intimate contact flowed together or coalesced into three or four minute, slightly hydrous particles.

Experiment 3. Experiment 2 was repeated with a somewhat more uniform clump. In this case, the substitution of barium ion for sodium ion caused the entire gelatinous mass to coalesce into a single particle.

Experiment 4. On account of the more gelatinous character of the precipitate obtained with lithium chloride, ultramicroscopic observations were made on a relatively large gelatinous clump as barium ion replaced the lithium ion. In this case there was a very marked shrinkage in volume, all the particles coalescing into a small uniform ball not more than 1/500 the volume of the original clump.

Observation of a projection of the motion picture film shows clearly the optical effects produced by the outflow of the adsorbed water. By visual observations in diffused light too dim to photograph, it is possible actually to see the convection currents in the water surrounding the clump. The striking character of this phenomenon can scarcely be imagined from the still pictures alone.

Experiment 5. Since potassium ion gives plastic sulfur, a clump formed with lithium ion was treated with potassium chloride. The loss of water and coalescence were identical in nature but the volume change was less marked than that observed in Experiment 4.

Experiment 6. Since the precipitate formed with caesium ion is more plastic than that formed with potassium, Experiment 5 was repeated, substituting caesium chloride for potassium chloride. In this case the original clump was constricted somewhat and the dehydration and coalescence caused complete segregation into two minute particles.

Reversibility of Precipitation. Attention has been called to the fact that the coagulum obtained with lithium or sodium ions is (1) gelatinous, (2) composed of the individual particles which have not coalesced and (3) readily reversible on washing out the precipitating ion. On the other hand, the precipitates obtained with potassium, caesium, and barium ions are (1) plastic, (2) formed by the coalescence of the ultramicrons and (3) practically completely irreversible. It has been shown also that clumps do not form if the neutralization of the ultramicrons is carried out in the shallow cardioid cell; instead, the individual particles settle out and remain at rest. This latter observation suggested experiments to show the factors which determine the reversibility of a precipitate. The method of procedure was as follows:

A monodisperse sol was placed in the cardioid cell, the excess sol was removed from the moat, which was filled with the solution containing the desired coagulating ion. After a sufficient amount of electrolyte had diffused into the cell to cause complete neutralization of the particles, the electrolyte was removed from the cell and pure water substituted. The electrolyte gradually diffused into the pure water, which was changed repeatedly.

Experiment 1. The sol was first neutralized by sodium chloride. After removing the excess electrolyte, the Brownian movement was resumed by all the particles, showing that the neutralization was completely reversible.

Experiment 2. Experiment 1 was repeated, substituting sodium hydroxide for sodium chloride. Identical results were obtained, the neutralization being reversible.

Experiment 3. A dilute solution of barium chloride was used as the precipitating electrolyte. In spite of repeated changing of the water through a period of 48 hours, the particles showed no signs of again taking on the Brownian movement. This experiment demonstrates quite clearly that the neutralization process is irreversible even in the absence of coalescence if the adsorption of the precipitating ion is too strong.

Experiment 4. Since potassium and barium ions give a similar type of precipitate when the particles are allowed to coalesce and since the adsorption of the univalent potassium ion is much weaker than that of the bivalent barium ion, it seemed possible that the precipitation with potassium ion in the cardioid cell, where there is no coalescence, would be reversible. This proved to be the case, the neutralized particles taking on the Brownian movement in 30 to 40 minutes after the beginning of the washing to remove the potassium ion.

As we have seen, Freundlich[1] attributes the characteristic properties of Odén's sol to the presence of pentathionic acid in the micelles. He is therefore led to the conclusion that the reversibility of sulfur precipitate depends on the formation of a stable pentathionate with the precipitating ion, that is, a pentathionate which does not decompose and thereby destroy the pentathionate ion. This view is not tenable, for in the case of potassium we have a precipitate which is reversible or irreversible depending on whether or not the particles are allowed to coalesce. In the case of sodium hydroxide we have a similar phenomenon. The partial reversibility of the precipitate formed by neutralization of the sol with sodium hydroxide is obviously due to some cause other than the destruction of pentathionic acid. It is probably related in some way to the influence of the excess OH ion on the amount of water adsorbed by the neutralized particles. Moreover, there appears to be no reason for believing that the lithium and sodium pentathionates should be any more stable than the corresponding potassium or barium salts. Certainly this is not true of the well-known, closely related dithionates.

The results of the above observations indicate that precipitation is irreversible (1) when there is coalescence of particles to form relatively large clumps and (2) when the precipitating ion is so strongly adsorbed that it is not readily removed by washing, irrespective of whether or not there has been a coalescence of ultramicrons.

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[1] Kolloidchem. Beihefte, **16**, 234 (1922).

Theoretical

From a survey of the observations recorded in the preceding section, it appears that the physical character of precipitated sulfur thrown down in the presence of alkali cations varies from gelatinous to plastic as we go down in the series from lithium to caesium. Likewise, the precipitate thrown down by alkaline earth cations changes in the same way as we go down in the series from magnesium to barium. In other words, precipitates formed in the presence of those ions which are generally recognized as the most highly hydrated, are the most gelatinous, and the precipitation is reversed by washing; while the precipitates thrown down in the presence of the less hydrated ions are dense and plastic, and the precipitation is not reversed by washing.

The order of hydration of the alkali cations is believed to be: Li > Na > K > Rb > Cs; and of the alkaline earth cations: Mg > Ca > Sr > Ba. Unfortunately, no one has yet succeeded in measuring quantitatively the ion hydration, much less its dependence on concentration, temperature, and the presence of foreign substances in the solution. Nevertheless, ion hydration numbers are frequently given. Thus, Remy[1] assumed that an ion moves like a sphere in a viscous liquid according to the well known Stokes formula, $u = 2/9 \cdot r^2(d_1 - d_2)g/\eta$, where u is the velocity, r the radius and d_1 the density of the sphere, and d_2 and η the density and viscosity of the medium, respectively. The mobility of the ions calculated in this way is too large when the atomic radius is assumed to be the radius of the ion. From the greater radius which must be assumed to obtain agreement with the Stokes formula—an increase which is attributed to a sheath of water—it is calculated that the lithium ion is associated with more than 120 molecules of water; the sodium ion with more than 66; potassium ion, 16; rubidium ion, 14; and caesium ion, 13. Hydrogen is assumed to be anhydrous. The order of magnitude of the hydration numbers determined from transference experiments by Washburn and Millard[2] is quite different from the results of Remy. Thus, if chloride ion is assumed to be anhydrous the number of molecules of water on the several cations is calculated to be: lithium, 4.7; sodium, 2; potassium, 1.3; caesium, 0.7; and hydrogen, 0.3. If the chloride ion is assumed to have 4 molecules of water, the values for the cations become: lithium, 14; sodium, 8.4; potassium, 5.4; caesium, 4.7; and hydrogen, 1. Recent theories of strong electrolytes would indicate that hydrogen is relatively highly hydrated. Thus Bjerrum[3] calculates the hydration number of hydrogen to be 8 and that of potassium 0. Jablczynski and Wisniewski[4] conclude from freezing-point measurements that lithium is combined with 11 molecules of water, sodium with 3, and potassium with 0. Schremer gives for hydrogen 10–11 and for lithium 6.5–7 molecules of water, respectively. On the assumption that hydrogen is monohydrated, Baborovsky[5] concludes that lithium holds 35

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[1] Z. physik. Chem., 89, 467 (1915).
[2] J. Am. Chem. Soc., 37, 694 (1915).
[3] Z. anorg. Chem., 109, 275 (1920).
[4] Roczniki Chem., 1, 116 (1921).
[5] Chem. Listy, 19, 297 (1925).

molecules of water, sodium 22 to 25, and potassium 6. Other investigators give still different values, but those recorded suffice to show that the absolute value for the degree of hydration of the ions under any special conditions, is not known. All observers agree, however, that the hydration falls off in the alkali series from lithium to caesium and in the alkaline earth series from magnesium to barium. Born[1] has shown further that the radius of the ions increases in the series from lithium to caesium, and Fajans[2] and Born[3] have calculated the heats of hydration of the ions from the lattice energies of binary salts and have found them to decrease from lithium to caesium and from magnesium to barium. This merely confirms the order of hydration of ions in the two series, but gives no indication of the degree of hydration. Indeed, Fajans is of the opinion that the so-called hydration of ions does not connote the formation of ion hydrates of definite stoichiometric composition,[4] but rather that, due to the electrostatic charge of the ions, the oppositely charged part of the polar water molecule is turned toward the ion and this in its turn exerts an attractive force on the next molecule. This type of dielectric polarization would proceed continuously in the water surrounding the ion. From this point of view it would follow that the so-called hydration values will be relative numbers only. For a series of ions having the same valence, the dielectric polarization will vary with the specific nature of the ion and with its size. In general, the concentration of the charge on a very small ion will exert a greater attractive force on the polar water molecules than the same charge on a larger ion.

Observations on the precipitation of sols with cations having the same valence, disclose that the adsorption of an ion, which determines its precipitating power, may be closely related to its degree of hydration.[5] If one accepts Fajans' view that the hydration consists in the formation of a polarized water envelope, the process being accompanied by a positive heat effect, one should expect the adsorption of an ion to be accompanied by a partial dehydration, the extent of which will be determined by the heat of hydration of the ions. Since we have seen that both the heat of hydration and the amount of hydration decrease in the alkali series from lithium to caesium and in the alkaline earth series from magnesium to barium, it follows that the adsorptive capacity and coagulative action should likewise decrease in the same direction, as the results show.[6]

It is of interest to enquire into the probable thickness of the film of water surrounding the sulfur particles. Pettijohn[7] found the maximum thickness of a water film on some glass pearls made in Germany to be about 128μμ. With another lot of glass of different origin the maximum was about 68μμ. With river sand the estimated thickness varied from 285μμ with 10-mesh

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[1] Z. Elektrochem, 26, 401 (1920).
[2] Verh. deutsch. physik. Ges., 21, 401 (1920).
[3] Z. Physik, 1, 45 (1920).
[4] Cf. also Baborovsky and Velisek: Chem. Listy, 21, 227 (1927).
[5] Cf. Lachs and Lachman: Z. physik. Chem., 123, 303 (1926).
[6] Cf. Weiser: J. Phys. Chem., 29, 955 (1923).
[7] J. Am. Chem. Soc., 41, 477 (1919).

sand to 114μμ with 60-mesh sand. From observations by Barus[1] on the formation of fog, it is calculated that the thickness of the water film under the conditions of the experiments is 0.1 to 0.8μ when the nucleus has a diameter of 2.6μ and 0.05 to 0.5μ when the nucelus has a diameter of 3.6μ. With sugar charcoal, Bijl[2] was able to show that the Gibbs layer of water was more dense than the main bulk of the liquid. He calculated the thickness of this layer to be 0.68μμ, which is below the limit of visibility with the ultramicroscope. Harkins and Ewing[3] found that when 10 grams of ignited charcoal was treated with 1 gram of water, the water was attracted onto the surface of the charcoal by an attractive force equivalent to 37,000 atmospheres, and that under this pressure, the water was compressed to 75 percent of its original bulk. The high visibility of the film between the discharged sulfur particles would seem to indicate that the density of the adsorbed water is relatively high, the refractivity being of a similar order to that of sulfur. The visual observation of ultramicroscopic convection currents accompanying the dehydration, supports this view. In a relatively dense gelatinous mass of sulfur precipitate, the thickness of the film of water between the ultramicrons appears to be, by comparison with the size of the ultramicrons, about 50μμ.

In the light of these considerations it seems reasonable to conclude that when the sulfur particles are partially neutralized by the adsorption of highly hydrated ions, the particles retain an envelope of water, so that the coagulated mass is an agglomerate of ultramicroscopic particles which have not coalesced. The film of adsorbed water together with the water entrained during the agglomeration process gives a flexible hydrous mass, which is known as a gelatinous precipitate. The ultramicroscopic observations on gelatinous sulfur formed by coagulation of the sol with highly hydrated lithium, sodium, or magnesium ion gives definite visual confirmation of the nature of a gelatinous precipitate deduced by Weiser[4] several years ago. E. Q. Adams called our attention to the fact that the coalescence in the presence of more strongly adsorbed, weakly hydrated ions may be due in part to a greater lowering of the charge on the ultramicrons than obtains in the presence of the less strongly adsorbed, highly hydrated ions.

Since the highly hydrated ions that yield gelatinous precipitates are not adsorbed strongly, and since the ultramicrons retain their individuality in such precipitates, it follows that washing out the excess of precipitating ion should cause repeptization. This is very readily accomplished with the precipitates formed with the univalent lithium and sodium ions. Practically complete repeptization of precipitates formed in the presence of magnesium and zinc ions can also be effected, but the washing must be more thorough because of the stronger adsorption of the divalent ions.

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[1] Phil. Mag. (6), 4, 24, 262 (1902).
[2] Rec. Trav. chim., 46, 763 (1927).
[3] J. Am. Chem. Soc., 43, 1787 (1921).
[4] Cf. Bogue: "The Theory and Application of Colloidal Behavior," 387 (1924).

Conditions are quite different if the neutralization of the particles is accomplished by the adsorption of ions that are not sufficiently hydrated to maintain a film of water of sufficient thickness or rigidity to prevent coalescence of the individual ultramicrons. This condition is realized with potassium, caesium, and barium ions. After neutralization, the ultramicrons collide and coalesce, giving a more or less uniform mass of plastic sulfur which cannot be repeptized to give a sol, no matter how thoroughly the precipitate is washed. If the individual particles are prevented from coming together by precipitating in the shallow cardioid cell, reversal can be accomplished by washing if the relatively weakly adsorbed potassium ion has been used to effect neutralization, whereas if the more strongly adsorbed, bivalent barium ion is employed it cannot be displaced by washing and reversal is impossible.

The formation of sulfur precipitates in quantity, either by neutralizing the sol by the addition of electrolytes or by carrying on the reaction between sulfur dioxide and hydrogen sulfide in the presence of electrolytes, can be visualized as follows: The first step following the formation of colloidal particles is their neutralization below the critical value necessary for agglomeration. When two or more such particles collide they either adhere or coalesce, the combination forming the nucleus for a larger clump. For the formation of a visible clump it is immaterial whether the particles actually coalesce or are held apart by a cushion of water. From the first collisions of discharged particles to form submicroscopic or microscopic nuclei the general mechanism is the same. A larger clump enmeshes a smaller one, and is in turn enmeshed by a clump larger than itself. The entire process resembles the accumulation of driftwood in a swollen stream. The growth of a clump therefore may be regarded as autocatalytic in nature. The shapes and sizes of the ultimate clumps depend upon the number and manner of chance collisions, except that the weakness of the binding forces in the gelatinous precipitates makes impossible the formation of very large clumps in the absence of packing. When the particles coalesce, the size of the clumps is limited only by the quantity of material available. The fundamental nature of the clumps, that is, whether they are flexible, gelatinous, and readily repeptized or are hard or plastic and nonpeptizable, depends on whether or not the conditions are favorable for the coalescence of the ultramicrons. This in turn depends on the nature and hydration of the adsorbed precipitating ion, in the manner above described.

Summary

(1) A discussion of the von Weimarn Law of Corresponding States for the Precipitation Process has been given. It has been shown that the law in its simplest form is frequently inapplicable, and that, in certain cases, it may be of little value for predicting the form of a precipitate in advance of the precipitation experiments.

(2) Among the factors other than the percentage supersaturation which influence the physical character of precipitates are: (a) the specific tendency

of the particles to adsorb the solvent; (b) the shape of the particles; and (c) the effect of the adsorption of ions.

(3) The element sulfur furnishes a satisfactory substance for studying the specific influence of the adsorption of ions on the form of a precipitate, since the physical character of precipitated sulfur varies more or less continuously from gelatinous and reversible to plastic and completely nonreversible when thrown down in the presence of the lyotropic series of ions from lithium to caesium and from magnesium to barium.

(4) Neutralization of Odén's sulfur sol below the critical value with a highly hydrated, weakly adsorbed ion, such as lithium or sodium, gives a gelatinous precipitate composed of the individual micelles separated by a film of adsorbed water. Such a precipitate is readily repeptized by washing out the neutralizing ion.

(5) When the sulfur sol is neutralized with a slightly hydrated, strongly adsorbed ion, a plastic precipitate is obtained in which the individual particles have lost their identity due to coalescence. A precipitate of this type is not reversed by very thorough washing.

(6) Ultramicroscopic observation of the change taking place when a highly hydrated cation is removed from a gelatinous sulfur clump, by displacing with a less hydrated, more strongly adsorbed cation, shows a very marked shrinkage as the result of the loss of adsorbed water and the coalescence of the particles. Ultramicroscopic convection currents in the surrounding liquid, due to the outflow of the adsorbed water, are visible during the change. Motion pictures have been made of this change in the physical character of the clumps under the influence of various ions.

(7) When the sulfur sol is neutralized in the cell of the cardioid ultramicroscope, so that the neutralized particles do not collide with one another, the precipitation is reversible or irreversible, depending on whether or not the adsorbed neutralizing ion may be removed by washing, and independently of whether the particles would coalesce if allowed to collide.

(8) It is concluded that: A reversible precipitate of any substance will be obtained when a sol is neutralized under such conditions as to prevent coalescence, either (a) by the intervention of a film of adsorbed solvent or (b) by preventing collisions of the neutralized particles. In either case it is essential that the adsorption of the neutralizing ion be sufficiently weak to permit its removal by washing.

(9) The shapes and sizes of the individual precipitated clumps of sulfur depend upon the number and manner of chance collisions during the precipitation process.

(10) The fundamental nature of the precipitated sulfur clumps depends upon whether or not the conditions under which the precipitation is carried out favor the coalescence of the ultramicrons, which is in turn dependent upon the nature and degree of hydration of the adsorbed neutralizing ions.

The Rice Institute,
Houston, Texas.

NEW BOOKS

Mechanochemistry and the Colloid Mill. *By Pierce M. Travis. 23 × 16 cm; pp. 191. New York: The Chemical Catalog Co., 1928. Price: $4.00.* At first sight it looks as though colloid chemistry were developing so rapidly that one form of mechanical disintegration had become a book in itself. A more careful examination shows that about 156 pages are devoted to colloid chemistry and about twenty-four to the colloid mill. That is more than anybody else has ever devoted to it; but it is not such a tremendous jump as it seemed at first.

The chapters are entitled: introduction; the colloidal state of matter from the physical-chemical viewpoint; the elementary structure of matter; the relation of viscosity and plasticity to the colloidal state; adsorption; electrical concepts and their importance in colloidal dispersion; the meaning of hydrogen-ion concentration and its importance in colloidal dispersion; orientation; gel structure and the Donnan theory of membrane equilibrium; the protective action of colloids in dispersion; the dispersion of solids and liquids in gas; the theory of emulsions and emulsification; dispersion of solids and liquids in liquids; the colloid mill and some of its applications; laboratory methods and physical testing of properties.

"Adsorption is an important factor in the wetting of some solids by liquids. If the solid particles are finely divided, they usually have a cushion of air about them, and when the fine powder is put into the liquid, the particles are airbound. That is, the little particles carry the air in with the powder, due to adsorption. This air may afterwards be displaced very slowly and this brings in the time factor. While we do not know what factors determine the amount of water adsorbed on fine crystals, there is no doubt but that different degrees of adsorption take place with various substances, hence the wetting power is entirely different. Some substances are easily wetted while others are resistant to wetting and, in a great number of instances, due to the affinity they have for adsorbing air upon the surface of the particle, the particles do not come in contact after the powder is agitated in the presence of such liquid. An excellent example of this is in the case of very finely divided calcium carbonate. If this is added to water and agitated, one may obtain a thick paste after the addition of about 25 per cent of carbonate. If this material is then passed through a so-called colloid mill, it is possible to shear off the air cushions and get a proper contact angle of the water with the powder. This dispersion, upon discharge from the colloid mill, will be found to be very fluid again, due entirely to the elimination of the air cushions. An additional 25 per cent of calcium carbonate can then be added to the dispersion and the operation repeated. A material will be obtained which is at least 50 per cent calcium carbonate and yet very fluid. This demonstrates that the original pasty condition was caused by the adsorption of air on the fine particles. Once this was eliminated and the liquid brought in true contact with the surfaces the dispersion was again quite fluid. Similar experiences are encountered with a great number of instances in a finely divided state. With the usual methods of mixing it is impossible to release the air cushions from the finely ground particles, but through proper mechanical treatment these may be removed and a large amount of such substance incorporated into the liquid medium. This is all due to the adsorption and the elimination of air from the surface of the finely ground solid material. Once it is wetted with the vehicle it will remain in a finely divided condition, provided there is not present an ion of opposite charge or some other condition of this sort to cause flocculation," p. 45. One wonders whether this means an error in Bingham's determinations of zero fluidity.

"Frequently, in colloidal dispersion, it is noticed that the material goes into the so-called colloid mill quite thin but is discharged from these mills in a thick condition, with more or less of a gel structure and the material is really plastic. This is always a pleasing indication to the operator of the machine and is usually attributed to fine dispersion, which is partially true. Nevertheless, the product must be in condition to have proper water adsorption or one would not get this gelatinous appearance," p. 89.

"The first users of pressure homogenizers were in the dairy industry. This use dates back to about 1905, when the homogenization of such dairy products as evaporated milk and light creams was accomplished by such means. Its purpose was just the reverse of that of a cream separator. Instead of separating the fat from the milk, it was possible with the homogenizer to incorporate fat into milk, thereby making any percentage of cream desired up to as high as 40 per cent, or what is known as heavy cream. It is a well-known fact in the dairy trade that homogenized cream cannot be whipped when prepared under regular conditions, such as the pressures above cited, nor will the fat separate out when passed through a cream separator. In other words, by this means one obtained almost a perfect emulsion of milk or cream."

"After the homogenizer had been used successfully in this field for a few years, it was next introduced into the ice-cream industry where it was used to incorporate the fat, milk solids, etc., into a homogeneous mass and develop a smooth ice-cream, thus bringing about a big improvement in the product. The practice of homogenizing was confined to the two above-mentioned industries for a number of years. It was then adapted by the pharmacist to the making of various types of emulsions, such as cod-liver oil, mineral oil-agar emulsions, etc. These machines made fairly satisfactory emulsions of the oil-in-water type for pharmaceutical manufacture and in the preparation of hand lotions and various face creams," p. 118.

"What the colloid mill really does is to deflocculate and, with a great number of substances, this is all that is necessary. This point might be illustrated with the dispersion of zinc oxide. It is well-known that when this substance is first manufactured, it is in a very finely divided state—what might, for commercial purposes, be classed as a colloidal state. In the packing of this product it groups or bonds together, so that the when the paint manufacturer uses it, all that is necessary is to deflocculate it in the presence of some vehicle. This is where the colloid mill is of value, for by dispersion through such a mill it is possible to obtain intimate contact of the vehicle with the small individual particles of the oxide, eliminate the air cushions brought about through adsorption, and replace these with direct contact of the vehicle with the power, in other words, increase its wetting power. Once these particles are deflocculated and are well wetted by the vehicle the dispersion is satisfactory for commercial application.

"This statement also covers a great number of other instances where it is sometimes said that the product is ground. One can readily prove this point by attempting to disperse carborundum or fused silica, where real grinding or disintegration would be necessary.

"It is hoped that this statement will help clarify the situation and will emphasize the point to prospective users, that if it is a case of deflocculating, the colloid mill may be of value to them, as it has proven to a great number of manufacturers. If it is a grinding problem, where it is necessary to really disintegrate or grind, no colloid mill has as yet been built which will do such work. Of course, as time goes on, it may be that it will be made possible to really grind by use of a colloid mill of the continuous type. From present evidence and study of the matter, however, the author is of the impression that in order to accomplish this it will be necessary to have enormous peripheral speeds, much beyond the mechanical limits of the continuous types of mill at the present time. The above facts, however, have not handicapped the progress of the colloid mill, which has found wide application throughout the chemical industry in various fields of operation," p. 149.

"The colloid mill is very frequently used as a sort of finishing mill the product having been previously treated through some other type of equipment, or else mixed thoroughly in some mixing device so that the colloid mill can handle the product, obtaining an unusually fine finish with large capacity. There might be other equipment which would accomplish the same work, but not with the same capacity or low cost of operation. It has frequently been found that with a colloid mill a manufacturer may increase his capacity to such a point that he operates this machine a few hours a week where with other equipment performing the same mission it was necessary to operate continuously. As a result, the manufacturer using the colloid mill can lower the cost of production enormously and undersell his competitor with another type of equipment.

"The following are typical examples of some of the uses to which the colloid or dispersion mills of proper design may be put in commercial operation:

1. Emulsification of vegetable, animal and mineral oils, resins, and waxes.
2. Manufacture of water paints, calcimines, etc.
3. Incorporation of pigments in the more fluid enamels and in paints such as outside white and flat white.
4. Homogenising of fat globules of milk for improvement in consistency and digestibility or for ice cream mix. Preparation of reconstituted milk from milk powder and sweet butter.
5. Extractions of oils, fats, resins, juices, etc., from vegetable or animal tissues as well as extraction of fibrous materials.
6. Purification of organic chemicals, liquids and solids.
7. Intimate mixing of creams, sauces and other foodstuffs where perfect blending is required.
8. Dispersion of some solids such as mica, certain oxides, fine clays, various dyes and other such materials which do not require the actual grinding operation.

"Many mineral colloids such as ferric hydroxide, silica gel, etc., contain water which is driven off on heating. Such material then becomes incapable of dispersion or suspension—for example, a clay heated above 100°C. Up to this temperature the natural moisture may be driven off, but there may be water of constitution, or that which is chemically combined, and after this is driven off, the residue no longer has the properties of the original material. Therefore, such material before excessive heating might disperse readily with the colloid mill, but such heating may make dispersion impossible. This, of course, is not always the case for there is no difficulty in dispersing a highly calcined magnesium oxide. In fact, this is a commercial process for making milk of magnesia. There are, however, a great number of substances to which this rule applies, especially those containing silica, iron etc. Very satisfactory dispersions have been made of chrome yellow, iron and zinc oxide, umber, lamp black, etc., of course, with the addition in most instances of a protective colloid," p. 164.

There is probably a misprint of wool for rayon in the statement, p. 47, that wool adsorbs relatively few basic dyes.

This is distinctly an interesting book. It gives a satisfactory outline of colloid chemistry from the non-teaching standpoint.

Wilder D. Bancroft

A Guide to the Literature of Chemistry. *By E. J. Crane and Austin M. Patterson. 23 × 16 cm; pp. v + 438. New York: John Wiley and Sons, 1927. Price: $5.00.* "The literature of chemistry is like a great, inspiring mountain with a core of rich ore. It is inspiring because the work of great men, of many earnest investigators, is recorded there. To obtain anything like full profit in its use one must learn how to climb this mountain and must know where and how to dig for the ore he needs. With the help of the many successful chemists who have generously contributed the results of their experience, we have attempted in this book to point the way."

The chapters are entitled: the problem and objectives; books; periodicals; patents; other sources; indexes; libraries; procedure.

"The question always arises as to how far back one should go in using the journal literature. This of course depends a great deal on the nature of the subject and of the search, as discussed in the chapter on Procedure (p. 217). Some searchers consider that it is usually safe to assume that everything of value in the journal literature has been made a part of the book literature after a period of about twenty years. A factor in such a decision is the realization that the development of a science is very rapid, so that much of the older literature is now close to useless because of discredited or at least greatly inferior methods, changed points of view, inadequate theories, and the like. Some even go so far as to assert that we would be better off if we could scrap the older literature as it becomes that. There are times when one will feel justified in ignoring all but the more modern literature but to do so always would be a mistake. The older literature is not always valueless by any means and books cannot be depended upon to glean everything that has a lasting value. Ideas and facts are still to be found there even though the methods, interpretations, and theories may practically all have been outgrown or carried over into the more recent literature. Just as it can be said that the journal literature is never out of date because of the continuous appearance of units of it, so it can also be said that the older parts of it are never really out of date because it is original material. A source book cannot be cast aside nor revised," p. 32.

If one is interested in the theoretical side of a subject, it is absolutely necessary to go back a good many years in the journal literature. As a broad statement, only those things get into the text-books which fit into the existing theory. As a typical case, how would any student learn from any modern text-book that a difference between solvent and solute was self-evident up to about forty years ago and that it dropped out only when and because the solvent was defined as the component which goes through the particular semipermeable membrane that one is considering?

From the reviewer's point of view one of the most important points in the book is the statement by a physical and metallurgical chemist, p. 227, that one should start with the most recent literature and work back. The counter-current method has two advantages. One picks up the references better in this way and is sure to be able to take them up in the reversed chronological order. The great advantage, however, is that one reads the earlier literature from the most recent point of view, which means that one detects flaws in reasoning of the earlier papers and omissions in the later ones in a way that could not be done otherwise.

The authors have got together a lot of valuable data which cannot be found anywhere else. The authors realize, and the reader will, that a study of this book will not in itself make him an expert at looking things up, though it ought to help him a great deal.

The authors themselves say, p. 152, that "skill in literature-searching involves skill in index-using and efficient index-using is an art in itself, a thing to be acquired." They might profitably have added that looking up a subject is an art in itself and one which calls for special ability as well as much practice. Since a scientific man looks up a subject primarily to find out what is of interest to him, the various news services are not and cannot be of much help to the research man though they may be, and apparently are, of great help to the technical man.

The authors have written a book which is a model of thoroughness from their point of view. Only time will tell whether people will get value out of it commensurate with the work that the authors have put in. *Wilder D. Bancroft*

Adsorption und Kapillarkondensation. *By Erich Hückel. 22 × 15 cm; pp. vi + 308. Leipzig: Akademische Verlagsgesellschaft, 1928. Price: bound, 20 marks; paper, 18 marks.* The book is divided into three parts: adsorption of gases and vapors by solids; surface tension of pure liquids and the wetting of solids by liquids; capillary condensation of vapors in porous substances. In Part I the four chapters are entitled: phenomenology and thermodynamics; molecular theory without reference to the nature of adsorbing forces (limiting case of small amounts adsorbed); the electrical significance of molecular forces; molecular theory for the case of large amounts adsorbed. There are three chapters in Part II: thermodynamics of the surface liquid-vapor; thermodynamics of the surface (pure) liquid-solid; theories of surface tension. In Part III we find: introduction and phenomenological; theory of capillary condensation.

The author approves of McBain's term 'sorption' when one does not know whether it is adsorption or absorption, and he believes that one should distinguish between adsorption and capillary condensation; but that is about all that he commits himself to definitely. Perhaps this is too severe. The author believes in the contact angle and that the order of adsorption of a vapor by a solid is either the order of boiling-points or a function of the van der Waals 'a'. He does not always play quite fair. He admits with reluctance that the van der Waals formula does not hold quantitatively, especially in the cases of polymerized vapors. Of course, not even van der Waals ever claimed that it would hold for gases like N_2O_4. The difficulty is that it does not hold quantitatively for any vapor.

There are 292 numbered equations and it seems incredible that one could write so much mathematics and say so little that could actually be tested. The author's acquaintance with the literature is nothing to brag about. It is hard to see what useful purpose this book will serve. *Wilder D. Bancroft*

THE FLOW OF CLAY PASTES THROUGH NARROW TUBES

BY G. W. SCOTT BLAIR AND E. M. CROWTHER*

After the classic equation of Poiseuille was put forward to account for the flow of fluids through narrow tubes, it was not long before various workers turned their attention to the modification which the equation would require in order that it might include within its scope those systems which are not true fluids, but have also some properties characteristic of solids. Trouton[1] for example, noted that the torsion-viscosity of certain "very viscous liquids" was not independent of the force of shear.

The first coherent attempt to produce a complete equation of flow for systems showing static rigidity was made by Bingham and Green.[2] These workers showed that a certain amount of pressure was required to overcome static rigidity, and that under suitable conditions, the Poiseuille equation could be applied, provided that the pressure term was taken as an excess over that amount required just to overcome the static rigidity. They pointed out, moreover, that flow curves plotted with the ordinates, " Amount of flow in unit time" and "Shearing stress applied" give for capillaries of different dimensions a family of straight lines, which, when extrapolated backwards over the region of low pressure (where the equation is not claimed to hold) all cut the "shear"-axis at a single point. This point gives a measure of the static rigidity of the system.

Bingham[3] points out that this linear relationship holds only at high rates of shear: "Fortunately, by using the higher rates of shear we can apparently always obtain the simple linear relationship. If later experiments prove that this is not the case, it will be time to use the more complex formulas." The constant corresponding to viscosity in the original Poiseuille equation, has been called by most workers by the unfortunate name of "Plasticity" and has the same dimensions as viscosity, although of course, it is not independent of pressure. Owing to the many different ways in which "Plasticity" has been used, we propose to term this constant "Pseudo viscosity." The reciprocal of this value (analogous to fluidity) is known as "Mobility."

Further, since no word has hitherto been adopted to describe the state of a substance exhibiting both static rigidity and fluid properties, we propose the term "pachoidal" with the corresponding noun "Pachoid" (Greek *παχὺσ* thick). This would include substances showing the above pseudo-viscosity or Bingham's plasticity and also de Waele's plasticity, (see below) should this prove to be a different phenomenon.

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* Soil Physics Dept., Rothamsted Experimental Station, Harpenden, Herts, England.

[1] Proc. Roy. Soc., 77A, 426 (1906).

[2] Bingham & Green: Proc. Am. Soc. Test. Mats., 1919, 641; Green: 1920, 450; Bingham: "Fluidity and Plasticity" (1922), and many papers.

[3] "Fluidity and Plasticity," 226 (1922).

Many American workers, especially ceramists, have made practical use of such high shear measurements, and have generally agreed with Bingham that conditions under low shears are too involved to justify serious investigations at present. (See especially Shearer.[1])

Reiner[2] has treated the whole question from the theoretical point of view basing his work on the postulate of a critical shearing stress which must be exceeded before plastic flow can start at any point and taking into account the fact that this critical stress is not attained at different distances from the centre of the tube at the same pressure but is attained first at a point nearest the wall. He accounts for the curved portion in the lower regions of the flow curve by considering the solid geometry of the "Extrusion figures" when the critical shearing stress has been attained only in part of the cross-section of the tube, so that the material is flowing as a solid plug within an envelope which is being sheared.

Buckingham[3] had previously arrived at a similar equation, but had also taken account of the fact that at low pressures, before the critical shear has been reached, the system tends to flow through the tube as a plug, surrounded by a truly fluid envelope which is thin, and adheres to both the wall, and the plastic material. This treatment leads to a flow curve of three portions: (1) a straight line passing through the origin (plug flow); (2) a curved portion (combined plug and plastic flow) approaching asymptotically (3), a final straight line (plastic flow).

As a final equation of flow, he gives,

$$V = \frac{\pi R^4 \mu}{8L}\left(P - \frac{4}{3}p + \frac{p^4}{3P^3}\right) + \frac{\pi R^3 \epsilon \Phi P}{2L}$$

where:—

V is volume of flows in ccs. per second*
R is radius of the capillary
μ is mobility
L is length of capillary
P is pressure applied
ϵ is thickness of liquid film through which plug flows
Φ is fluidity (1/ Viscosity) of this liquid film
p is pressure corresponding to critical shearing stress (f).

* Buckingham actually prefers to write "v/t" where *v* is the volume flowing in *t* secs.

The equation is qualified by the conditions that "the last term vanishes when there is no slip at the wall, and the first is to be omitted when $P < (2f/R) = p$." Buckingham appears to have advanced no experimental evidence for this theory.

De Waele,[4] finding that experimental flow curves are parabolic rather than linear, has questioned the whole treatment, and has shown that his

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[1] J. Am. Ceramic Soc., 11, 542 (1928).

[2] Kolloid-Z., 39, 80 (1926), and other papers.

[3] Proc. Am. Soc. Test. Mats., 1921, 1154.

[4] Oil and Colour J.. 1923, 33; 1927, 232; J. Am. Chem. Soc., 48, 2760 (1926); Kolloid-Z., 36, 332 (1925).

equation, in which pressure is set as proportional (over a wide range) to a power of the flow, is valid at the very high pressures used by him. Many other workers (chiefly of the Ostwald school) claim that such an equation fits well the experimental facts at much lower rates of shear, and Green has pointed out that such a result would be expected on the Green-Buckingham theory if the experiments were carried out at insufficiently high rates of shear for the material investigated. It will be shown elsewhere that the results of the Ostwald school, when subjected to an alternative—and simpler—form of treatment, support the views to be given in the present paper.

In this paper the authors propose to give: (1) quantitative evidence to show that an equation only slightly modified from that of Buckingham holds under certain conditions of shear; and (2) qualitative evidence in favour of the Buckingham theory for those regions where quantitative measurements have not been practicable. This evidence has been obtained from experiments on the behaviour of certain clays (chiefly agricultural) in a modified Bingham plastometer.

The Apparatus

The plastometer used in this work is essentially that used and described by Bingham and Green, the only modifications of importance being: (1) that there are two bulbs, the clay being sheared alternatively from one to the other; (2) that the level of clay in the two bulbs is kept the same so that no correction is required for hydrostatic head.

The air is forced by a foot pump into a reservoir, being released through a sensitive valve. When the clay paste is flowing under constant air pressure as measured on a mercury or water manometer, the air displaced by the clay is allowed to escape through one of a series of capillaries selected of a size convenient for the velocity to be measured. The extremely small pressure behind this capillary (proportional to the amount of air flowing through it) is read on a sensitive alcohol manometer inclined at an angle of about 1:10. To obtain the velocity of flow in cm^3/secs, the alcohol manometer readings need only be multiplied by a constant dependent on the dimensions of the air-capillary and determined by measuring the times required to shear a known volume of glycerine at constant rates. The pressures used varied from 1mm. water to nearly 50 cm. Hg. and the rates of flow could be measured with accuracy from 0.0002 – 2.0 cm^3/secs. The whole apparatus was enclosed in a thermostat at 25°C.

It will be seen from Fig. 1 that the apparatus is not geometrically regular. In order to be sure that the flow of a true fluid through the apparatus was closely in accordance with Poiseuille's law, experiments were done with glycerine, kerosene, and water, and the flow curves obtained were found to be good straight lines passing through the origin.

Although satisfactory results are obtained with natural clays and most soils, from which only the coarse sand has been removed, all the data given in this paper were obtained with separated clay fractions. Unless otherwise stated, the clay fractions were prepared from a heavy clay taken at a depth of 3 feet below Broadbalk Field, Rothamsted. All the clay fractions were prepared by making a suspension in dilute sodium carbonate and decanting the top 8.5 cm. after sedimentation for 24 hours. The stable suspensions from a number of such repeated decantations were flocculated with dilute acetic acid, and filtered. The flocculated clay was washed with distilled water, thoroughly mixed and bottled. For each series of experiments, a quantity of the paste was gently rubbed once or twice through a wire sieve with apertures of 0.2 mm. side. All comparisons are between samples taken from a single batch; separate batches were used for Tables I, II and III. The concentration figure given is the number of grams of dry matter in 100 grams wet clay after drying for one hour at 165°C.

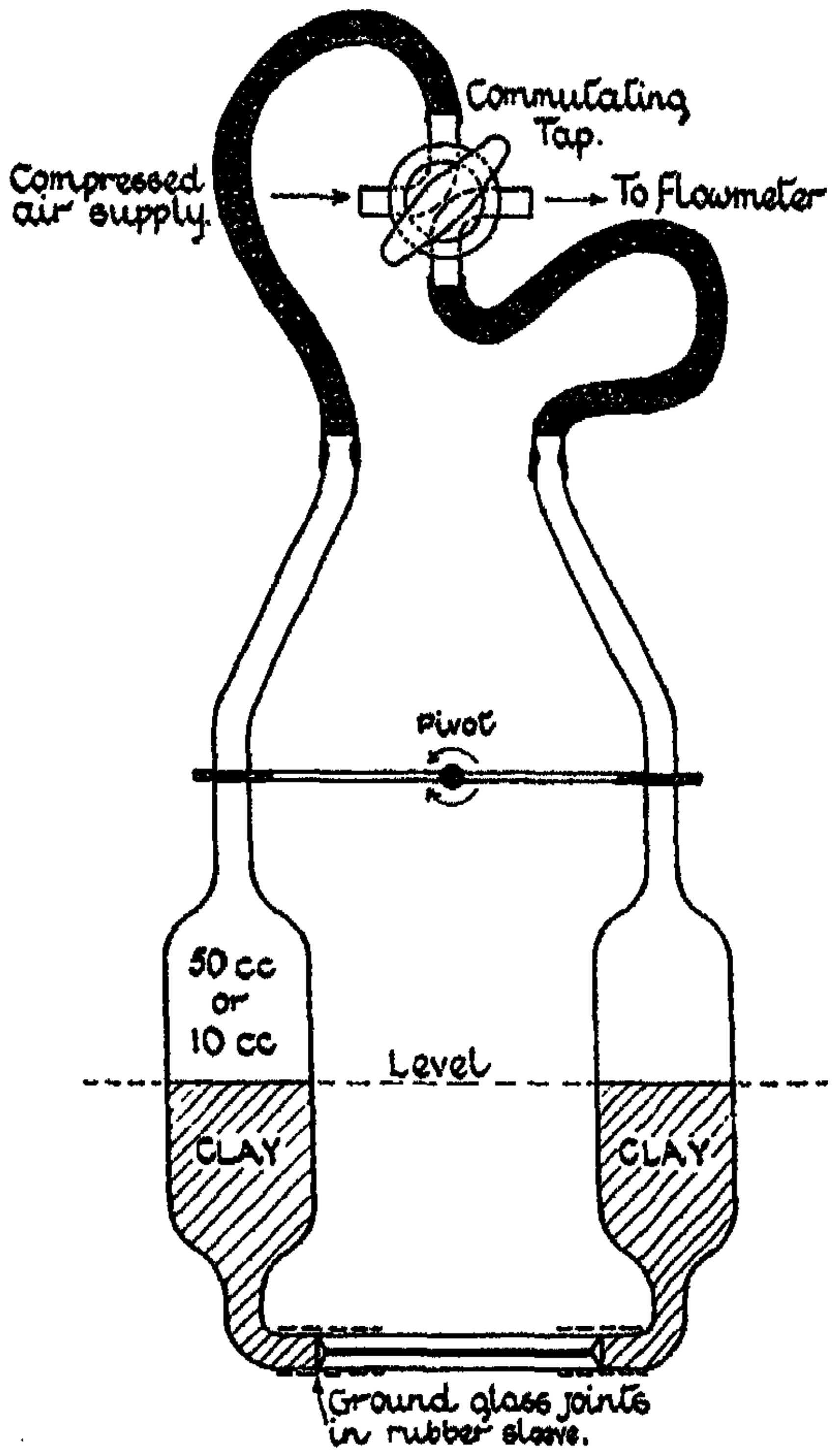

FIG. 1
Plastometer Bulbs and Capillary

The bentonite used for the dyed clay experiments was a commercial sample kindly given by Mr. A. de Waele. It was made up directly with distilled water without preliminary purification. It was then passed once more through the wire sieve. The dyed bentonite was washed until the wash-water was quite colourless.

For high shears, about 40 cc. of clay paste were sucked into the plastometer bulbs having a capacity of about 50 cc. each, and for low shears, about 8 cc of paste were used with bulbs of about 10 cc capacity. For high rates of flow a single reading, and for low rates, as many as six readings were obtained from each shearing from bulb to bulb. Under all the conditions considered in this paper, the number of shearings to which the clay had been subjected had no effect on the flow curve. Duplicate samples gave closely concordant results.

The Experimental Flow Curves

A typical flow curve is given in Fig. 2. Owing to the wide range of rates of flow, the curve is divided into two portions with rates given in mm^3/secs and cm^3/secs. respectively. It was generally found convenient to use different capillaries for exploring these two portions of the curve, but, for simplification, in presentation, the data in Fig. 2 are taken from experiments on a single capillary. It was of course necessary to change the air-capillary of the flow meter in order to cover such a wide range. Even smoother curves than those in Fig. 1 were obtained when different capillaries were used for the two portions.

It is at once apparent from this figure that there are four separate stages in the behaviour of a clay paste subjected to increasing pressures. These are indicated in the diagram, and will be discussed separately.

Curves of the same type have been obtained for all the clays studied with the exception of kaolin, which gave serious irregularities due in part to seepage. In certain cases, as with clays of the bentonite type, stage II covered only a small range of pressures. After the removal of the coarse sand fraction, most soils gave curves similar to, and as regular as those of clays, but the concentration had to be much more carefully chosen.

On increasing the pressure gradually a number of different phases or regimes were obtained on the flow pressure diagrams.

Stage I. There was no motion until a well-defined critical shearing stress was reached.

In order to be certain that the initial point of flow was really sharply defined, a pressure of only a few per cent less than the observed critical pressure was applied, while the flow-meter air-capillary was completely blocked up. No rise at all was noted although the merest movement would have given a very large displacement in the flowmeter; the addition of an extra 1-2 mm. Hg pressure gave a definite reading with the unblocked air-capillary.

It will be seen from Table I that for flow in long narrow plastometer capillaries (with L/R greater than about 110) the values obtained by multiplying the pressure of initial flow (a) by the ratio R/L gave a constant (A) which was independent of the size of the capillary. For shorter and wider tubes, this constancy did not hold. Further, for long and narrow capillaries the constant A was independent of the shape and size of the container bulbs, but with shorter and wider capillaries, as the ratio L/R was reduced below about 110, the critical pressures for initial flow began to show variations with changes in the form of the containers and approximate calculations indicated that the resistance of the bulbs themselves became significant.

If we follow Buckingham in assuming a plug flow at low shears through an envelope of constant thickness, the existence of a critical shearing stress for the start of the flow, can only be interpreted by assuming either (1) that the fluid layer comes into being suddenly when a definite stress is reached, and attains at once its constant thickness or (2) that the layer is not truly fluid, but itself exhibits static rigidity or (3) that some bonds or forces exist across the fluid layer (already present) which are broken down on the attainment of a certain critical shearing stress.

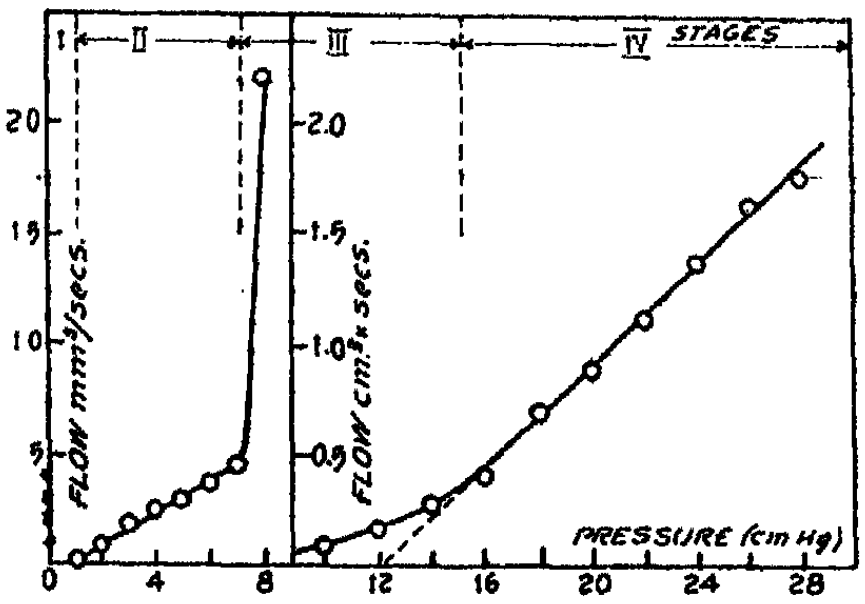

Fig. 2

A Typical Flow Curve

Clay paste 18.1%. Capillary No. 7. R = 0.060 cm. L = 10.60 cm.

TABLE I

Stage I. Constancy of critical shearing stress (A) for long narrow capillaries. Capillaries for which L/R < 110, or R/L > 0.09 are marked*

Tube No.	Radius cm.	Length cm.	10R/L	Initial flow pressure cm. Hg "a"	Critical shearing stress. 10.(A)
2*	0.102	8.00	0.128	1.4	.18
8*	0.087	7.20	0.121	1.3	.16
3*	0.100	10.70	0.094	1.4	.13
6	0.088	10.65	0.083	1.5	.12
5	0.086	13.00	0.066	1.5	.10
13	0.049	8.00	0.061	1.6	.10
7	0.060	10.60	0.057	2.1	.12
11	0.049	10.00	0.049	1.9	.09
10	0.050	10.60	0.047	2.1	.10
12	0.049	12.90	0.038	2.7	.10

Alternative (3) seems the most probable, but the matter requires further investigation. The fact that readings can be taken repeatedly on both sides of the initial flow pressure indicates a reversibility which makes alternative (1) seem improbable.

Stage II. In this stage the clay paste moves as a rigid plug through the tube and the flow curve is linear over a considerable range.

Fig. 3 shows a photograph of a tube in which a paste of bentonite dyed fast with crystal violet was pressed through a capillary containing natural white bentonite of approximately the same moisture content. The sharp line of demarcation indicates a true "plug" flow.

Over this stage, the experimental points fall on a straight line within the limits of experimental error.

Table II shows as an empirical fact that the slope ($dv/dP = x$) multiplied by L/R^3 gives a constant (a) which is independent of the dimensions of the capillary, provided that L/R exceeds about 50. The significance of this in its bearing on Buckingham's theory is dealt with below.

TABLE II

Stage II. Constancy of X ($= xL/R^3$ where x is slope) for different capillaries

Tube No.	Radius (cm)	Length (cm.)	$L/10^4R^3$	x	$10^{-4}X$
4	0.132	10.80	0.47	1.8	0.85
3	0.100	10.70	1.07	0.80	0.86
8	0.087	7.20	1.10	0.82	0.90
6	0.088	10.65	1.56	0.60	0.93
7	0.060	10.60	4.92	0.18	0.88
10	0.050	10.60	8.49	0.11	0.90

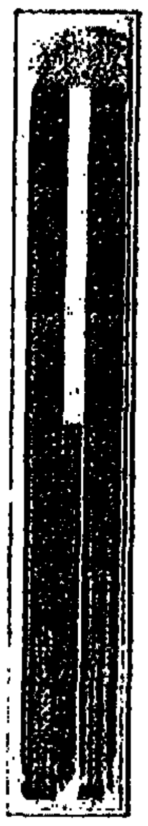

FIG. 3

Stage III. The clay flows as a central plug within a stream-line shell of increasing thickness and the flow curve bends rapidly upwards.

Qualitative evidence of the dual type of flow was obtained by a further experiment with dyed bentonite. Fig. 4 shows the cross-section of a capillary tube after the stress had reached the critical value, so that the dyed bentonite was now advancing as a central plug through a residual ring of undyed bentonite. That the dyed bentonite represents a plug rather than part of a streamline system is indicated by the fact that the flow curve has a definite curvature.

Stage IV. For the highest rates of shear studied the flow curves become linear and the flow is streamline throughout.

It is found that the slope of the flow curve (y) multiplied by L/R^4 gives a constant (Y) independent of the capillary.

When the flow curves are extrapolated to the pressure axis, the intercepts (c) multiplied by R/L give a constant (C) independent of capillary. (Table III)

TABLE III

Stage IV. Constancy of C (= cR/L where c is extrapolated intercept) and Y = (yL/R^4 where y is slope) for different capillaries.

Tube No.	10R/L	L/10^6R^4	C(cm Hg)	C	y	10^{-6}Y
3	0.094	0.107	7.5	.71	7.5	.80
6	0.083	0.178	8.5	.70	4.7	.84
7	0.057	0.820	11.7	.67	1.1	.90
10	0.047	1.70	14.2	.67	0.50	.85

(Slopes are expressed in the same arbitrary units throughout.)

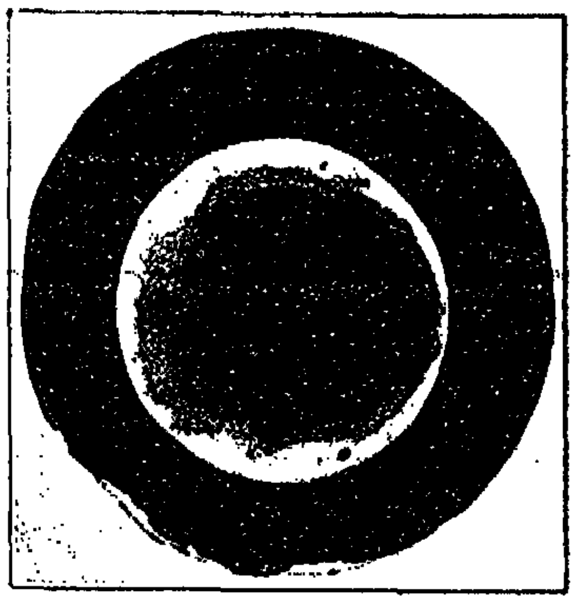

FIG. 4

(C) The Linear Portions of the Flow Curves

Further evidence of the essential physical difference between the types of flow over the linear portions of the flow curves in Stages II and IV was obtained by experiments in tubes which had been roughened internally by means of a mixture of ammonium fluoride and hydrofluoric acid. The roughening of the capillary would be expected to interfere seriously with the thin envelope through which the plug flows in Stage II but to have little or no effect on the streamline flow of Stage IV.

Fig. 5 gives the flow curves in both stages for a smooth and a roughened capillary of approximately the same diameters, together with curves calculated from the constants of the smooth tube for a tube of the same dimensions as the roughened one. In the streamline regime (Stage IV.) the experimental points for the roughened tube approximate to the calculated curve. But in Stage II there is a wide divergence and the rate of flow for a given pressure is greatly reduced. Further the flow curves were often more irregular than in the example given, indicating that the envelope was not only considerably reduced in thickness but was also less uniform.

The constants (X and Y) derived from the slopes in Stages II and IV (Tables II and III) were found empirically to be connected, in that the ratio X/Y for a wide range of concentrations of the same clay was constant within the limits of experimental error. Clays of widely different geological types gave slight but significant differences in values of X/Y. (Table IV).

Such a relationship between X and Y was indicated in the work of St. John[1] who made comparisons with flour suspensions between a low-shear plastometer of his own design and the Bingham high-shear plastometer. Although St. John regarded both cases as instances of streamline flow, it seems probable that the low shear apparatus was giving a plug flow and that

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[1] Ind. Eng. Chem., 19, 1348 (1927).

the correlations obtaining between the two sets of results for different flours depend on a somewhat similar relationship between X and Y.

A correlation of certain of the above plastometric constants for soil pastes with agricultural factors, such as the resistance of the soil to the plough, has been found and will be discussed elsewhere. It may be mentioned that some soils showed visible "seepage"* and a consequent failure to give reproducible results on repeated shearing. Experiments are also in progress on the plastometric behaviour of clays and soils, with special reference to flocculation, exchangeable bases, and the effect of lime and fertilisers on soil tilth.

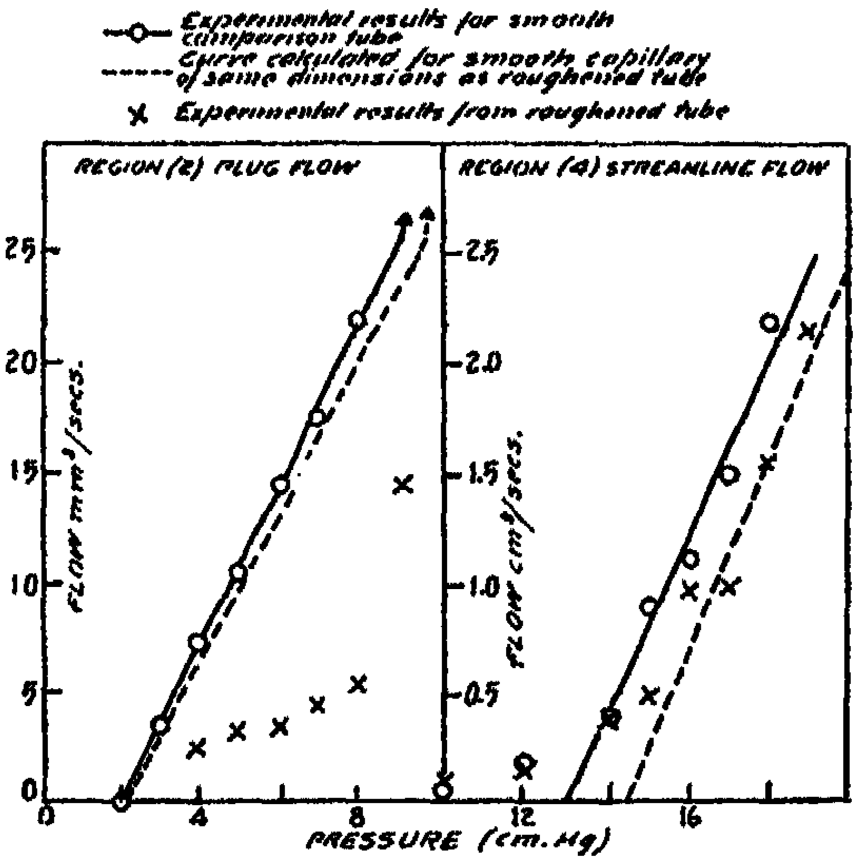

FIG. 5
Effect of Roughened Capillary Surface on Flow Curves

TABLE IV
Values of Ratio X/Y for different concentrations of three clays
Clay A. Clay from Broadbalk Field, Rothamsted
Clay B. Oolitic Clay Clay C. Liassic Clay.

Clay A Concentration	X/Y	Clay B Concentration	X/Y	Clay C Concentration	X/Y
21.9	2.2	24.8	1.5	24.5	1.7
19.3	1.8	23.8	1.5	20.8	1.7
18.4	2.0	19.5	1.5	18.3	1.4
18.2	2.2	18.2	1.1	16.4	1.6
15.5	2.3	17.2	1.6	12.6	2.0
14.3	2.0	14.6	1.0		
11.8	2.1	13.7	1.5		
10.7	2.3				
Mean	2.2		1.4		1.7

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* "Seepage" is defined as the condition in which the liquid suspension medium flows more rapidly than the bulk of the solid matter.

Modification of Buckingham's Equation

Although the experimental data presented are not sufficient to test the whole range of Buckingham's equation, the constants derived from the two linear portions are in agreement with it, provided that it is modified to cover the initial region of no movement. This involves altering his assumption that the lubricating envelope acts as a true fluid for very low pressures. It is necessary to assume that a critical shearing stress must be obtained before any motion takes place and to deduct the equivalent pressure before applying the equation. This new shearing stress must not be confused with Buckingham's critical shearing stress (f), which refers to the beginning of streamline flow in the paste itself (Stage III).

The above modification in the hypotheses in Buckingham's equation would lead theoretically to the expression

$$v = \frac{\pi R^4 \mu}{8L}\left(P - \frac{4}{3}p + \frac{p^4}{3P^3}\right) + \frac{\pi R^4 \epsilon\phi (P - a)}{2L}$$

The relationships between this expression and the constants derived from the above experimental data are as follows,

Stage I and II. a = the pressure equivalent to the critical shearing stress.
Stage III $\epsilon\phi = x = (L/R^3)$. slope.
Stage IV $4/3P = c$ (= extrapolated intercept.)
and $\mu = Y = L/R^4$. slope.
$1/Y$ = pseudo-viscosity

Our thanks are due to Dr. B. A. Keen for his interest and criticisms throughout the progress of this work, and also to Mr. A. de Waele for advice in the earlier stages, especially in connection with the design of the plastometers.

Summary

(1) A modified plastometer of the Bingham and Green type has been devised, suitable for experiments on small amounts of clay and soil pastes over a range of applied pressure of from 0.05 to 50 cm Hg, and rates of flow of from 0.0002 to 2.0 cm^3/secs.

(2) The flow curves fall into four stages. In the first stage there is no flow; in the second the value of dV/dP is constant; in the third it increases rapidly and in the fourth it is again constant. The movements are successively—plug flow, plug flow with stream line flow in an outer sheath, and entirely streamline flow.

(3) This behaviour is shown qualitatively by experiments with dyed clays and for the most part quantitatively from the constancy of the plastometric functions to agree with an equation slightly modified from Buckingham's theoretical equation.

(4) It is found as an experimental fact that the ratio of the constants derived from the slopes of the plug and streamline stages respectively is constant over a wide range of concentration for a single clay. For clays of widely different geological origin variations in this ratio are small, but probably significant.

PHOTO-VOLTAIC CELLS WITH SILVER-SILVER BROMIDE ELECTRODES. PART I*

W. VANSELOW AND S. E. SHEPPARD

A review of all the work which has been published bearing on the subject of photo-voltaic cells would be a task in itself. To review and scrutinize all of the literature relative to photo-voltaic cells having silver halide electrodes is in order but for the fact that the data published have been obtained under somewhat incomparable conditions. The present investigation was taken up in order to investigate indirectly the formation of the visible and latent photographic images with silver halides.

Thus it is not the object herein to criticize others' results but merely to present the methods and results obtained by using a photo-voltaic cell consisting of silver-silver bromide electrodes immersed in an electrolyte having the bromide ion. Nor do we offer herein a complete interpretation of all data presented. Such interpretations and theoretical discussions will follow in another publication.

Two recent investigators, Allen Garrison[1] and Carl W. Tucker,[2] have published results of experiments with photo-voltaic cells using silver halides as the photo-sensitive material. Wildermann[3] has also done considerable work on this photo-voltaic cell. He finds the photo-potential gradually reaches a maximum, and after the exposure has ended, the potential falls to its original dark potential difference.

Scholl[4] has studied the behavior of silver iodide in the photo-cell in various spectral regions. A number of processes take place during the illumination of silver iodide in a salt solution. Moisture increases the liberation of electrons when silver iodide is illuminated. Goldmann[5] has devoted some attention to the photo-electric effects in photo-voltaic cells using solutions of eosin, fluorescein, *etc.* The strength of the photo-electric current is proportional to the light intensity and to the illuminated area and is within wide limits independent of the magnitude of the resistance of the circuit.

Going still further back into years, we come to another investigator whom we will mention,—Minchin.[6] Retreating still further we come upon the investigator to whom credit for the discovery of the phenomenon is due,—Ed. Becquerel.[7]

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* Communication No. 362 from the Kodak Research Laboratories.

[1] J. Phys. Chem., **28**, 333 (1924).

[2] J. Phys. Chem., **31**, 1357 (1927).

[3] Z. physik. Chem., **59**, 553, 703 (1907)

[4] Ann. Physik, (4), **16**, 417 (1905).

[5] Ann. Physik, (4), **27**, 449 (1908).

[6] Phil. Mag., (5), **31**, 207 (1891).

[7] La Lumière, II, 129 (1868).

When two metallic electrodes are coated with a photo-sensitive material and are immersed in an electrolyte, if one of these electrodes is illuminated while the other is kept dark, an electromotive force is set up. This phenomenon has been termed the Becquerel effect, after its discoverer. Becquerel, in his work, observed that in the case of the photo-voltaic cell having silver-silver iodide (silver iodide layer upon silver) electrodes, one of which is illuminated while the other is kept dark, that the photo-potential was not always in the same direction. Garrison's statement regarding Becquerel's work reads . . . "If the silver iodide coating was not too thick on the electrode he found that the photo-potential was always positive, that is, the light caused the electrode to take a positive charge from the liquid. But when the coating had reached a critical thickness there appeared a negative light effect which was only temporary and was ordinarily followed by the positive effect." These facts agree in part with those we have observed in the case of the photo-voltaic cell using silver-silver bromide electrodes. We might state that up to a certain thickness of silver bromide layer on the silver the photo-potential was momentarily negative and then positive. But it must be borne in mind that there is little justice for a comparison because all conditions of experiment were not similar. Becquerel had used his silver-silver halide electrodes in a solution containing a small amount of sulfuric acid. The electromotive force of the photovoltaic cell depended in part upon the thickness and uniformity of the silver halide layer.

The definitions of the positive and the negative effects are not the same for all investigators. Some have the reverse meaning, *i.e.*, positive to some is the negative to others.

In reviewing briefly Tucker's article, one must recall that Tucker and Minchin have adopted opposite meanings of positive effects. Minchin's results regarding the electrical effects observed are rather indefinite. Tucker quoted Minchin exactly: "In nearly every cell that I used with thin plates—whose surfaces, as stated above, had not been treated in any way—the exposed plate was positive to the unexposed; but after a time varying from a few minutes to a few hours, it was found that this positive current died out and was replaced by an apparently stronger current, in which the exposed electrode was negative. Thus there was a change in the sign of the e.m.f. produced by the continuous action of light. This again reminds me of M. Becquerel's observation about the thickness of sensitive layers. There seemed to be almost no exception to the rule that the exposed electrode begins by being positive and ends by being negative, the negative regime lasting for many days of prolonged exposure to light." Minchin found that the photo-potential sign is dependent upon the nature and thickness of the photo-sensitive material upon the metal electrode, upon the electrode metal and upon the photo-cell electrolyte. Tucker performed various series of experiments with cuprous oxide and silver halide photo-voltaic cells, using a potentiometric method for the measurement of the photo-potentials. Tucker used this potentiometric method because "practically no current passes through the cell when this method is used, the occurrence of a secondary electrode polarization is prevented."

It may be stated here that the authors of this paper used the potentiometric method at the outset of the problem but soon adopted the vacuum tube voltmeter method because the potentiometric method was slow for making readings required for this particular voltage-time curve. Tucker set forth a group of generalizations as a basis for explaining and predicting the behavior of a given voltaic cell. Three of these generalizations are:

1) In a photo-voltaic cell with electrodes consisting of the same metal from which the metallic constituent of the photo-sensitive material is derived, illumination tends to produce a photo-chemical reduction of the photo-sensitive substance.

2) If the photo-sensitive substance is on the illuminated electrode as a uniform layer, local cell formation on the illuminated surface will be at a minimum and the exposed electrode will be an anode.

3) If the photo-sensitive substance is on the illuminated electrode as a non-uniform layer, local cell will be set up in the illuminated electrode. If these local cells tend to polarize, the illuminated electrode will eventually become a cathode after continued illumination. If these local cells do not polarize but are completely reversible, the electrical behavior of the illuminated electrode will be determined by the oxidizing solution or reducing nature of the cell solution. In an oxidizing solution or a neutral solution the illuminated electrode will be a cathode while in a reducing solution, the illuminated electrode will be an anode.

From these generalizations one may at the outset gather that there is a possibility of the initial negative photo-potentials being caused by local cell reaction on the illuminated electrode. This thought can be discarded upon examination of the results given.

Garrison, too, found that the sign of the photo-potential was dependent on the thickness of the silver iodide layer over the electrode and also on the ratio of the concentration of silver ions to that of iodide ions in the electrolyte.

The results given in this paper were, with a few exceptions which were obtained by a potentiometric method, obtained through use of the vacuum tube voltmeter. Work is now in progress on this problem whereby measurements are being made with the oscillograph.

Apparatus Section

Electrodes.

The photo-voltaic cell or in short the photo-cell consisted briefly of two silver-silver bromide electrodes immersed in an electrolyte. The method of preparation of silver-silver bromide electrodes which would render reproducible results is far from perfection. Reproducibility of results caused by minute differences in electrodes is the chief difficulty encountered in photochemical work of this type. Perhaps, one might state, that some previous investigators in the field of photo-cells have been reluctant about disclosing any difficulties they might have encountered in preparing "reproducible electrodes."

At the outset of this investigation it was hoped to develop a method for the preparation of reproducible electrodes of silver-silver bromide. Electrodes giving fairly reproducible results can be prepared. The "quality" of the "reproducibility" will be evident after examination of the results presented herein. The problem of reproducible metal-metal halide electrodes, it may be said, is still in general unsolved and worthy of extensive investigation.

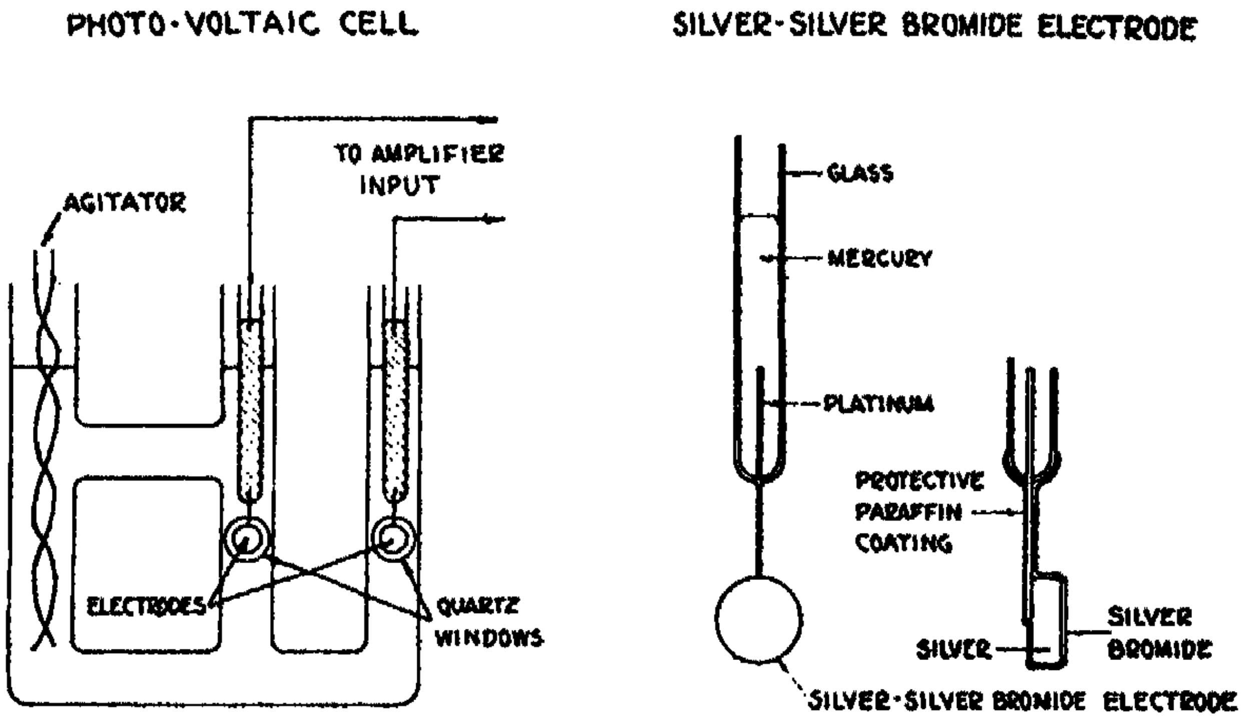

Fig. 1

It would be wearisome to relate all the unsuccessful attempts in obtaining reproducible silver-silver bromide electrodes. Therefore, merely a few diverse methods will be given in brief; but that method yielding the best results will be described completely. The electrodes were all of silver about 1.5 to 2 mm. in thickness and 10 mm. in diameter. Silver obtained from two different sources was used: 1) silver used by the Eastman Kodak Company, and 2) silver obtained from the U. S. Mint, Philadelphia.

The results from the two sources were indistinguishable. In Fig. 1 is represented the electrode employed. The electrodes were fused onto a platinum wire which was sealed into the end of a glass tube making it possible to make contact through a mercury well.

Many attempts were made to obtain electrodes which would give reproducible results. Variations in the method of polishing of these silver electrodes included wet polishing on 400 mesh carborundum paper, annealing or not, polishing dry on blotting paper with levigated aluminum oxide, or dry or wet on silk broad-cloth using "Shamva," magnesium oxide. Paraffin was used for insulating the backs and edges of the electrodes from the electrolyte in the photo-cell.

The silver surface was prepared from bromination by polishing, sputtering silver, or electroplating.

The various methods of forming the silver bromide onto the silver electrode included:

1) Bathing in solutions of bromine in water or in carbon tetrachloride for periods upwards to three hours.

2) Bathing in liquid bromine.

3) Electrochemical formation of silver bromide. Most of these methods give poor results.

The method finally adopted for the preparation of the silver-silver bromide electrode is this: The silver electrodes are ground flat in 400-mesh carborundum paper under water. A fairly good polish can thus be obtained. They are then annealed. Wildermann[1] states: "Gradually heat the silver up to 120° to 140°C. and allow to cool over the course of several hours."

Unfortunately during the annealing process a thin layer of silver oxide is formed. The backs and edges of the electrodes are paraffined by immersing them into melted paraffin kept only just above its melting point. It might be thought this rewarming of the electrodes would destroy the anneal they had just received, but experiments showed this is not the case. The paraffin is wiped off the front of the electrode with cotton. It is then polished on silk broadcloth, using water and Shamva so as to remove the very thin layer of silver oxide formed during the annealing process. Immediately after polishing, the electrode is washed in distilled water and then immersed in water until the second one of its set has been polished. The two electrodes, forming a set, are now washed in a solution identical to that used for brominating, and then transferred to the brominating apparatus. The silver bromide is formed electrochemically at once so as to avoid reoccurrence of the oxide film.

A set of two electrodes is brominated at one time so as to have the two electrodes more nearly duplicates of each other, and thereby increase the possibility of having a zero difference of potential between them when they are used in the photo-cell. The electrolyte used in the formation of the silver bromide was of two concentrations: *A* electrolyte consisted of 5% KBr and 1.2% HBr in water; *B* electrolyte consisted of 0.5% KBr and 0.12% HBr in water. The set of electrodes served as the anode and the platinum sheet as cathode in the electrochemical formation of AgBr on the silver electrode.

The silver bromide contents of a series of silver-silver bromide electrodes were determined. The following is the scheme for analysis of the electrodes: The silver-silver bromide electrode was placed in ammonium hydroxide solution and allowed to stand until the silver bromide was dissolved off completely (say 5 minutes). This solution was diluted to a definite volume

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[1] Z. physik. Chem., 59, 574 (1907).

and the silver converted into silver sulfide. The color of this solution was compared with that of standard silver sulfide solution in the micro-colorimeter.[1]

TABLE I

Concentration of solution used in electrochemical formation of AgBr	Period of AgBr formation (seconds)	Wt. of AgBr on electrode (mgr).	Thickness of AgBr layer on electrode mm.
5% KBr – 1.2% HBr	1	0.43	0.00085
	5	.63	.00124
	10	1.08	.00213
	15	1.55	.00305
	30	2.61	.00515
	60	3.96	.0078
	120	7.2	.0142
	240	11.6	.0229
0.5% KBr – 0.12% HBr	1	.076	.00015
	5	.20	.00039
	10	.27	.00053

The set of two electrodes having been coated with silver bromide is washed at once in a portion of the solution of the photo-cell electrolyte in which it is to be used. The electrodes are then allowed to hang immersed in a bottle containing some of the photo-cell electrolyte. At first the electrodes of each set were short-circuited and allowed to stand over varying periods of time. In some cases even after a short-circuiting period of a week, the difference of potential between the two electrodes was so great that they could not be used in a determination. It was found in this work that short-circuiting the electrodes of a set did not assist in obtaining better results. It is to be noted that in this work it was always a matter of measuring the difference of potential between two electrodes (as near identical as could be obtained experimentally), one of which was exposed and the other kept in the dark. It was found that if there was a large difference of potential between the electrodes (both dark), the results of the photo experiment were also very poor and were discarded.

Apparatus

The apparatus, in general, consisted of three parts: the optical system, photo-cell, and the system for measuring the potential difference between the illuminated or exposed electrode and the dark electrode.

The optical system, if one may call it such, consisted of a Cooper Hewitt quartz mercury vapor arc enclosed in a ventilated lamp house. A quartz-windowed water cell of 1 cm. thickness between the arc and photo-cell served to eliminate heat effects in the photo-cell. An Ilex shutter is used to control the period of exposure of the electrode in the photo-cell.

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[1] These analyses were performed by Mr. A. Ballard, according to a method described by Sheppard and Ballard: J. Franklin Inst., 205, 659 (1928).

Photochemical relations, in general, have a temperature coefficient of nearly unity and so a thermostat is not so important as far as the photochemical reaction is concerned; but in making potential measurements on a cell it is of importance to have no temperature difference between the two electrodes. For this reason alone a thermostat is necessary if voltages are to be read beyond the third decimal place. An aqueous layer in the thermostat serves as a filter for some infra-red radiations and minimizes that source of error. The thermostat was sufficiently large to contain a metal box containing a standard cell, the photo-cell; a heating and cooling system, and an agitator. The water in the thermostat was maintained at a temperature of 25 ± 0.1°C. The whole thermostat was so constructed as to be light proof.

Photo-cell

Two different photo-cells were used in this work. The first photo-cell consisted of a large *U*-tube in each arm of which a silver-silver bromide electrode was supported so as to be opposite a quartz window. The resistance of photo-cell with electrolyte was approximately 800 ohms. It was thought that agitation of the electrolyte in the photo-cell might be desirable and so a second photo-cell was made, Fig. 1.

The electrodes and their method of preparation have been described previously. The nature of the photo-cell electrolytes will be considered with the particular experiments described.

Total Energy reaching the Silver-Silver Bromide Electrode

The distance from the arc to the face of the electrode was 20 cm. The complete emission spectrum of the Cooper Hewitt quartz mercury vapor arc passing through the optical system as described was employed in illuminating the electrode. It is desired to know approximately the amount of energy reaching an electrode under the conditions specified in spite of the fact that but a small portion is photochemically effective. The same optical system was used except a thermopile was adjusted in place of the electrode. Inasmuch as most of the experiments were conducted using a photo-cell electrolyte of 0.1 N-KBr saturated with AgBr, a layer of this electrolyte of the same thickness as that in front of the electrode in the photo-cell, was introduced in the path of the light in front of the thermopile. A Moll thermopile was used in connection with a Leeds and Northrup high sensitivity galvanometer which system had been calibrated against a radiation standard purchased from the Bureau of Standards. The system for measuring the energy was as identical to the experimental system as could be desired, except for the fact that a neutral wedge of density 4.0 had to be introduced into the path of light so as to reduce the intensity of radiations sufficiently to make them measurable by the thermopile.

The thermopile was calibrated against a Radiation Standard C 52 obtained from the Bureau of Standards. The energy reaching the surface of an electrode was 14.6×10^6 ergs per second.

Apparatus for Photo-Potential Measurement

At the outset of the exposure period it was observed that the potential was negative with respect to that obtained after about the first minute or less. At this time a Leeds and Northrup type K potentiometer was employed in making the voltage measurements. The time required by the operating technique of a potentiometer is far too great to permit of making a satisfactory reading within this period. In order to investigate this initial effect, which was known to occur during the first minute of exposure, a vacuum tube voltmeter was designed and constructed. Some of the results obtained by this vacuum tube voltmeter will be presented herein. With this instrument it was possible to obtain an e.m.f. time curve accurately after the first five seconds of exposure. The negative effect still occurred during this first portion of the curve. In view of the high period of vibration of the microammeter, it was impossible to obtain the absolute values of the initial negative effect during the first second of exposure, however, somewhat relative values were obtained by noting the sudden surge of the microammeter needle. At present accurate data are being obtained on this initial effect through use of an oscillograph.

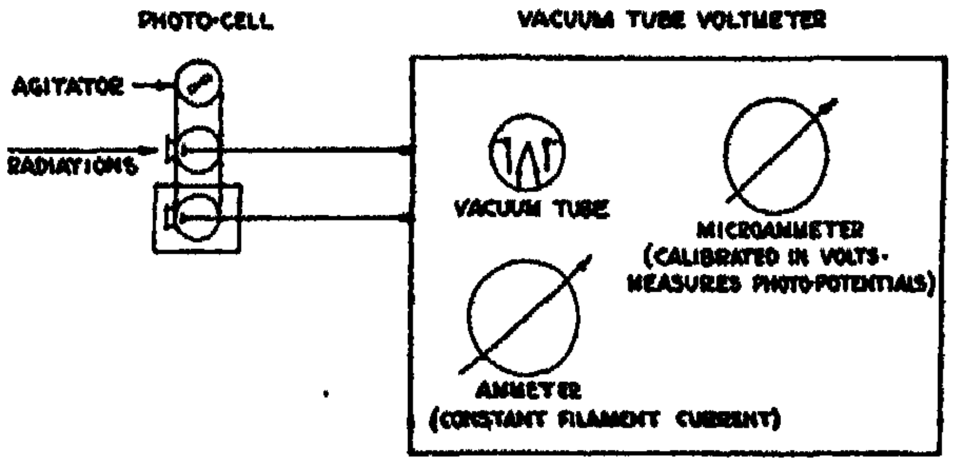

PHOTO-CELL-VACUUM TUBE VOLTMETER SYSTEM

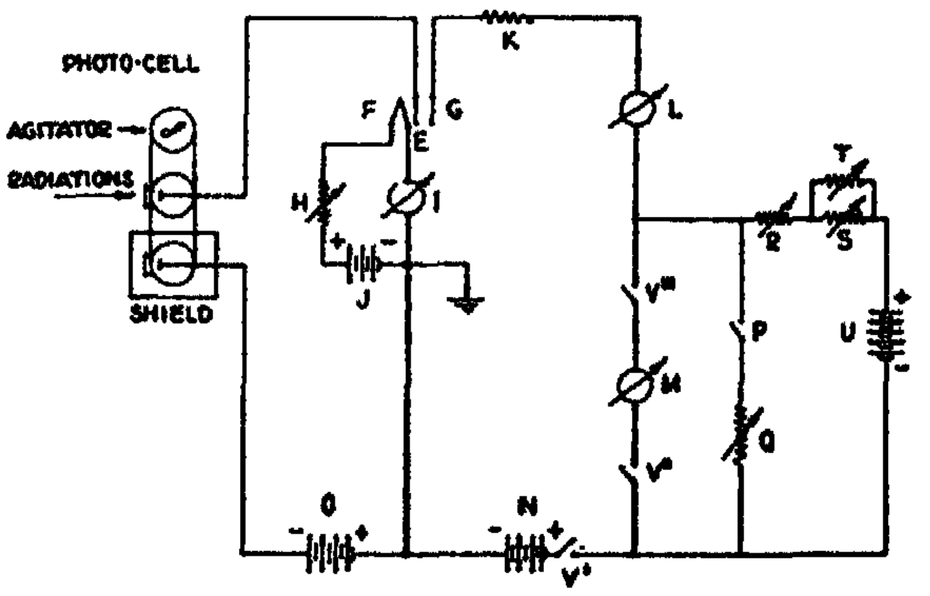

PHOTO-CELL - VACUUM TUBE VOLTMETER CIRCUIT

FIG. 2

The vacuum tube voltmeter which was used in making most of these photo-potentials will be described. The potentiometric method needs no further remarks because the operation of the L & N type K potentiometer is described fully by its manufacturers.

Vacuum Tube Voltmeter

This instrument was constructed and installed by Mr. V. C. Hall of the Physics Department of these laboratories, to whom we express our grateful thanks.

Fig. 2 shows the important features of the photo-cell-vacuum tube voltmeter system and also the circuit. The electrode of the photo-cell receiving the radiations is the positive one and is connected to the grid *E* of the 205 D Western Electric vacuum tube by as short a connection as possible. The current through the filament *F* is maintained at 1.5 amperes. The rheostat *H* and the vacuum tube are incased in a grounded metal shield. *K* is a 3000 ohm resistance which aids in stabilizing the system. *L* is a Weston milliammeter, scale 0.50. *M*—Weston d. c. microammeter, Model 322, 300 microampere range. (This is replaceable by a similar meter of 25 microampere range. *N*—B battery, 240 volts. *O*—C battery, 12 volts. *U*—24 volts, storage batteries.

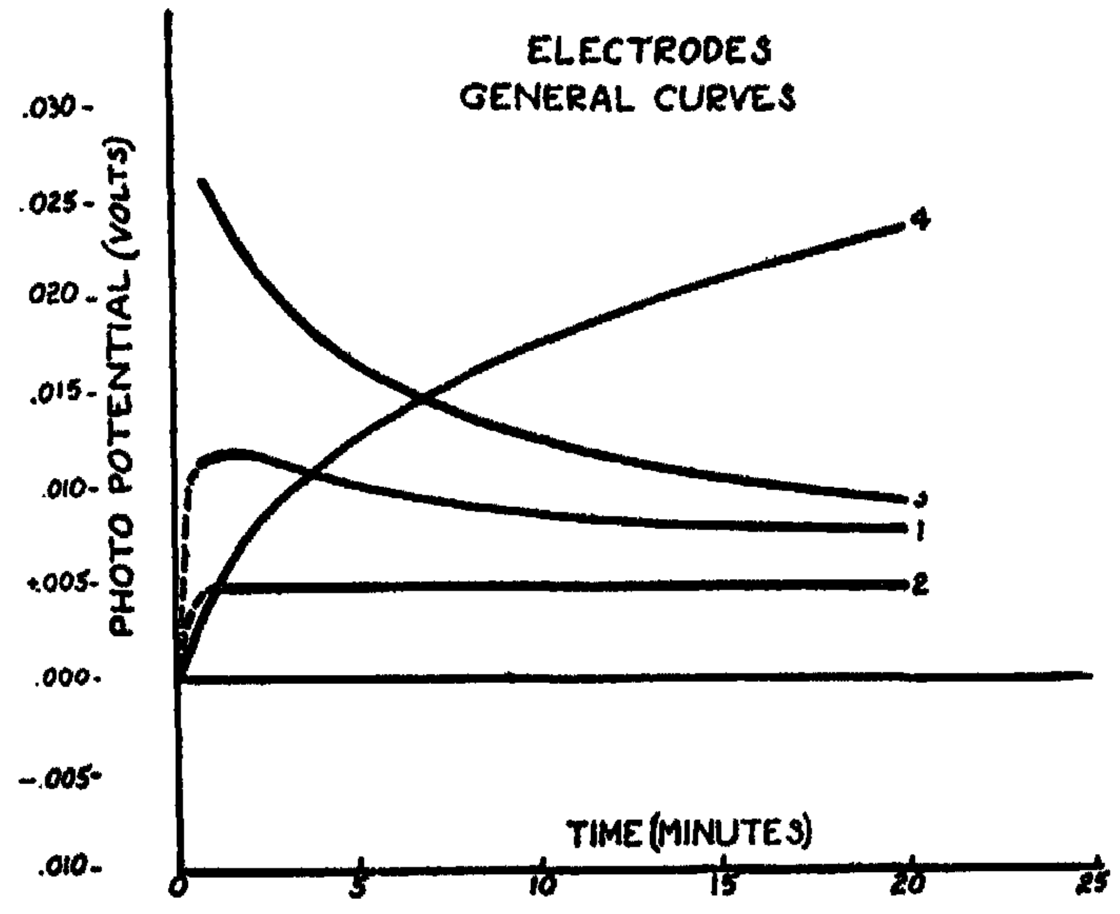

Fig. 3

To use the voltmeter the filament of the tube is lighted and *N* adjusted so as to have about 10 milliamperes plate current indicated by *L*. The shunt *PQ* is closed during these adjustments so that no current flows through the microammeter *M*. *Q* is increased slightly and *R* adjusted until *M* reads zero.

While Q is now being gradually increased, M is always adjusted to zero, until finally the switch P is opened when the full sensitivity is obtained. T and S are now adjusted so that the microammeter reads zero and is ready for use. Whenever an adjustment is being made on the voltmeter, the microammeter must be shorted.

The vacuum tube voltmeter was calibrated with a potentiometer. Its readings were microamperes while the values read by the potentiometer were volts. The relationship between the amperage and voltage was almost linear for a range of 0 to 16 volts. The voltmeter calibration curve did not change over a six month period of service. The grid current of this voltmeter is remarkably small. It is so small that if it does produce polarization in the photo-cell it is insufficient to interfere with the results. If there were polarization taking place, the microammeter needle would have a large drift but the drift is too small to influence the photo-potentials measured.

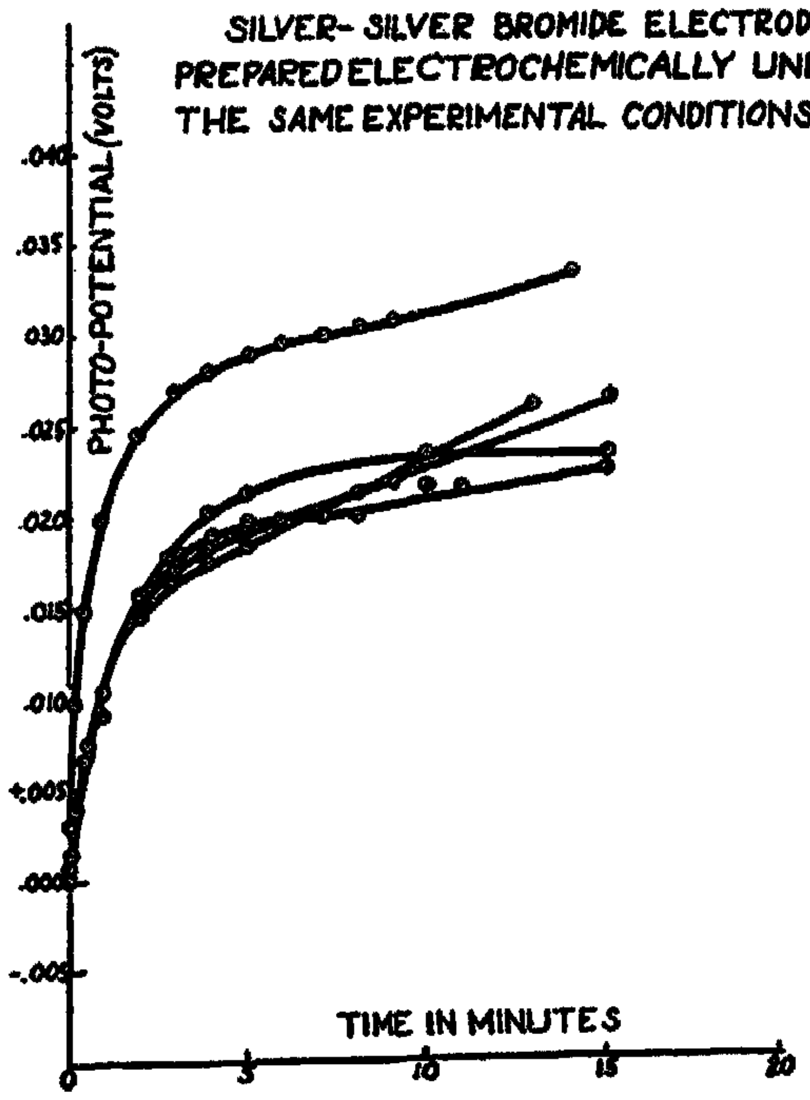

Fig. 4

Experimental Results

Results obtained by electrodes prepared by different methods.

In general there are four differently shaped curves. It may be said the shape is dependent upon the thickness of the layer of silver bromide and upon the crystal size of silver bromide. These curves were obtained with the potentiometer. The four general shaped curves are:

1) Gradual increase in voltage up to a maximum at about the second minute exposure, Fig. 3, Curve 1.

2) A horizontal line after the first minute, Curve 2.

3) A maximum reached during the first minute exposure and a continual decrease in voltage following, Curve 3.

4) A continual increase in voltage dependent, however, upon thickness of AgBr, Curve 4.

The methods of AgBr formation on the silver electrode were widely different yet the curves obtained could be classified according to the curves in Fig. 3.

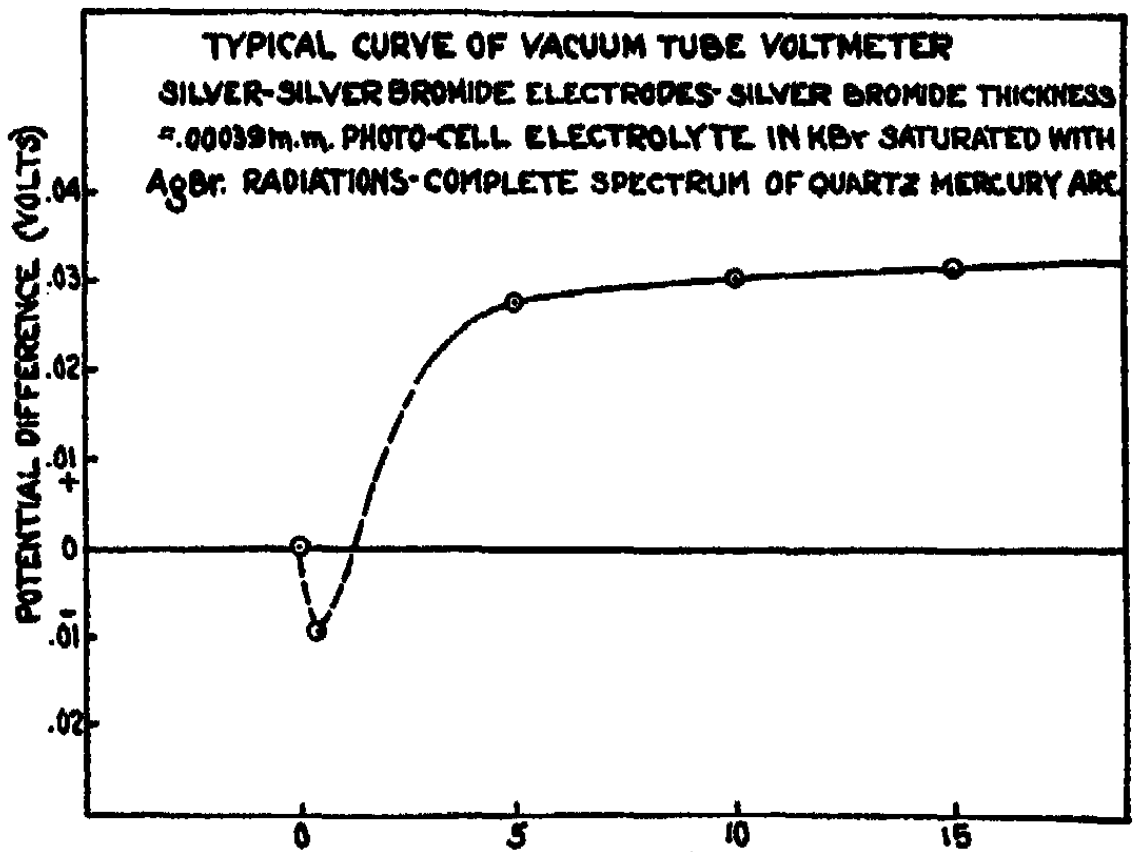

FIG. 5

TABLE II

Method of Silver Bromide Formation

Curve	Time	Solution
1	15 minutes	2½% bromine in CCl_4
	3 hours	saturated bromine water
	1 hour	⅓ saturated bromine water
2	—	not brominated
	10 minutes	bromine
	2 minutes	⅓ saturated bromine water
3	1 hour	saturated bromine water
	15 minutes	saturated bromine water
	10 minutes	⅓ saturated bromine water
4	—	electrochemically

It is unsafe to make any general statement regarding the shape of the curve as related to the period of bromination because the various methods of bromination are not comparable and further, the purity of the silver-silver bromide electrodes is an uncertainty dependent upon the method. The exact thicknesses of the silver bromide layers were not determined in these experiments because we were searching for a method which would offer possibilities of reproducibility. Electrodes prepared electrochemically gave the best results. The curves are presented to show the discrepant results obtainable from electrodes of Ag-AgBr prepared by different methods and hence the difficulty of comparing different observer's results.

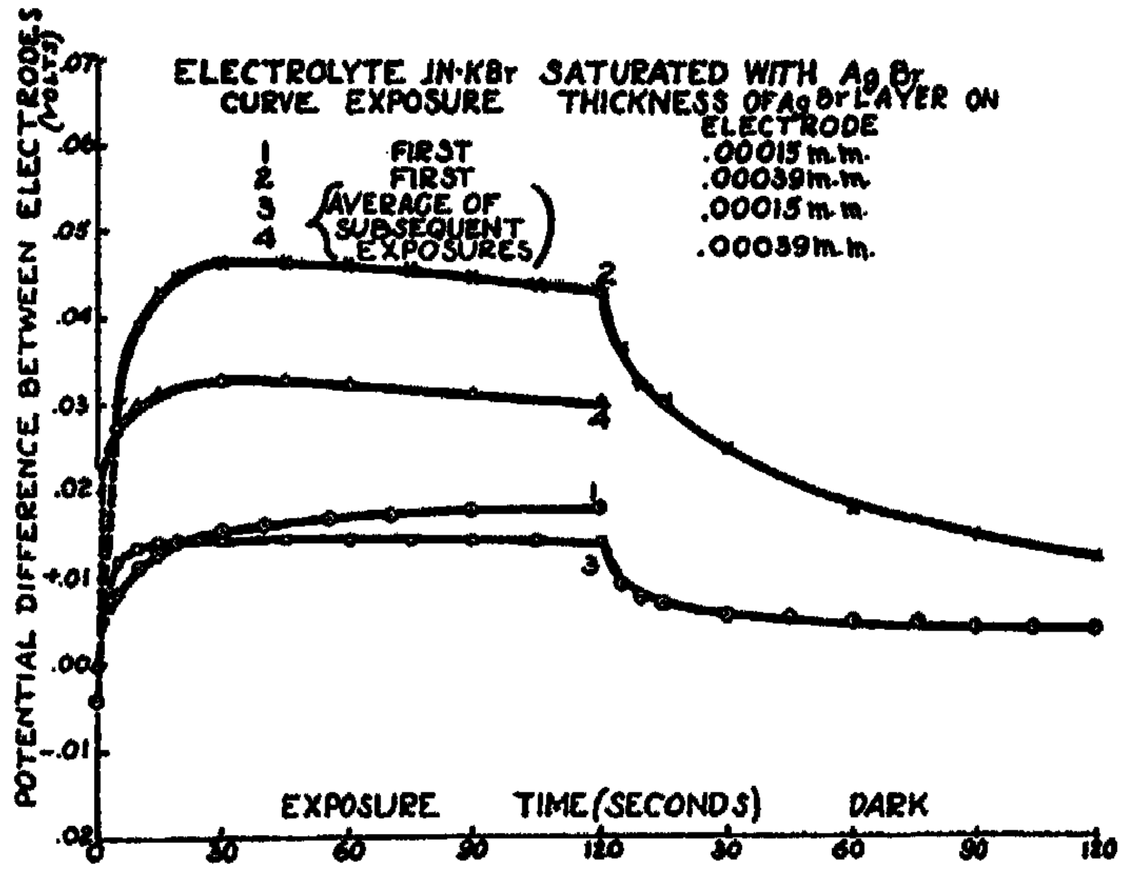

Fig. 6

Fig. 4 represents five determinations in which the electrodes were brominated alike electrochemically. In four out of the five curves, the parts for the first minute exposures are in agreement. The curves in Fig. 4 illustrate well what changes in potential can be effected by very slight—yet outwardly imperceptible—differences in the electrodes.

Effect of the Thickness of the Silver Bromide Layer on the Electrode upon the Photo-Potential.

For these determinations two types of electrolytes in the photo-cell were used. A 0.1 N KBr solution, and a 0.1 N KBr saturated with AgBr, were used as cell electrolytes. Only a few experiments were conducted with the 0.1 N KBr because the solution of the silver bromide of the electrodes is sufficient to affect the photo-potentials of the cell. For this reason it is best to work with photo-cell electrolytes which are saturated with respect to the photo-sensitive material of the electrode. As the thickness of the silver bromide layer increases, the photo-potential curve assumes a more steady e. m. f. after about the first 30 seconds' exposure. This effect caused by the solution of the silver bromide is brought out very distinctly by a very thin layer of AgBr. when the photo-cell electrolyte is saturated with respect to AgBr, the photo-potential reaches a steady e. m. f. after approximately the first 30 seconds and maintains this e. m. f. for a period of at least 90 seconds.

In case of some of the electrodes, a negative effect was observed at the very beginning of the exposure. Fig. 5 is a typical curve. In the case of the negative effect, the values given are merely relative because they represent *surges* of the microammeter needle. This initial negative effect is practically inertialess. An Ilex shutter set to 1/100th second exposure period was opened for that period and the ammeter needle surged. Some negative effect was still observed after five successive 1/100th second exposures. Actual e. m. f.-time records are now being obtained of this period of exposure by means of an oscillograph.

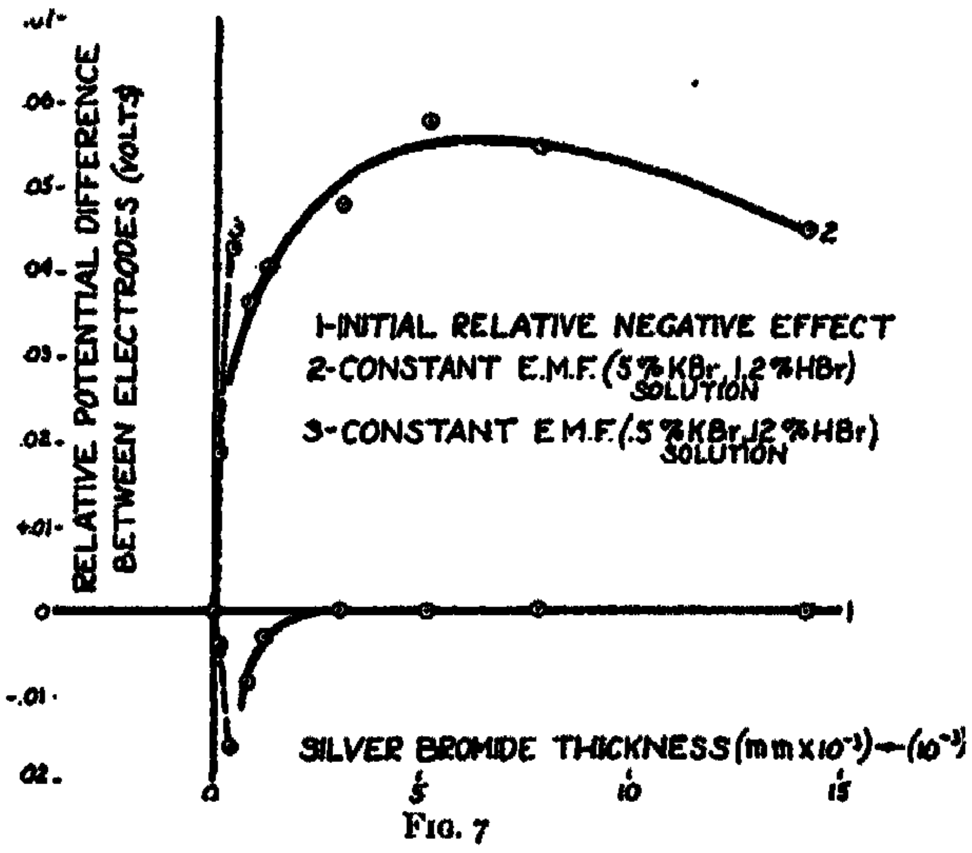

FIG. 7

In general, it can be stated that the curves obtained for the initial exposure of a set of electrodes differs somewhat from the curves obtained for subsequent exposures. Compare Curves 1 and 2 with 3 and 4 respectively in Fig. 6.

Fig. 7, Curve 1, represents the initial relative negative effect as the thickness of the AgBr on the silver electrode varies in this particular concentration of photo-cell electrolyte. At a thickness of 0.0025 mm., the curve reaches the zero axis. In all probability the negative effect curve approaches the axis more gradually but this vaccum tube voltmeter does not indicate such perhaps because of its insensitivity.

Fig. 7, Curve 2 is a curve representing the potential differences when they have become constant or nearly so when the photo-cell is illuminated. Curve 3 represents the same feature. In the case of Curve 2, the electrodes were prepared in the (5% KBr, 1.2% HBr solution) while in the case of Curve 3, they were prepared in the 0.5% KBr, 0.12% HBr solution. The rate of AgBr formation apparently affects the crystal size of the silver bromide which is evidently somewhat responsible for the difference between the two curves.

Fig. 8 deals with the rate at which the potential difference between the electrodes returns to the initial value which existed before exposure. Immediately after the exposure of the cell was ended, thereby causing both electrodes to be dark, the e.m.f.-time curve was obtained. The drop at first was rather rapid and sufficient precautions were not taken to make the most accurate measurements in consideration of this rapid initial drop. However, it appeared as though some relation existed between thickness of silver bromide layer and rate of return to zero difference of potential. As a result the times required for the e.m.f.'s to drop 10% of the steady e.m.f.'s shown in Fig. 7, Curve 2, were plotted against thickness. The curve is an approximation, but it indicates a nearly linear relation.

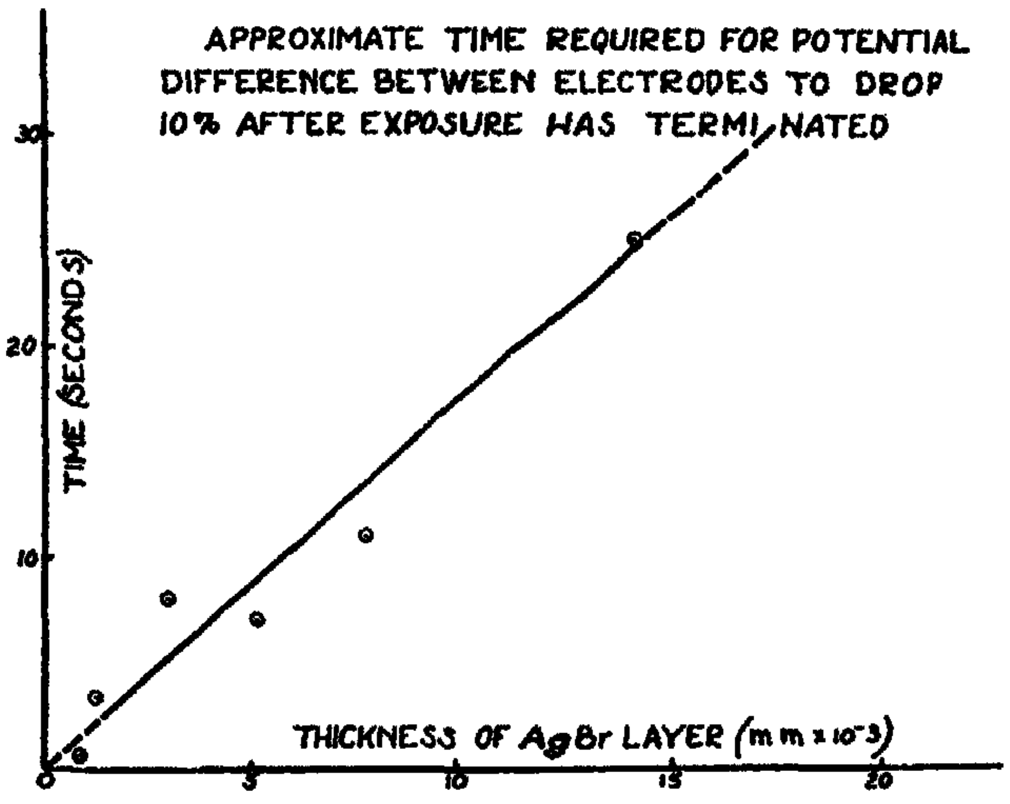

FIG. 8

The Relation of Electromotive Force of the Photo-cell to Concentration of Electrolyte.

A series of experiments were made wherein the variable factor was the photo-cell electrolyte. The electrodes were all the same, having an AgBr layer of 0.00039 mm. thickness. All the photo-cell electrolytes used were saturated with respect to AgBr. Fig. 9 represents the results of nine different concentrations of the electrolyte. The negative effects are, as has been previously stated, merely relative. That the variations in these curves are not caused to any great amount by varying amounts of light absorbed is proved by the experiments conducted. The electrolytes 1 N-KBr and saturated KBr contained a relatively large amount of silver bromide when saturated with respect to AgBr as compared to the AgBr content of the lower KBr concentration electrolytes. Their curves are decidedly different also. The absorption of light by the AgBr in these concentrated KBr solutions is not responsible for the greater part of the difference in the curves.

A photo-cell containing electrolyte of 0.0001 N-KBr saturated with AgBr, and AgBr electrodes of 0.00039 mm. thickness were used. The potential differences between the exposed and dark electrodes were obtained by the vacuum tube voltmeter under the following conditions:

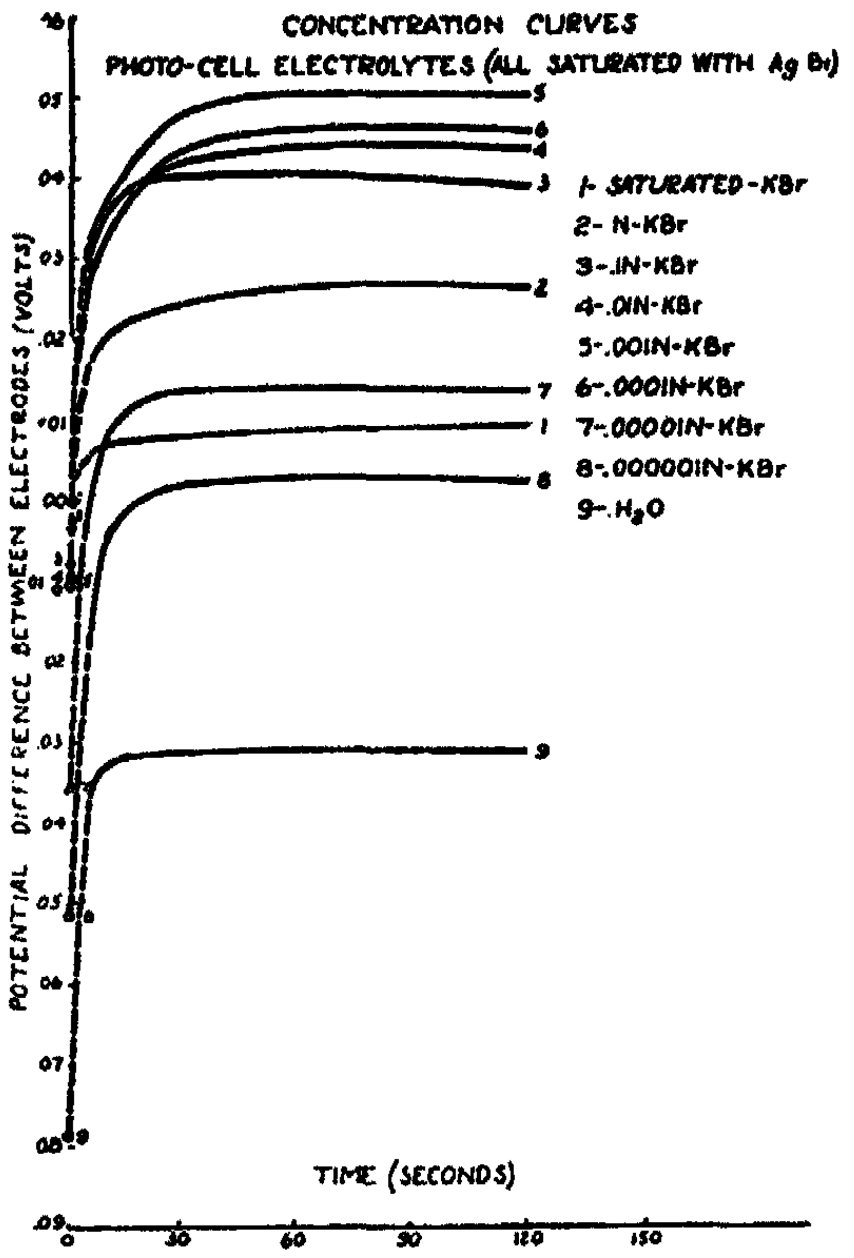

Fig. 9

a) Without a filter cell in front of the window of the exposed electrode.
b) With a quartz cell (1 cm. thickness) in front of the exposed electrode. The filter cell contained:

6 N KBr saturated with AgBr
5 N KBr
4 Saturated KBr, saturated with AgBr
3 Saturated KBr
7 Nothing

Compare these curves with Curves 1 and 2 and it becomes obvious that this large difference is not due to difference in light absorbed. It appears that as the concentration of KBr and AgBr increases, a direct effect upon the electromotive process is produced.

The four parts of Fig. 11 represent the *relative* initial (negative) Curves 2 and 4, and steady (positive) Curves 1 and 3, potentials for various concentrations of KBr in the photo-cell electrolyte.

The Electromotive Processes

Examination of the general shape of the p.d.-time curves shows them to consist of two initially important portions. These are a quasi-instantaneous negative portion, or negativization of the electrode, followed by or passing into a positive portion (positivization).

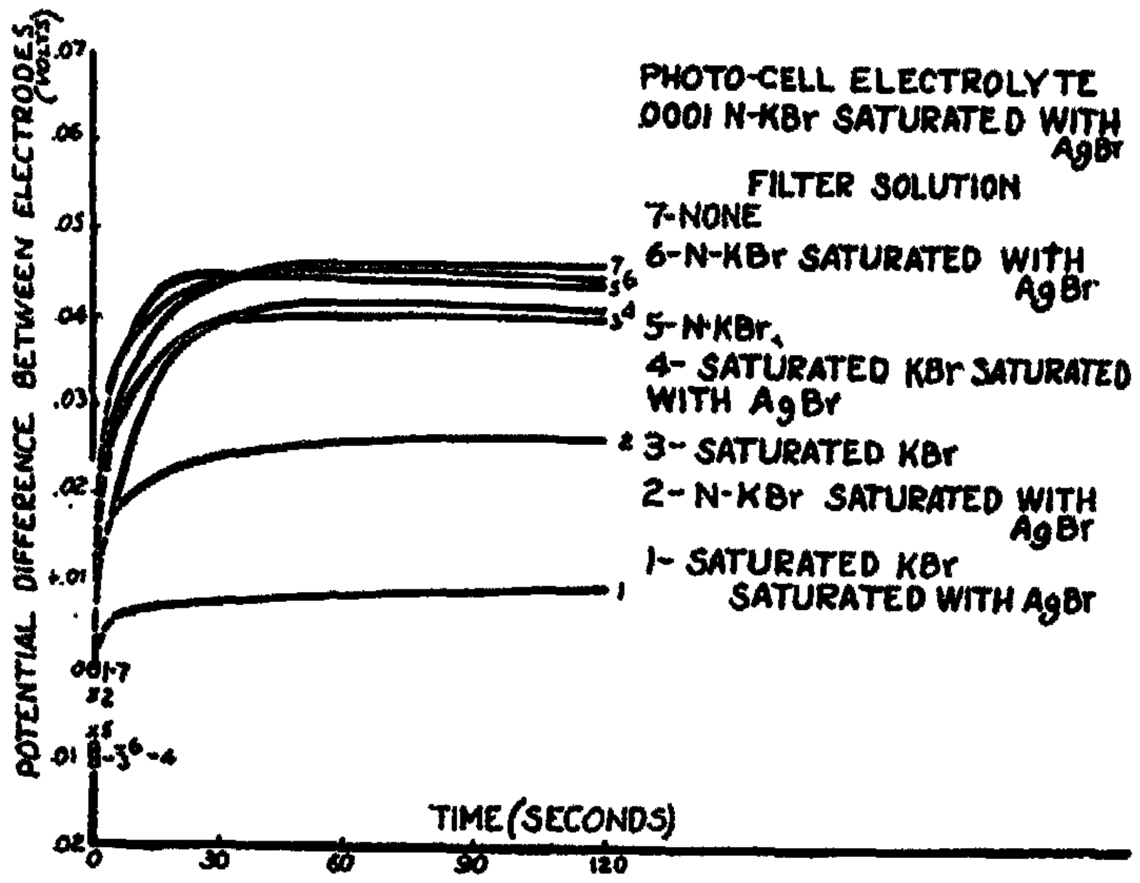

Fig. 10

It is reasonable to assume that the negative process is not eliminated when the positivizing process comes into being but that the p.d.'s then are the resultant differences of two effects.

It was observed that the thinner the layer of AgBr on the silver electrode, the more marked was the initial negative effect.

To explain this characteristic of the p.d.-time curves, the following hypothesis was assumed. It has been proposed by Sheppard and Trivelli[1] and independently by Fajans[2] that the primary photochemical effect of light upon silver halide, which form ionic or heteropolar lattices, is to discharge an electron from a bromide ion, which is then accepted by a silver ion, forming silver atoms and bromine atoms. The former are aggregated to metallic silver, the latter to bromine molecules. This may be represented as follows:—

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[1] Phot. J., 61, 403 (1921).

[2] Chem. Ztg., 666 (1921); Z. Elektrochemie, 28, 499 (1922).

$$\overset{-}{\mathrm{Br}} + h\nu = \mathrm{Br} + \Theta$$

$$\overset{+}{\mathrm{Ag}} + \Theta = \mathrm{Ag}.$$

Supposing this primary action of light upon the $\overset{-}{\mathrm{Br}}$ ion to occur in the silver bromide of the photo-cell, then at first both electrons and bromine (as atoms or molecules) may be supposed to move in the direction of the light ray toward the silver electrode (*cf.* Fig. 12).

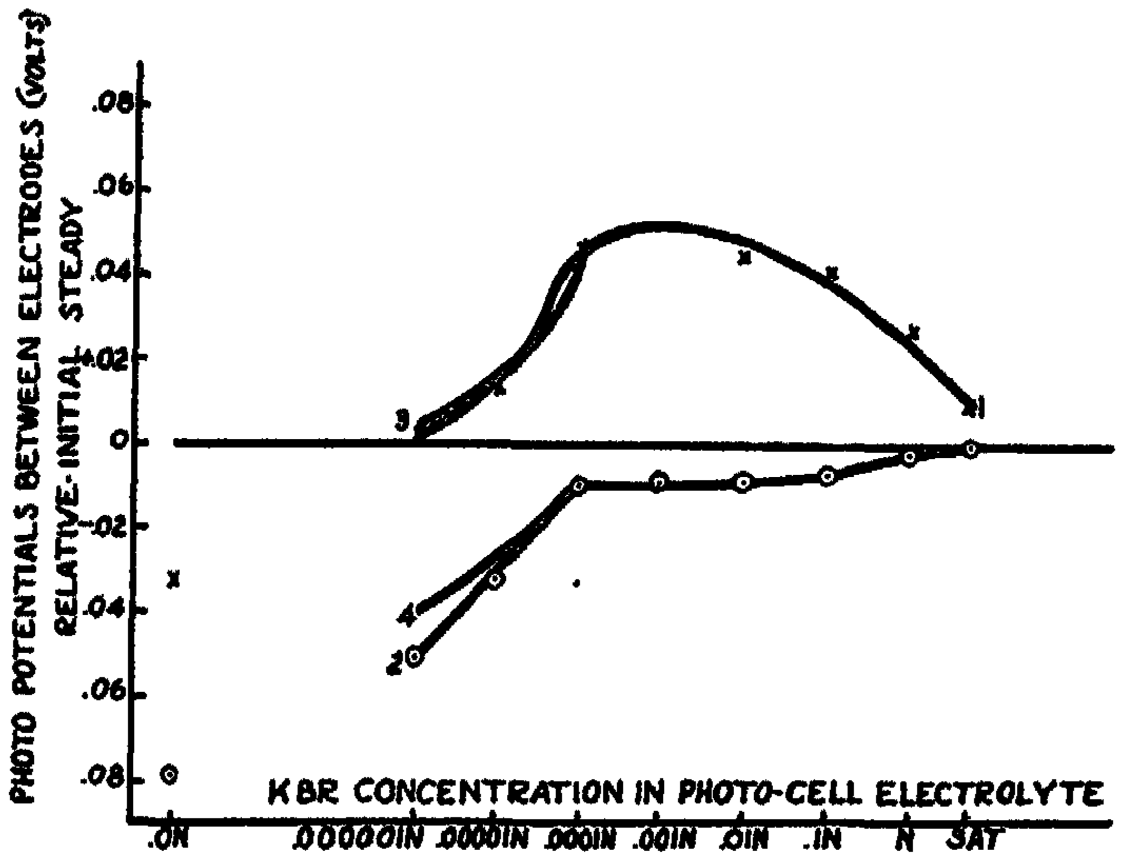

FIG. 11

The electrons penetrating into the silver electrode increase the electron pressure and thereby produce the initial negative surge. Meanwhile the slower moving bromine on reaching the electrode attack this, according to the equation

$$1/2(\mathrm{Br_2}) + \mathrm{Ag} = \overset{+}{\mathrm{Ag}}\overset{-}{\mathrm{Br}}$$

giving the positive potential.

Before proceeding to the more quantitative aspects of this hypothesis, we shall describe certain semi-quantitative and qualitative tests to confirm it. These will deal first with the positive p.d. ascribed to bromine.

It is evident that the relation of the fall of the positive p.d. with time on darkening, to the thickness of the AgBr layer is in agreement with a diffusion resistance directly proportional to the thickness of layer.

Effect of Halogen Acceptors

If the hypothesis is correct, introduction of other halogen acceptors than the silver of the electrode should eliminate or reduce the positive p.d. and leave the negative p.d. more in evidence. The experiments confirmed this prediction, as is shown in Fig. 13.

The thickness of the AgBr layer was 0.00039 mm. in each case, the electrolyte 0.1 N KBr saturated with AgBr. The concentration of the bromine acceptor was 0.1 M.

It is evident that the effect of the halogen acceptor depends upon its velocity of reaction with the bromine. Further experiments are planned on this, trying other acceptors, including gelatin. The problem of securing their presence in the silver halide layer is a difficult one.

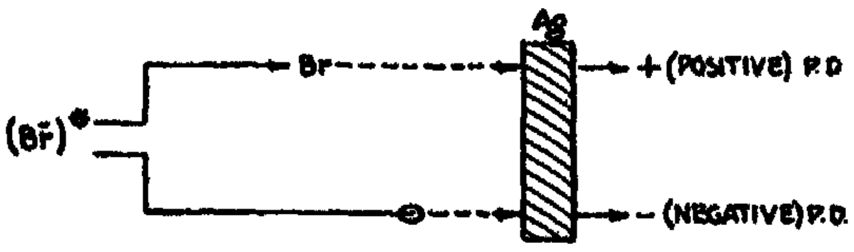

FIG. 12

Direct Bromine Potentials

Assuming bromine to be the active agent of the positive p.d. process, similar results should be obtained with bromine itself. A similar photo-cell was used, but entirely darkened, and one electrode exposed to bromine allowed to diffuse from a solution through the AgBr layer. The cell contained the two silver: silver bromide electrodes (*cf.* Fig. 1) and a solution of 0.1 N KBr saturated with AgBr. The negative electrode was surrounded with an alundum crucible to protect it from the bromine solution about the positive electrode, but giving a capillary electrolyte connection.

The experiment was conducted as follows: The two electrodes of the cell were connected to the vacuum tube voltmeter, the positive electrode to the grid. The solution of X c.c. of 0.1 N-KBr saturated with AgBr about the positive electrode was agitated vigorously throughout the experiment, thereby later mixing the solutions rapidly and maintaining a constant concentration of bromine. When the system was in equilibrium, (*i.e.*, microammeter's needle was steady), X c.c. of 0.1 N-KBr saturated with AgBr and containing a double concentration of bromine were added quickly to the solution about the positive electrode, and the microammeter readings taken. The double concentration of bromine became a single concentration about the positive electrode. These experiments are preliminary in nature yet they answer the question.

Experiments were conducted using three concentrations of bromine with three different thicknesses of silver bromide electrodes. The electrodes having a thickness of 0.0078 and 0.00124 mm. were prepared using a solution of 5% KBr and 1.2% HBr, whereas the electrodes whose thickness was 0.00039 mm. were prepared using a solution of 0.5% KBr and 0.12% HBr.

It was observed that the results obtained from electrodes prepared with the dilute solution differ from the others. Crystal size of AgBr is perhaps again an influencing feature. Some of these results are shown in Fig. 14.

In view of the fact that the microammeter reads zero, it is known that the members of the photo-cell were in equilibrium. The curves of the positive photo-potential and those obtained by bromine diffusing through the silver

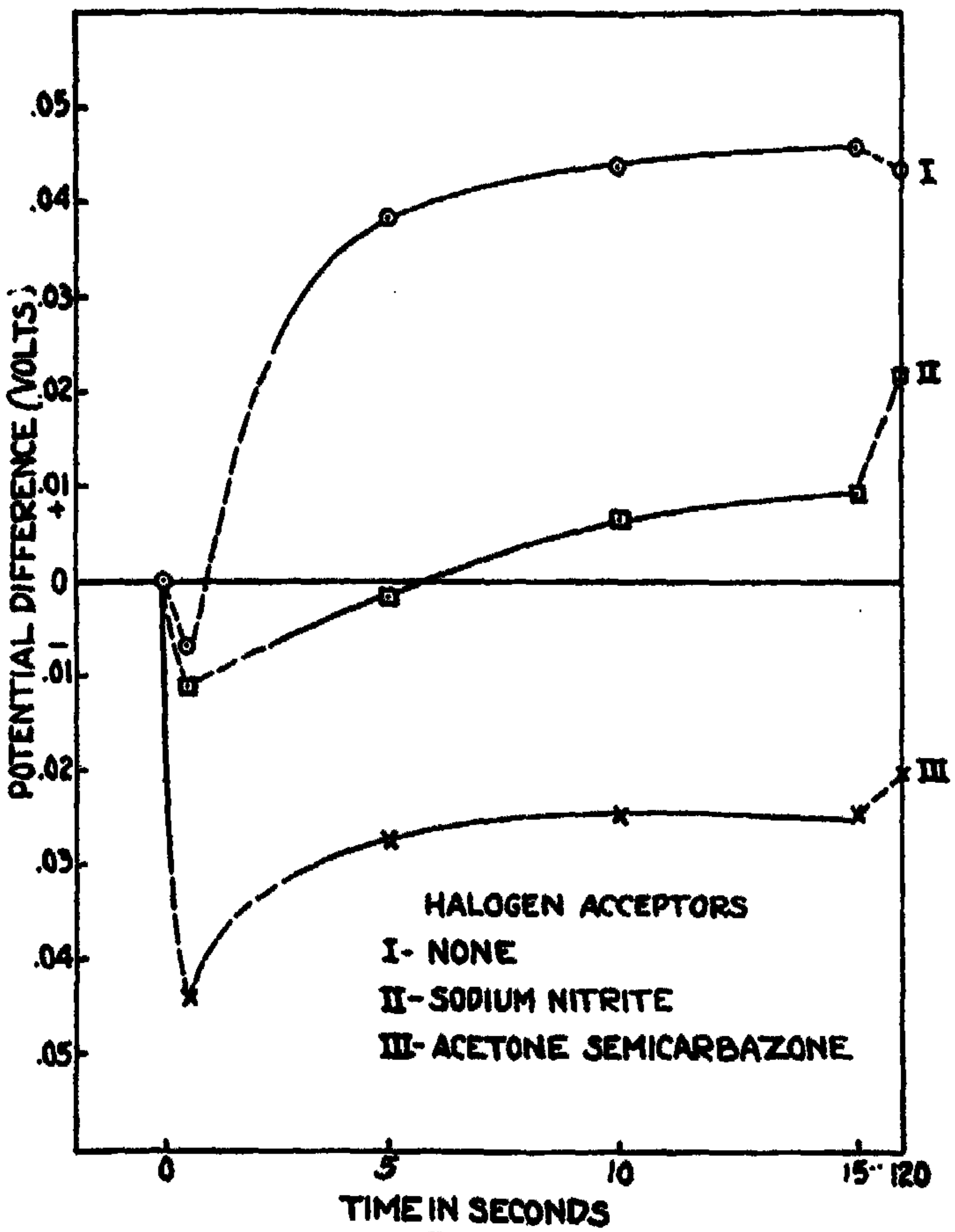

Fig. 13

Table III

C_{Br}	Steady e.m.f.	$(C_{Br})^{1/2}$
1.0%	0.074	1.
.5	0.066	.706
.1	0.058	.316
.05	0.0433	.223
.01	0.0285	.1
.005	0.0253	.0706
.001	0.0153	.0316

bromide layer of the silver bromide electrode are evidently very similar in magnitude and in shape. The steady e.m.f. values for the different bromine concentrations have been read on Fig. 14 and tabulated.

Assuming the reaction to be

$$1/2\,Br_2 + Ag \rightleftharpoons \overset{+\;-}{AgBr}$$

we have for equilibrium

$$k = \frac{[Br_2]^{1/2}\,[Ag]}{[Ag^+\,Br^-]} \quad \text{or} \quad \frac{[Br_2]^{1/2}\,[Ag]}{[Ag^+][Br^-]}.$$

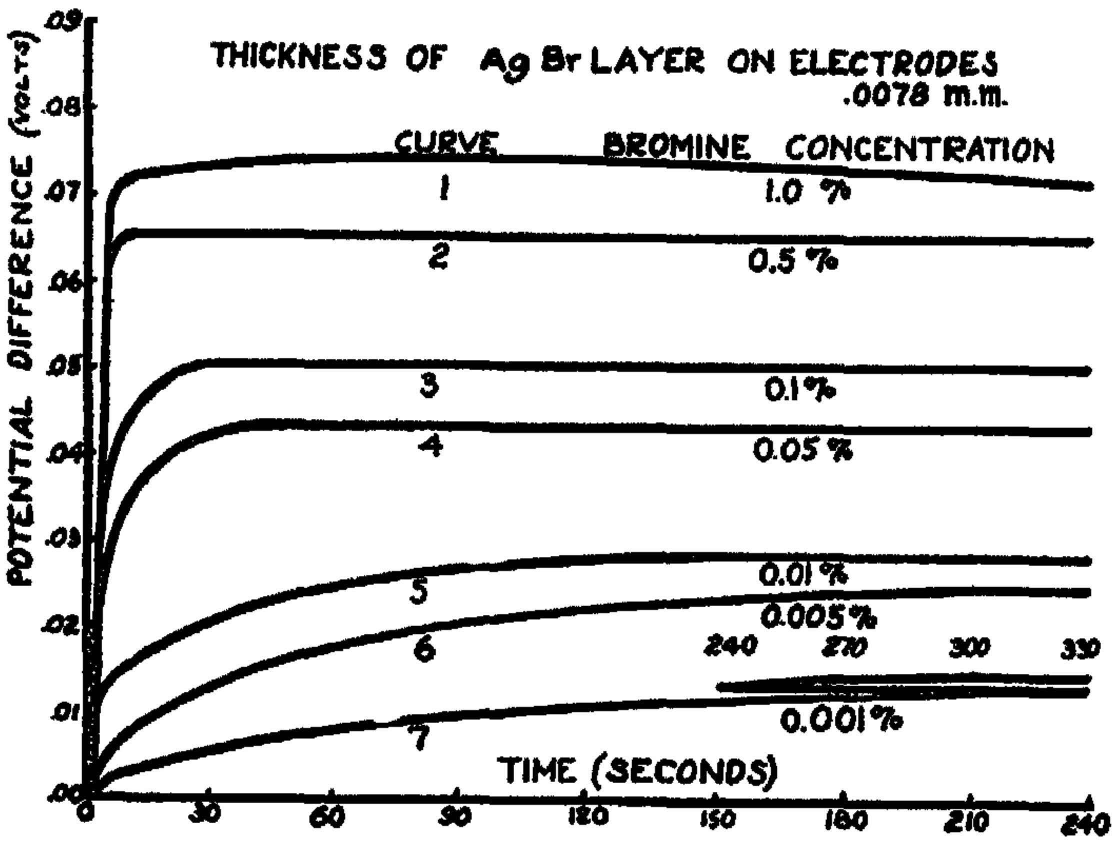

Fig. 14

From Kolthoff's work[1] it appears that electromotively the expression $[Ag^+][Br^-]$ is constant. Assuming [Ag] in presence of solid phase also constant, this gives

$$k = K\,(Br_2)^{1/2}.$$

From Nernst's equation, the e.m.f. should be

$$E = E_0 - \frac{RT}{nF}\log k$$

$$= E_0 - RT\log K \cdot [Br_2]^{1/2}.$$

On plotting the steady e.m.f. against log $[Br_2]^{1/2}$, the curve in Fig. 15 was obtained.

This is a straight line until the lowest concentrations of bromine are reached. In the calculation, neither the hydrolysis

$$Br_2 + H_2O \rightleftharpoons HBr + HBrO$$

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[1] Kolthoff and Furman: "Potentiometric Titrations," 166 (1926).

not the complex formation

$$\mathrm{Br_2} + \overset{-}{\mathrm{Br}} \rightleftharpoons \overset{-}{\mathrm{Br_3}}$$

have been allowed for, which may introduce deviations increasing as the concentration of $\mathrm{Br_2}$ becomes smaller. It seems possible that later experiments may yield information on these points and on the adsorption of $\mathrm{Br_2}$ and Br to AgBr. In any event, the experiments confirm the production of the positive p.d. by the action of bromine.

Discussion

The last experiments described confirm the hypothesis that the positive p.d. is due to bromine. With regard to the negativization, it must be borne in mind that the photo-cell seldom exhibits a zero p.d. in darkness. The illuminated electrode is usually slightly positive with regard to the other. On exposure it *instantly* becomes less positive, *i.e.*, the p.d. is diminished and negativized during the first fraction of a second in light. In view of the zero reading of the microammeter, it appears that the members of the photo-cell prior to illumination were in equilibrium, *i.e.*, the osmotic pressure of silver ions and the solution pressure of the electrode. The initial negative effect due to light corresponds with a decreased solution pressure of $\mathrm{Ag^+}$ ions or an increased electron pressure in the metal.

The reactions proceeding in the silver halide in light may be represented according to our present ideas by the following schemes:

I	II
1) $\overset{-}{\mathrm{Br}} + h\nu \longrightarrow \overset{-*}{\mathrm{Br}}$	1) $\overset{-}{\mathrm{Br}} + h\nu \longrightarrow \overset{-*}{\mathrm{Br}}$
2) $\overset{-*}{\mathrm{Br}} \longrightarrow \begin{cases} \mathrm{Br} + \Theta^* \\ \mathrm{Br}^* + \Theta \end{cases}$	2) $\overset{-*}{\mathrm{Br}} + \mathrm{Ag^+} \longrightarrow \mathrm{Ag} + \mathrm{Br}$ or Br^*
3) $\mathrm{Ag^+} + \Theta \longrightarrow \mathrm{Ag}$	3) $\mathrm{Ag} + \mathrm{Br} \longrightarrow \mathrm{Ag^+Br^-}$
4) $\mathrm{Br} + \mathrm{Br} \longrightarrow \mathrm{Br_2}$	
5) $\mathrm{Ag} + \mathrm{Br} \longrightarrow \mathrm{Ag^+Br^-}$	

A similarity in the two reaction schemes is that in both cases the first action of light is to produce an excited bromide ion. In Scheme I the excited bromide ion is supposed to lose an electron, either yielding a normal bromine atom and a high-speed electron, or an excited bromine atom and a low speed electron. In Scheme II, the excited bromine ion is supposed to react directly with a silver ion, giving a silver atom and a bromine atom (either normal or excited). There is evidence for the production of relatively free internal photo-electrons in insolated silver halides from the photo-conductance experiments of Arrhenius,[1] but particularly from those of Scholl,[2] and more recently of Gudden and Pohl.[3] We may therefore assume provisionally that Scheme I is the more probable.

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[1] Ann. Physik, (3) 32, 566 (1887); Wien. Ber., 98, 12, 831 (1887).

[2] Ann. Physik, (3) 16, 193, 417 (1905).

[3] Z. Physik, 6, 248 (1921).

The reactions expressed by I (1) and I (2) are taking place throughout the thickness of the silver bromide layer, but with a probability depending upon energy density, *i.e.*, upon the *intensity* of the light at a given thickness. The reactions I (4) and I (5) represent the recombinations; of these the recombination of bromine with silver can occur both with the silver reduced by reaction I (3) or with the silver of the electrode. The hypothesis which we are proceeding to test for the production of the photo-potentials is the following. We may assume that both the photo-electrons from I (1) and I (2) and the bromine atoms will move in the direction of the light ray, *i.e.*, will diffuse towards the silver electrode, in so far as they are not removed by recombination. Supposing the photo-electrons to have considerably greater velocity than the bromine atoms, some of them reach the silver electrode before the bromine and increase the electron pressure, or negative potential, thus giving the negative movement in the first second of exposure (*Cf.* Fig. 12.) This could hardly continue, because the removal of the electrons from the silver bromide will be building up a corresponding excess positive charge, soon restraining transfer of electrons. On the other hand, the bromine diffusing to the silver surface will be attacking this and producing, in virtue of the reaction:

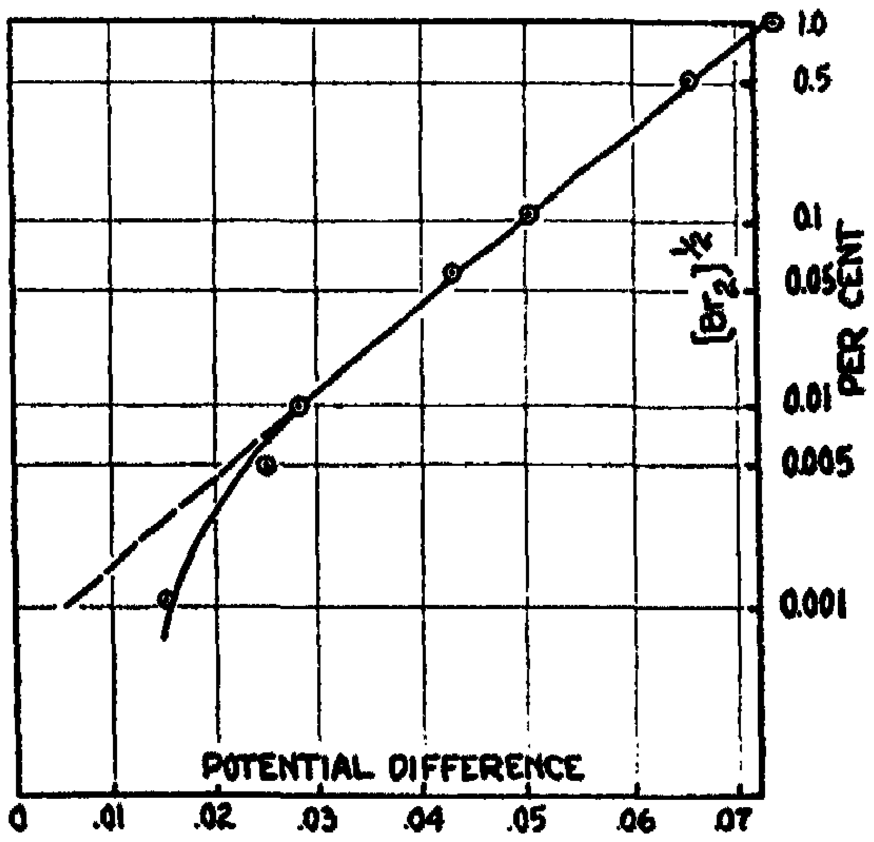

Fig. 15

$$Br + Ag \longrightarrow Ag^+Br^-,$$

an electromotive force which we believe corresponds to the main or positive photo-potential measured. The bromine diffusion experiment confirms this belief. Further, the presence of halogen acceptors, such as acetone semicarbazone, sodium nitrite, sulfite, *etc.*, should interfere with the production of the positive potential. This, too, has been confirmed by experiment.

Fig. 16 shows diagrammatically the processes taking place *at the illuminated electrode.*

In view of the fact that after a two minute exposure to the light, the silver bromide layer on the electrode is already gray in color, apparently due to the silver formed, certain consequences appear definite. Bromine must be released, and first a negative electrification of the silver electrode, then a positive one occurs, in light. The fall of the potential, which occurs after exposure had ended, is such that the time required to fall to a fraction of the steady positive value is a linear function of the thickness of the silver bromide layer, or the velocity of fall is an inverse function of the thickness. This agrees with the potential being due to the bromine attacking the silver electrode. We have now taken up the study of the negativization process with an oscillograph and this will be reported in a second communication as well as the spectral relations.

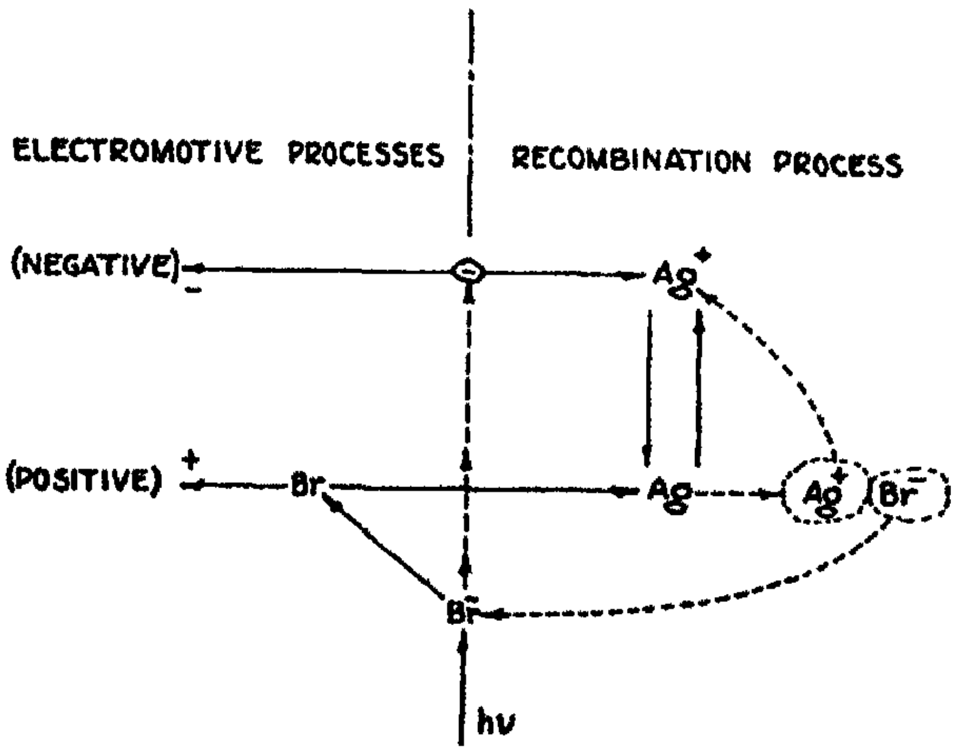

Fig. 16

Summary

Photo-voltaic cells consisting of silver:silver-bromide electrodes in solutions of potassium bromide have been studied. The p.d.-time curve obtained is the resultant of two effects, *viz.*, an initial negative effect on which is superimposed a positive effect. A hypothesis was developed explaining these in terms of the liberation of electrons and bromine atoms for bromide ions on absorption of light. In agreement with this it is shown that the positive effect can be suppressed, the negative effect made more pronounced, by addition of bromine acceptors. The positive effect is shown to be similar to that produced by allowing bromine to diffuse through the AgBr layer to the silver.

Rochester, N. Y.
Kodak Research Laboratories,
July 12, 1928.

AN EQUATION OF STATE FOR ETHYLENE GAS*

BY LOUIS J. GILLESPIE

In the present paper the equation of state of Beattie and Bridgeman[1] is utilized to smooth and to correlate, as far as is possible, the pressure-volume-temperature data for ethylene gas. The available data are those of Amagat[2] which extend over a large range of pressure and temperature into the liquid phase; the 24.95° isotherm of Masson and Dolley,[3] and about four points on each of four isotherms by Mathias, Crommelin and Watts.[4] Data on the normal volume of ethylene at 0° and 1 atmosphere are collected and reviewed by Blanchard and Pickering.[5]

No equation of state has apparently been presented for ethylene, with the exception of virial *pv* expansions. Aside from the general usefulness of equations of state, especially for gases of considerable chemical activity, an equation for ethylene is especially desirable in view of the work on mixtures of ethylene and argon by Masson and Dolley, which have permitted the calculation of partial molal free energies of the constituents of these binary mixtures.[6] The present work was in fact undertaken with a view toward a more complete thermodynamic investigation of these data than has been hitherto possible.

Interpolation of the Isothermals

For each temperature the *pv* products of Amagat were graphically smoothed as a function of the density, using an appropriate deviation function and large scale coordinate paper, and values of the pressure were interpolated for even values of the density in moles per liter (0.5, 1.0, 1.5, etc.). The transfer from Amagat units of density to moles per liter was effected through the normal density given by Batuecas[7] and chosen by Blanchard and Pickering,[5] namely 1.2604 grams per liter.

By a similar procedure, the data of Masson and Dolley and of the Leiden laboratory were interpolated to the same even density values, thus permitting a comparison of data. In the former case the transfer of density units required a knowledge of the ratio of the volume at 24.95° to that at 0°, both volumes at 1 atmosphere. From Amagat's data this ratio, V_{25}/V_0, was calculated to be 1.0936, from Masson and Dolley's data, 1.0932. The mean

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* Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 216.

[1] J. A. Beattie and Oscar C. Bridgeman: J. Am. Chem. Soc., **49**, 1665 (1927).

[2] Ann. Chim. Phys., (6) **29**, 68 (1893).

[3] Proc. Roy. Soc., **103A**, 524 (1923).

[4] Cinquième Congrès International du Froid, Rome; Première commission internationale de l'Institut Internationale du Froid, Rapports et Communications. Leiden, 1928.

[5] Sci. Paper U. S. Bureau of Standards, No. 529 (1926).

[6] Gibson and Sosnick: J. Am. Chem. Soc., **49**, 2172 (1927).

[7] J. Chim. phys., **16**, 322 (1918).

value 1.0934 was chosen. At a subsequent period it was found that the higher ratio was yielded by the equation of state finally derived, but it was found that the effect of the difference, 0.0002, was practically negligible in all relations under consideration.

It was observed in this isothermal interpolation that the pv data at 24.95° do not approach RT at low pressures in a perfectly smooth way around 1 atmosphere. The data are smoother at all higher pressures. These data were already smoothed once before publication,[3] but probably without the aid of a value of RT, which in fact could not be obtained without knowledge of the ratio V_{25}/V_0. A like situation obtained with reference to the Leiden isotherms; no way being discovered of smoothing these together with RT values without assuming in this case rather large experimental errors.

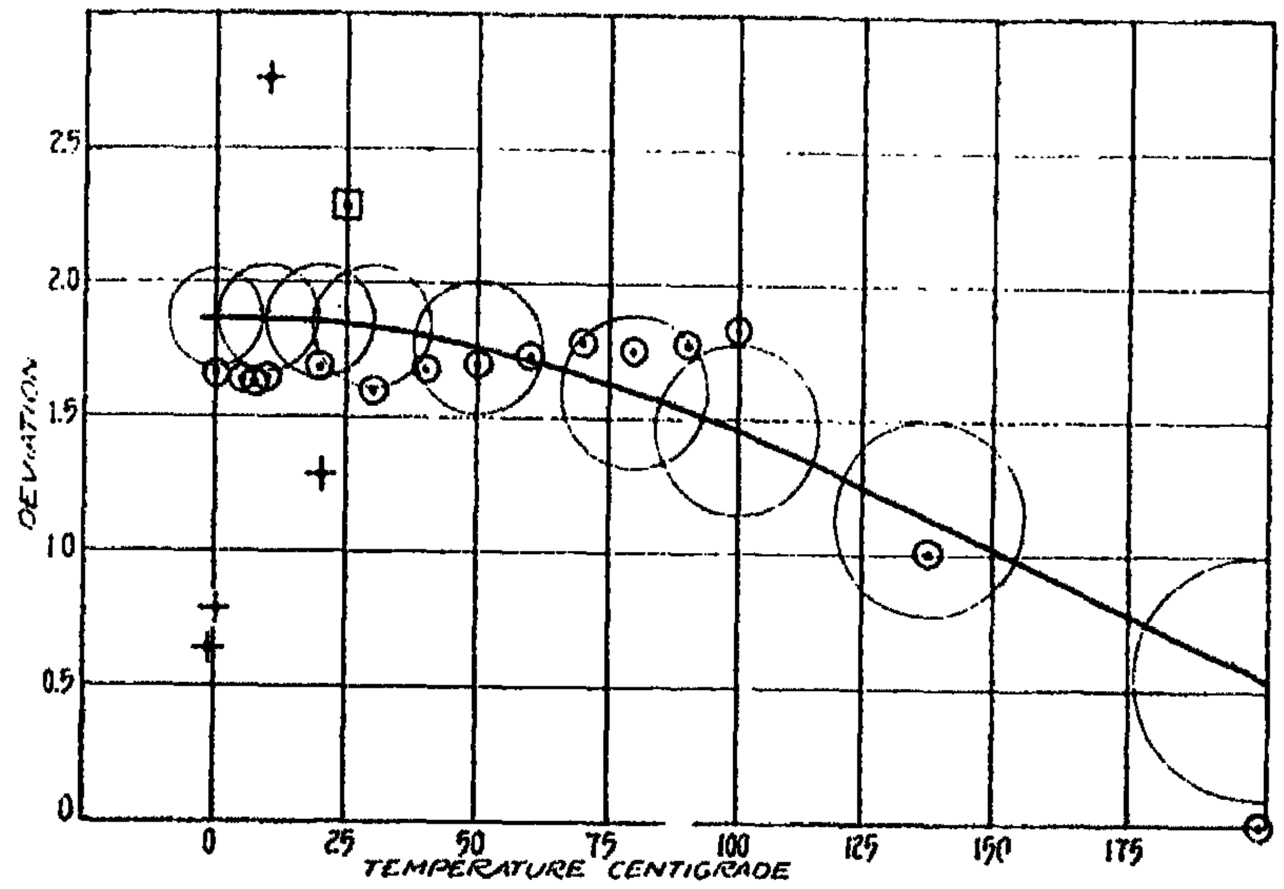

FIG. 1

Typical plot of an unsmoothed isometric $(2.5 \frac{\text{moles}}{\text{liter}})$ showing the isothermally smoothed points due to Amagat (circles), Masson and Dolley (square), and Mathias, Crommelin and Watts (crosses). The plot shows the value of the deviation,—$p - 34 - 0.275\,16t^\circ$ as a function of the temperature Centigrade. The line is furnished by the equation of state finally selected. The circles centered on this line are drawn with radii equal to 0.5% of the calculated pressures.

The interpolated values of the pressures, which are hereafter described as the observed pressures, were now grouped as isometrics for the next step.

Representation of the Isometrics

For each density, the pressure was plotted as a function of the absolute temperature. Fig. 1 shows a typical plot, that for 2.5 moles per liter. The line, shown for comparison only, was calculated from the final equation. It

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[3] See Fig. 2, ref. No. 3, where irregularities in the original data are obviously not entirely removed in the smoothing.

is clear that the results of Masson and Dolley, of the Leiden Laboratory, and of Amagat differ too much to permit utilization of all data in the final smoothing. Only the Amagat data are extensive enough to determine an equation of state; such an equation must be based on Amagat's data alone. It is also clear from the line drawn that the equation does not include a certain trend in the Amagat data. This trend, evidenced by an inflection of the isometrics, suggests at first a discordance between the high temperature (137°, 198.5°) and the low temperature (0-100°) data. Exclusion of the high temperature data would however leave d^2p/dt^2 positive, whereas this is as a rule negative (above the critical volume)[9]. It seemed best therefore to include all temperatures and to assume such a curvature of the isometrics as would keep them within about 0.5 percent of the measured pressures. Following the procedure of Beattie and Bridgeman[10] a value of *c* was found which would secure this, at least from a density of zero to about 7 moles per liter, with some difficulty as regards the highest temperature-pressure corner of the field. The other constants of their equation were then determined as described by them.

The constants so determined are given in Table I.

TABLE I

Constants in Beattie-Bridgeman Equation of State for Ethylene.

R	A_0	a	B_0	b	c	Mol. Wt.
0.08206	6.152	0.04964	0.12156	0.03597	$22.68 \cdot 10^4$	28.031

The equation is $p = RT(1 - \epsilon).(v + B)/v^2 - A/v^2$

Where $A = A_0 (1 - a/v)$

$B = B_0 (1 - b/v)$

$\epsilon = c/vT^3$

v = volume in liters of a mole

p = pressure in international atmospheres

$T = 273.13 + t°C.$

The agreement of the equation with the observed pressures of Amagat is exhibited in Table II, which lists the observed pressures and the deviation Δp (observed minus calculated pressure) in atmospheres. The average deviation (taken without regard to sign) over the entire range considered is 0.45 per cent. This range goes to a density 8 mols per liter, slightly higher than the critical density. The agreement is fair. The equation holds very well indeed up to 7 mols per liter, the average deviation being 0.36 per cent.

Table III shows the magnitude of the disagreement, already noted by Masson and Dolley, between their results and those of Amagat. There is agreement only at low densities. It is however precisely at such low densi-

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[9] Onnes and Keesom: Encyklopädie der mathematischen Wissenschaften, Art. V 10, page 756 (1912); also Communications from the Phys. Lab. Univ. of Leiden, **11**, Supplement 23, p. 142, Leiden (1912).

[10] Proc. Am. Acad. Arts Sci., **63**, 229 (1928).

TABLE II

Comparison of Observed Pressures of Amagat with Those calculated for the Equation of State

t°/density		0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0
0	p obs.	10.31	18.90	25.91	31.46	35.66	38.61	40.4	—	—	—	—	—	—	—	—	—
	Δ p	0	−.01	−.04	−.09	−.20	−.41	−.8	—	—	—	—	—	—	—	—	—
5	p obs.	10.54	19.39	26.67	32.50	37.02	40.4	42.8	44.5	45.6	—	—	—	—	—	—	—
	Δ p	+.01	+.01	−.02	−.10	−.22	−.4	−.5	−.5	−.3	—	—	—	—	—	—	—
7.5	p obs.	10.63	19.52	26.91	32.92	37.69	41.4	44.0	45.9	47.0	47.6	47.8	48.8	48.0	—	—	—
	Δ p	−.01	−.10	−.16	−.20	−.24	−.2	−.3	−.3	−.4	−.5	−.5	−.5	−.2	—	—	—
10	p obs.	10.74	19.81	27.34	33.48	38.40	42.3	45.2	47.3	48.7	49.6	50.1	—	—	—	—	—
	Δ p	−.01	−.04	−.10	− 17	−.22	−.2	−.2	−.2	−.2	−.1	−.1	—	—	—	—	—
20	p obs.	11.17	20.70	28.77	33.55	41.2	45.8	49.5	52.5	54.7	56.6	58.2	59.4	60.4	61.4	62.2	63.2
	Δ p	−.02	−.08	−.15	−.19	−.2	−.1	−.1	0	0	+.1	+.3	+.3	+.1	−.1	−.8	−1.7
30	p obs.	11.62	21.65	30.24	37.57	43.8	49.2	53.9	57.7	60.9	63.5	65.8	68.0	69.9	71.8	73.7	75.6
	Δ p	−.01	−0.07	−.16	−.25	−.3	−.2	+.1	+.3	+.4	.3	.3	.4	.1	−.2	−.9	−1.9
40	p obs.	12.04	22.56	31.73	39.73	46.7	52.8	58.1	62.6	66.6	70.1	73.2	76.1	79.2	81.9	84.8	88.0
	Δ p	−.02	−.09	−.15	−.16	−.1	0	+.2	.2	.3	.3	.2	0	−.2	−.6	−1.2	−2.0
50	p obs.	12.46	23.50	33.25	41.8	49.5	56.3	62.3	67.7	72.4	76.8	80.8	84.8	88.7	92.5	96.4	100.5
	Δ p	−.04	−.08	−.10	−.2	0	+.1	.3	.4	.4	.4	.3	.3	+.2	−.3	−.9	−1.9
60	p obs.	12.93	24.48	34.78	44.0	52.2	59.7	66.5	72.6	78.0	83.0	88.0	92.9	97.8	102.6	107.5	112.7
	Δ p	−.01	−.03	−.04	0	0	+.1	.3	.4	.3	.1	.1	.1	0	−.4	−1.1	−1.9
70	p obs.	13.40	25.48	36.36	46.2	55.0	63.1	70.5	77.4	83.7	89.6	95.4	101.2	107.1	113.1	119.4	126.0
	Δ p	+.02	+.05	+.07	+.1	+.1	.2	.2	.4	.3	.2	.1	.1	.1	−.1	−.3	−.8
80	p obs.	13.88	26.48	37.90	48.3	57.8	66.5	74.5	81.9	88.9	95.8	102.5	109.2	116.0	123.1	130.5	138.4
	Δ p	.07	.12	.14	.2	.2	.2	.1	0	−.1	−.1	−.1	−.2	−.2	−.2	−.3	−.4
90	p obs.	14.29	27.41	39.42	50.4	60.5	69.9	78.7	86.8	94.6	102.3	110.0	117.7	125.5	133.7	142.2	151.1
	Δ p	.04	.12	.22	.2	.2	.2	.3	.1	0	0	+.1	+ 1	+.2	+.3	+.4	+.3
100	p obs.	14.71	28.33	40.9	52.6	63.3	73.4	82.9	91.8	100.4	108.8	117.2	125.9	134.9	144.3	153.9	163.9
	Δ p	.02	.12	.2	.4	.3	.4	.4	.3	+.1	0	0	.2	.5	.9	1.1	1.1
137.5	p obs.	16.35	31.71	46.2	59.9	72.9	85.4	97.5	109.3	121.0	132.8	144.6	156.6	168.8	181.7	195.4	210.2
	Δ p	.02	.04	0	0	−.1	−.1	−.2	−.2	−.1	+.1	.3	.5	.7	+1.2	2.0	3.2
198.5	p obs.	18.97	37.23	54.8	71.9	88.6	105.0	121.2	137.5	153.9	170.6	187.7	205.3	223.7	243.3	264.2	286.5
	Δ p	−.01	−.07	−.2	−.4	−.6	−.8	−1.0	−1.0	−.9	−.6	−.1	+.5	1.6	3.3	5.8	8.9
Average ±	Δ p, %	0.16	0.28	0.34	0.41	0.39	0.46	0.55	0.43	0.37	0.29	0.27	0.31	0.26	0.48	0.96	1.59

Grand average ± Δ p% is 0.45

Grand average Δ p% excluding density of 7.5 and 8.0 is 0.36

ties (1.1 to 2.3) that the Leiden data differ, and at all temperatures, from the equation, as is shown in Table IV, for which the unsmoothed Leiden data were utilized. The data deviate more strongly than those of Masson and Dolley and in the opposite direction. If the percentage deviation is plotted as a function of the density, it is found not to approach zero asymptotically at zero pressure. This is not attributable to a defect in the equation. Even though the purity of Amagat's ethylene was not so great as it is now possible to obtain, the fact is important that the equation furnishes numbers, smooth in two dimensions, which must be considered to approach correctness, in smooth fashion, as the pressure approaches zero.

There exist relations in which the disagreement between Masson and Dolley and Amagat, which reaches 4.6% up to a density of 8, is not so important as might appear from Table III alone. Compare the discrepancy of 3% at a density of 4.5 with the error of 85%, which is the percentage deviation of the perfect gas law from the observed value. At a density of 6, the perfect gas law is in error by 122%.

TABLE III

Comparison of Calculated and Observed (Masson and Dolley) Isotherms at 24.95°

$$\Delta p, \% = 100\,\frac{\text{obs.} - \text{calc.}}{\text{calc.}}$$

Density	p calc.	Δp, %	Density	p calc.	Δ p, %
—	1	−0.02	7	66.7	4.6
0.5	11.41	−0.2	7.5	68.7	4.2
1	21.25	+0	8	71.2	3.1
1.5	29.66	+0.3	8.5	74.1	1.6
2	36.77	0.6	9	77.8	− 0.3
2.5	42.71	1.0	9.5	82.4	− 2.5
3	47.63	1.5	10	87.9	− 4.7
3.5	51.7	1.9	10.5	94.7	− 6.9
4	54.9	2.7	11	102.8	− 8.7
4.5	57.6	3.1	11.5	112.3	−10.0
5	59.8	3.7	12	123.5	−10.7
5.5	61.7	4.0	12.5	136.6	−10.5
6	63.3	4.6	13	151.6	− 9.0
6.5	65.0	4.6			

TABLE IV

Percentage deviations between Leiden experimental values and the values calculated. The calculated pressure is always greater.

Temp./Serial order	1	2	3	4	5
−1.36°C	1.3	1.4	1.6	2.0	——
+0.10°	0.9	1.0	1.2	1.5	1.8
10.17°	1.1	1.0	1.3	1.6	——
20.18°	1.0	1.0	1.2	1.4	——
Density at 20.18°	1.1414	1.3356	1.6474	2.2644	——

Calculation of the Normal Density

The equation does not necessarily furnish upon calculation the same value of the density at 0° and 1 atmosphere as that which was used to obtain it, but may give a better value.

Table V shows the summary of Blanchard and Pickering (5) with the addition of the value calculated from the equation.

TABLE V

Normal Density of Ethylene, in grams per liter

Source	Density	Source	Density
Leduc	1.2605	Batuecas	1.2604
Stahrfoss	1.2610	Equation	1.2599

Blanchard and Pickering selected the value of Batuecas. This selection is supported by the value here found.

Calculation of Critical Data

In the isothermal smoothing of the *pv* values under the critical temperature it was noticed that the calculated pressures became almost a zero function of the density and indeed, without great care in the smoothing, the pressures actually decreased with increasing density. When the equation was derived it was thought interesting to see whether it would exhibit this trend. It was found that the equation gave a 7.5° isotherm with an inflection at about 7 moles per liter. By a succession of trials it was found that an inflection occurred at as high a temperature as 8.5°, but not at 8.55°, when the pressures were calculated with a precision of 0.002%. The critical temperature is therefore given by the equation as 8.5°, to the nearest 0.1°. Pickering[11] selects the value 9.7°, a difference of 0.4% on the absolute temperature, which is of course the quantity calculated by the equation. Since this selection, Masson and Dolley (3) obtained 9.35°, the lowest recent experimental value.

The critical pressure calculated is 49.19 atmospheres against 50.9 selected by Pickering, a difference of 3.4%. The critical density calculated is 6.4 to 6.5, selected value 7.9 in moles per liter. Here the errors seem to accumulate, making a positive disagreement.

Equations which represent the measured pressures are not generally expected to furnish correct critical constants (nor do those which are derived from critical constants represent the measured pressures), so that the success of the equation for ethylene in furnishing at least the critical temperature is surprising. The agreement may of course be accidental.

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[11] Sci. Papers, U. S. Bureau of Standards, No. 541 (1926).

Summary

The constants in the equation of state of Beattie and Bridgeman have been determined for ethylene gas from the data of Amagat. Using atmospheres, liters per mole, $T = 273.13 + t°C$, $R = 0.08206$, they are $A_0 = 6.152$, $a = 0.04964$, $B_0 = 0.12156$, $b = 0.03597$, and $c = 22.68 \cdot 10^4$.

The representation of Amagat's data is good up to a density of 7 moles per liter and fair to 8, slightly above the critical density; the average deviations being 0.36 and 0.45 per cent respectively.

The equation does not represent closely the isotherm of Masson and Dolley, except at low pressures, in accordance with their statement that this isotherm does not agree with interpolations from Amagat's data.

The critical temperature calculated from the equation agrees to 0.4% with that observed, the difference being 1.2°; the critical pressure calculated is 3.4% in error.

The normal density calculated from the equation, 1.2599, supports the value of Batuecas as against that of Stahrfoss, being lower than either.

RAOULT'S LAW*

BY WILDER D. BANCROFT AND H. L. DAVIS

Using a van't Hoff cycle we can calculate the osmotic work done when we squeeze out of a solution one gram of the pure solvent by means of an ideal piston which is permeable to the solvent and impermeable to the solute. If we work with such a large mass of solution that we may ignore the change of concentration when one gram of solvent is removed reversibly, if the vapor of the solvent follows the gas law at that temperature, and if we can ignore the volume of one gram of liquid solvent relatively to the volume of one gram of solvent as vapor, we have

$$PV_g = \frac{RT}{M_2}\ln\frac{p_2}{p'_2} \text{ or } PV_m = RT\ln\frac{p_2}{p'_2}, \qquad \text{I}$$

where P is the osmotic pressure, V_g is the volume of one gram of the solvent in the solution,[1] M_2 is the gram-molecular weight of the solvent as vapor, p_2 is the vapor pressure of the pure solvent, p'_2 is the partial pressure of the solvent in the solution, and V_m is the volume of one gram-molecular weight (as occurring in the vapor) of the solvent in the solution. The first equation holds for the pressing out of one gram of the solvent and the second for the pressing out of one gram-molecular weight (as defined) of the solvent. The gram-molecular weight of the liquid solvent does not appear in the formula.

If we squeeze out the amount of solvent in which one gram-molecular weight of the solute (in the solution and not as vapor) is contained, we get the equation as given by van't Hoff

$$PV_1 = \frac{N_2}{n_1}RT\ln\frac{p_2}{p'_2}, \qquad \text{II}$$

where $N_2 = G_2/M_2$ and $n_1 = G_1/M_1$, G_2 and G_1 being the masses in grams of the two components in the solution, M_2 being the gram-molecular weight of the solvent as vapor, and M_1 the gram-molecular weight of the solute in the solution. The gram-molecular weight of the solute as vapor does not appear in the equation. V_1 is the volume occupied in the solution by N gram-molecules (as defined) of the solvent. It is necessary to be as meticulously explicit as this because many physical chemists do not know just what the terms mean in the van't Hoff formula.

If we assume that $PV_1 = RT$, equation II becomes

$$\frac{n_1}{N_2} = \ln\frac{p_2}{p'_2}, \qquad \text{III}$$

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*This paper is part of the programme now being carried out at Cornell University under a grant to Professor Bancroft from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[1] Bancroft and Davis: J. Phys. Chem., 32, 1 (1928).

which is, of course, true only within the limits for which the assumption holds. For very small values of n_1 we can write, with a loss of accuracy,

$$\frac{n_1}{N_2} = d \ln p_2 = \frac{p_2 - p'_2}{p_2}$$

An empirical study of his data led Raoult to write this last formula

$$\frac{n_1}{N_2} = k\frac{p_2 - p'_2}{p_2} \qquad \text{IV}$$

As a result of van't Hoff's theoretical deductions, Raoult made $k = 1$. Since the resulting equation becomes an absurdity when $n_1 = N_2$ because we must then have $p'_2 = 0$, the equation was changed empirically to read

$$\frac{n_1}{N_2 + n_1} = \frac{p_2 - p'_2}{p_2}. \qquad \text{V}$$

For values of n_1 negligible with respect to N_2, Equations III and V are practically identical. It is only for such conditions that we can substitute $(p_2 - p'_2)/p_2$ for $\ln(p_2/p_1)$ without introducing a serious error.

Equation V has practically no theoretical basis when applied to any considerable range of concentrations, because it contains the two assumptions, contrary to fact, that $PV_1 = RT$ and that $\ln(p_2/p'_2) = (p_2 - p'_2)/p_2$. It has not been shown by anybody that introducing n_1 into the denominator nullifies the effect of the two errors. Speyers[1] was one of the first people to try to substitute Equation V for Equation III.

If we define an ideal solution, for the moment, as one in which each component has the same molecular weight in the liquid phase as in the vapor phase, and as one in which the two components mix in all proportions without change of volume and without any heat effect, we find empirically that the change of partial pressures over the whole range of concentrations can be expressed accurately by the equations

$$\frac{N_1}{N_1 + N_2} = \frac{p_2 - p'_2}{p_2} \text{ and } \frac{N_2}{N_1 + N_2} = \frac{p_1 - p'_1}{p_1} \qquad \text{VI}$$

where the M_1 and M_2 concealed in N_1 and N_2 refer to the gram-molecular weights of the two components respectively as vapors.

Equation VI is called Raoult's law by the California school,[2] following the lead of Speyers, because Equation V reduces to it for the case, and only for the case, that the molecular weight of the solute is the same in the liquid as in the vapor, in which case $n_1 = N_1$. In fact Hildebrand puts the cart before the horse by saying, p. 59: "We may, therefore, follow G. N. Lewis in defining an ideal solution as one which obeys Raoult's law

$$\frac{p_0 - p_1}{p_0} = \frac{n}{N + n}$$

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[1] J. Am. Chem. Soc., 21, 725 (1899).

[2] Cf. Hildebrand: "Solubility," 24 (1924).

at all concentrations and pressures, a definition which has some important consequences. It follows from it, as Lewis has shown, that the formation of such a solution will take place from its component liquids without any heat of mixing and without any change in volume."

It seems to us that the identity between Equation VI and the special case of Equation V is purely formal and not real. In Equation V, it is certain that one molecular weight refers to one substance in solution and the other molecular weight to the other substance as vapor. We believe, and expect to show in this paper, that the molecular weights for both components in Equation VI refer to the vapor phase and not to the solution phase. Of course this makes no difference in the ideal case, where there is no polymerization in the liquid phase. The difference between tweedledum and tweedledee becomes very important when one wishes to include other binary systems. Hildebrand did not have any very striking success in discussing non-ideal solutions on the assumption that what he calls Raoult's law has to do with molecular weights in solution. Consequently, it will be wise to find out what can be done on the assumption that both the molecular weights in Equation VI refer theoretically to the vapor phase.

By doing algebraic transformations we can change Equation VI into

$$\frac{N_1 + N_2}{N_2} = \frac{p_2}{p'_2} \text{ and into}$$

$$\frac{N_1}{N_2} = \frac{p_2 - p'_2}{p'_2} = \frac{G_1}{G_2}.\frac{M_2}{M_1} \qquad \text{VII}$$

TABLE I

Ethyl Alcohol and Water at 25°

$$0.61 \log \frac{G_{alc.}}{G_{water}} - \log \frac{p_w - p'_w}{p'_w} = \log K_1 = 0.6670$$

$$0.55 \log \frac{G_{water}}{G_{alc}} - \log \frac{p_A - p'_A}{p'_A} = \log K_2 = 0.0030$$

Gram % alcohol in liquid	log K_1 calc.	p' water found mm	p' water calc. mm	log K_2 calc.	p' alcohol found mm	p' alcohol calc. mm
0	——	23.73	23.75*	——	0.0	0.0*
12.36	0.8030	22.67	22.39	$\bar{1}.8034$	10.50	15.1
20.51	0.6847	21.78	21.70	$\bar{1}.9185$	16.66	19.07
28.40	0.6653	21.15	21.13	0.0035	22.27	22.26
33.90	0.6697	20.79	20.77	0.0028	24.90	24.25
39.32	0.6636	20.36	20.38	0.0260	26.85	27.3
50.46	0.6791	19.60	19.50	0.0048	30.73	30.68
56.50	0.6724	19.01	18.95	$\underline{0}.0160$	32.16	31.73
71.09	0.6678	17.31	17.30	$\bar{1}.9948$	36.64	36.89
78.07	0.6663	16.18	16.19	0.0037	39.53	39.51
90.12	0.4979	10.68	12.98	0.0829	47.40	45.50
100.	——	0.0	0.0*	——	59.01	59.01*

*These values have no significance because they are given by every equation of this type.

In Equation VII each side of the equation varies from zero to infinity as we change from $G_1 = 0$ to $G_2 = 0$. We can tell whether this equation holds by plotting the data on logarithmic co-ordinates and seeing whether we get a straight line. Since M_2/M_1 is a constant when the vapor of each liquid follows the gas law and when the mixtures follow Dalton's law, it is immaterial whether we plot the concentrations in grams or in molecular weights.

We have found empirically that a number of systems can be represented with an unexpected degree of accuracy by the modified equation

$$a \log \frac{G_1}{G_2} = \log \frac{p_2 - p'_2}{p'_2} + \log K_1 \qquad \text{VIII}$$

In Table I are the data by Dobson[1] for ethyl alcohol and water. The data for the partial pressures of water agree with the calculated values within the experimental error through 78% alcohol. There is quite a discrepancy between the calculated and found values for ninety percent alcohol. Special experiments will have to be made to discover the cause of the discrepancy. In any event the equation describes the facts at least up to a mol fraction of 0.6, which is a long way beyond the orthodox limit of tenth-normal. The partial pressures of alcohol agree very well except for the two dilute solutions and for the most concentrated solution. In view of the good agreement for water vapor in the two dilute solutions, it is possible that the discrepancy with the alcohol pressures for these two solutions may be due to experimental error.

TABLE II

Methyl Alcohol and Water at 30.90°

p_1 = partial pressure and N_1 = number of mols of alcohol

p_2 = partial pressure and N_2 = number of mols of water

$$0.9 \log \frac{N_2}{N_1} - \log \frac{p_1 - p'_1}{p'_1} = \log K_1 = 0.100$$

$$0.95 \log \frac{N_1}{N_2} - \log \frac{p_2 - p'_2}{p'_2} = \log K_2 = 0.0030$$

Mol percent alcohol in liquid	p' alcohol found mm	p' alcohol calc. mm	p' water found mm	p' water calc. mm
0	0.0		55.0	
5	20.2	21.3	52.8	52.7
10	39.8	38.7	50.7	50.7
20	74.4	69.2	45.1	46.5
30	101.1	96.4	41.9	42.2
40	122.8	121.5	37.7	40.3
50	143.7	145.1	32.8	32.8
60	165.3	167.9	27.5	27.4
70	188.0	190.1	21.0	21.7
80	210.4	212.1	14.8	12.1
90	235.0	234.7	7.8	6.7
100	260.5		0.0	

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[1] J. Chem. Soc., 27, 2866 (1925).

In Table II are given the data by Ferguson and Funnell[1] for methyl alcohol and water. The equations fit the data very well over the whole range with the exception of the alcohol values for the twenty and thirty molecular percents alcohol solutions. When plotted on logarithmic co-ordinates, the values for these two concentrations lie well off the curve. Professor Ferguson says that the curve does have a hump in it over this range. It remains to be seen to what this is due. The value for the pressure of water vapor in equilibrium with forty molecular percent of alcohol is also not what it should be; but this might well be experimental error, though Professor Ferguson does not concede this.

Some preliminary data by Morton[2] for methyl alcohol and acetone, Table III, came out pretty well except for the most dilute solutions, where the formula exaggerates any experimental error very much. Similar data by Morton for water and acetone gave moderately good results for the partial pressures of acetone; but the corresponding figures for water vapor were not satisfactory enough to be worth giving. As a matter of fact the logarithmic data in Table IV could be represented better by a curve than by a straight line. It is probable, however, that more accurate data will give a really good straight line.

We had hoped to use the data of Wrewsky[3] on ethyl alcohol and water; but inspection shows that they are too inaccurate to be of any real value. At 39.76° for percentage concentrations of ethyl alcohol of 15.92, 18.25, 30.25, 31.88, 36.42, 42.0, 43.75, and 47.54, Wrewsky found 44.3, 44.6, 45.95, 45.5, 45.4, 44.7, 49.3, 44.8, and 43.8 respectively for the partial pressures of water vapor expressed in millimeters. This is quite impossible, since alcohol and water do not form two liquid layers at this or any other temperature.

In Tables V and VI are given the data by Sameshima[4] for acetone and ethyl ether at 30° and at 20°. The calculated values for acetone in ether do not agree any too well with the experimental values and there is the painful possibility that the logarithmic graph is really a flat curve which has been made to fit fairly well by a judicious placing of the straight line. The values for the partial pressures of acetone, however, are a joy to the soul. At each of the two temperatures the equation represents the facts with considerable accuracy over the whole range of concentrations.

Since methyl alcohol, ethyl alcohol, and water are highly associated liquids with normal vapors, the fact that Equation VIII appears to hold very well for these liquids and also for acetone, which is a slightly associated liquid shows that it is not the molecular weight in the liquid phase that counts. Any polymerization in the liquid phase will show in the exponent. If the exponent is unity and if $K = M_1/M_2$, Equation VIII reduces to Equation VI, the so-called Raoult law. All ideal binary solutions therefore form a special case under Equation VIII, and we have at least made a start towards a

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

[2] J. Phys. Chem., 33, 384 (1929).

[3] Z. physik. Chem., 81, 1 (1912).

[4] J. Am. Chem. Soc., 40, 1482 (1918).

TABLE III

Methyl Alcohol and Acetone at 20°

$$0.83 \log \frac{G_{Alc}}{G_{Ac}} - \log \frac{p_{Ac} - p'_{Ac}}{p'_{Ac}} = \log K_1 = 0.14$$

$$0.62 \log \frac{G_{Ac}}{G_{Alc}} - \log \frac{p_{Alc} - p'_{Alc}}{p'_{Alc}} = \log K_2 = 0.03$$

% acetone in liquid	log K_1 calc.	p′ acetone found mm	p′ acetone calc. mm	log K_2 calc.	p′ alcohol found mm	p′ alcohol calc. mm
0.0	——	0	——	——	96.0	——
10.0	0.0710	28.6	32.7	0.1834	82.2	75.7
24.2	0.1235	57.0	62.5	0.0642	67.5	65.8
30.0	0.1361	72.4	73.8	0.0188	61.8	62.4
40.0	0.1419	89.2	88.8	0.0407	56.2	55.6
49.8	0.1416	103.8	103.6	0.0449	50.5	49.9
60.0	0.1475	118.8	118.1	0.0384	44.1	43.6
70.1	0.1337	131.6	132.1	0.0558	38.2	36.8
80.1	0.1118	144.2	146.0	0.0162	29.3	29.9
90.1	0.1625	161.4	160.6	1.9698	17.6	20.6
100.0	——	179.2	——	——	0	——

TABLE IV

Water and Acetone at 20°

$$0.9 \log \frac{G_w}{G_{Ac}} - \log \frac{p_{Ac} - p'_{Ac}}{p'_{Ac}} = \log K_1 = 0.39$$

% acetone in liquid	log K_1 calc.	P_{Ac} found mm	P_{Ac} calc. mm
0	——	——	——
10.3	0.3210	41.2	46.5
20.0	0.3811	73.2	74.1
29.3	0.4102	95.5	95.4
39.0	0.4274	115.8	113.8
58.3	0.3954	138.1	137.7
79.6	0.2245	152.5	160.1
100.	——	179.2	——

general equation which shall be valid for all concentrations of all pairs of liquids. We have got away from the tyranny of dilute solutions, without making use of the activity concept.

It is not claimed or believed that Equation VIII will represent the data with absolute accuracy over the whole range of concentrations for all pairs of consolute liquids which are not electrolytes in the usual sense of the term; but it is hoped that Equation VIII will do this for some solutions in addition

TABLE V

Acetone and Ether at 30°

$$0.9 \log \frac{N_{Ac}}{N_{Et}} - \log \frac{p_{Et} - p'_{Et}}{p'_{Et}} = \log K_1 = 0.147$$

$$0.88 \log \frac{N_{Et}}{N_{Ac}} - \log \frac{p_{Ac} - p'_{Ac}}{p'_{Ac}} = \log K_2 = 0.17$$

Mol % acetone in liquid	log K₁ calc.	p' Ether found mm	p' Ether calc. mm	log K₂ calc.	p' Acetone found mm	p' Acetone calc. mm
0.0	—	646.0	—	—	0.0	—
3.867	0.4149	632.5	621.5	0.1601	21.8	22.3
13.27	0.1458	570.8	571.0	0.2029	66.2	62.4
25.09	0.1470	510.2	510.1	0.2011	106.7	102.0
34.54	0.1131	464.6	466.6	0.1772	132.4	131.2
49.58	0.1789	390.3	378.9	0.1675	167.5	167.9
65.07	0.1883	301.5	287.3	0.1556	201.2	203.2
70.47	0.1771	266.0	255.9	0.1663	213.7	214.0
83.81	0.1883	166.5	156.4	0.1593	243.1	243.8
93.37	0.1254	71.0	74.2	0.2224	266.8	265.0
95.28	0.1457	55.3	55.5	0.2048	270.6	269.4
97.99	0.0419	20.8	26.4	0.1712	276.6	276.6
100.00	—	0.0	—	—	282.7	—

TABLE VI

Acetone and Ether at 20°

$$0.9 \log \frac{N_{Ac}}{N_{Et}} - \log \frac{p_{Et} - p'_{Et}}{p'_{Et}} = \log K_1 = 0.17$$

$$0.88 \log \frac{N_{Et}}{N_{Ac}} - \log \frac{p_{Ac} - p'_{Ac}}{p'_{Ac}} = \log K_2 = 0.20$$

Mol % acetone in liquid	log K₁ calc.	p' Ether found mm	p' Ether calc. mm	log K₂ calc.	p' Acetone found mm	p' Acetone calc. mm
0.0	—	443.5	—	—	0.0	—
5.2	0.1629	422.2	422.6	0.1828	19.6	20.3
12.71	0.1487	394.1	396.2	0.2012	41.8	41.7
24.90	0.1599	350.5	352.2	0.1916	70.2	71.0
45.70	0.1738	281.8	280.8	0.1706	105.2	106.8
61.21	0.1888	224.4	219.6	0.1623	126.8	127.5
66.62	0.1800	198.8	196.3	0.1677	135.2	137.9
84.16	0.1769	111.1	109.8	0.1544	160.5	162.6
88.83	0.1611	79.7	82.6	0.1946	167.9	168.1
93.17	0.1084	48.3	54.7	0.2137	174.5	174.2
93.58	0.1139	46.3	51.9	0.2103	175.0	174.8
97.90	0.0577	15.4	19.7	0.2032	181.4	181.3
99.59	0.0472	1.8	4.7	0.1244	184.1	184.3
100.00	—	0.0	—	—	185.2	—

to the ideal solutions. It is hoped that Equation VIII is the one which binary solutions of consolute liquids should follow and that we can evaluate the disturbing factors best by studying the variations from the normal curve which they produce. The hump in Mr. Ferguson's curve for acetone and methyl alcohol may be genuine, as he believes; but it was the application of Equation VIII that brought out clearly the fact that there is a hump in the curve which must either be eliminated or accounted for.

In so far as Equation VIII holds for two pairs of consolute liquids having one liquid in common, we can predict the distribution ratio for the common liquid in case the other two liquids can be kept immiscible in some way. For the two pairs of liquids Equation VIII becomes

$$a_1 \log \frac{G_1}{G_2} - \log \frac{p_2 - p'_2}{p'_2} = \log K_1$$

$$a_3 \log \frac{G_3}{G'_2} - \log \frac{p_2 - p'_2}{p'_2} = \log K_3.$$

The two pairs of liquids will be in equilibrium with respect to the second liquid—denoted by G_2 and G'_2—when the partial pressure of this liquid is the same for each liquid phase, in other words when

$$a_1 \log \frac{G_1}{G_2} - a_3 \log \frac{G_3}{G'_2} = \log(K_1/K_3)$$

Rearranging this, we have

$$a_3 \log G'_2 - a_1 \log G_2 = \log(K_1K_3/) - a_1 \log G_1 + a_3 \log G_3$$

Dividing both sides by a_3 and keeping G_1 and G_3 constant, the whole right side of the equation becomes a constant and we have, if we clear of logarithms and call $a_1/a_3 = n$

$$G'_2/G_2^n = \text{const.} \qquad \text{IX}$$

Equation IX is Henry's law expressed in mass concentrations instead of in the volume concentrations which unfortunately are usually used. It is thus evident that the exponents in Equation VII are some measure of the polymerizations, becoming unity when the polymerizations are zero, as with ideal solutions. The value of log K depends on the units employed and on the solubilities.

In Equation VIII we may of course write $k^n = K$, in which case we have

$$\frac{G_1^n}{k^nG_2^n} = \frac{p_2 - p'_2}{p'_2}$$

We can make k_1^n disappear either by writing $S = G_1/k$ or $S = kG_2$. It will be more general to eliminate k^n by changing both numerator and denominator. If S_1 and S_2 are values of the masses so adjusted that k^n disappears, we have

$$\frac{S_1^n}{S_2^n} = \frac{p_2 - p'_2}{p'_2}. \qquad \text{IX}$$

By a simple transformation this becomes

$$\frac{S_1^a + S_2^a}{S_2^a} = \frac{p_2}{p'_2} \qquad \text{X}$$

which is probably the form that will be used when, and if, it comes to a thermodynamical deduction because RTln p/p′ is the work term when the pressure of an ideal gas varies reversibly between those two limits.

Water and methyl alcohol pass slowly through a rubber membrane while acetone passes through rapidly. By using a rubber diaphragm and working rapidly, it should therefore be possible to determine the distribution of acetone between water and methyl alcohol considered as immiscible liquids. This has been done in the Cornell laboratory by Morton.[1] The exponents from Tables III and IV are 0.83 and 0.9. For the ratio we have 0.9/0.83 = 1.08, while the directly determined exponent was 1.09, as good an agreement as one can ask until we learn to measure vapor compositions more accurately than has yet been done. An attempt to do this is now being made at Cornell; but the question of the validity and the limitations of Equation VIII is so important that we hope that many other laboratories will contribute their share to the work.

We are especially interested in Equations VIII and IX because they tie in with the work on three-component systems begun by one of us[2] and carried through with accuracy by Lincoln[3] for ethyl alcohol, benzene, and water.

The general results of this paper are as follows:

1. When the so-called Raoult equation is applied to concentrated solutions, the molecular weights are theoretically those of the two components in the vapor state. In the equation actually used by Raoult there comes in the molecular weight of one of the components in the liquid phase. The error has not been recognized, because, in ideal solutions, the molecular weights in the liquid and in the vapor are supposed to be the same.

2. Owing to the failure to recognize the real meaning of the so-called Raoult equation, $\frac{N_1}{N_1 + N_2} = \frac{p_2 - p'_2}{p_2}$, most of the work dealing with variations from this equation will probably have to be revised.

3. It has been found experimentally that the equation $\left(\frac{G_1}{G_2}\right)^a = K\frac{p_2 - p'_2}{p'_2}$ describes the facts with unexpected accuracy over a wide range of concentrations for several pairs of liquids even when both components are associated liquids.

4. When the exponent is unity and $K = M_1/M_2$, the new equation reduces to the so-called Raoult law. Consequently, the behavior of all ideal solutions is covered as a special case under the new equation.

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[1] J. Phys. Chem., 33, 384 (1929).

[2] Bancroft: Phys. Rev., 3, 21, 114, 193 (1895).

[3] J. Phys. Chem., 4, 161 (1900); 8, 248 (1904).

5. In the new equation the exponent, a, is some measure of the relative polymerization and is independent of the units, while the constant, K, depends on the units used, the molecular weights in the vapor phase, the solubility, and perhaps on other factors.

6. The data for ethyl alcohol and water obtained by Dobson in Masson's laboratory, have been calculated up to a mol fraction of 0.6 for alcohol without having recourse to variations from the gas laws or to the activity concept.

7. From the new equation it is possible to calculate the equation of the distribution of one liquid between two other liquids, each consolute with the first, provided these other two liquids are kept immiscible. This has been realized experimentally by Morton in the Cornell laboratory for acetone, methyl alcohol, and water, using a rubber diaphragm to keep the methyl alcohol and water from mixing.

8. Henry's law and Nernst's distribution law should be expressed in mass concentrations and not in volume concentrations, as is usually the case.

9. Many experiments by many laboratories are needed in order to determine the validity and limitations of the new equation.

10. The new equation ties in with the work done at Harvard and Cornell many years ago on dineric equilibria in systems consisting of two non-miscible liquids and a third liquid consolute with each of the others.

Cornell University.

THE FORMATION OF THIN FILMS OF ORGANIC COLLOIDS ON MERCURY SURFACES[*]

BY R. L. KEENAN[**]

Introduction

The investigation described forms parts of a series of studies on molecular orientation in relation to colloid structure which are being carried out in these laboratories. One object is to develop quantitatively a hypothesis proposed by S. E. Sheppard[1] concerning so-called emulsoid colloids, also termed "high molecular" substances. A preliminary note on the present work was communicated to *Nature*.[2]

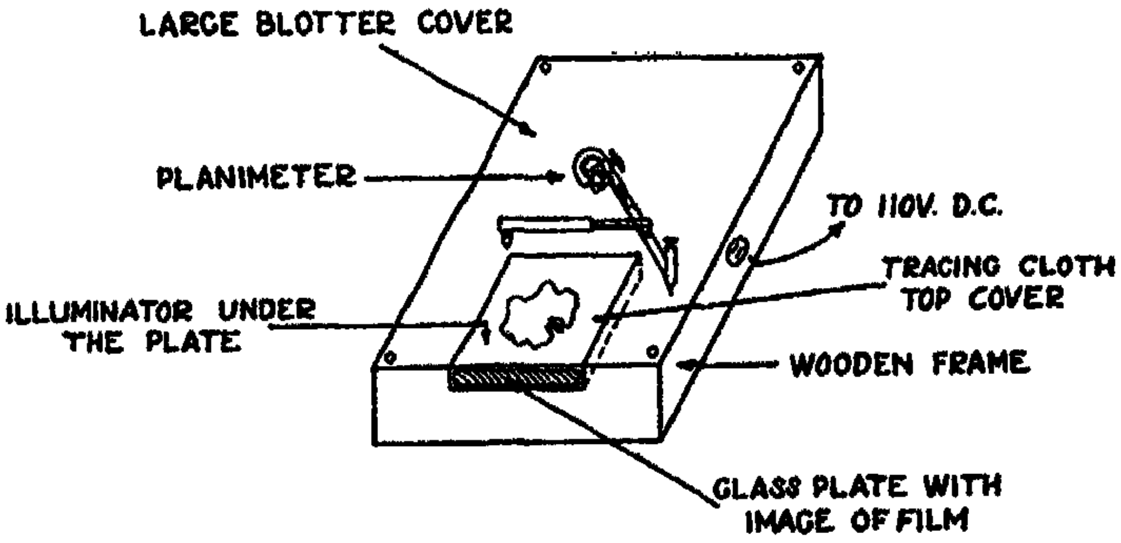

Fig. 1

Studies of "high molecular" bodies, such as cellulose, rubber, and proteins, have been made from various angles, *i.e.*, viscosity, X-ray crystal structure, molecular weight, polarized light, and chemical reactions. Each of these methods has given interesting pictures of these supposed large molecules. There is, however, one property of materials which has given extraordinarily vivid pictures of the sizes and shapes of many long chain compounds, such as the fatty acids and their esters. It was thought that this property, the spreading of materials on liquid surfaces, might be of use in the study of organic colloids.

Langmuir[3] showed that when films of fatty acids were extended to their limit, the molecules were oriented so that their carboxyl groups were in the water and the hydrocarbon group extended up from the surface. Knowing the weight of material, its density, and the area it covers, the thickness of the films, or in other words, one dimension of the molecule, could be determined.

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[*] Read at the Swampscott meeting of the Am. Chem. Soc. Colloid Division, Sept., 1928.

[**] Communication No. 363 from the Kodak Research Laboratories.

[1] The Nature of the Emulsoid Colloid State, Nature, 107, 73 (1921).

[2] S. E. Sheppard and R. L. Keenan: Nature, 1928, 982.

[3] Langmuir: J. Am. Chem. Soc., 39, 1869 (1917).

If solutions of these polymers could be spread on a suitable support, there was a possibility of measuring at least one dimension of the molecule.

Previous Work

Dewhurst[1] wishing to obtain as thin a film as possible for his rapid bolometer was successful in getting collodion films from ether-alcohol solutions by allowing them to spread on a clean mercury surface. These films were many molecules thick and useless for our purpose.

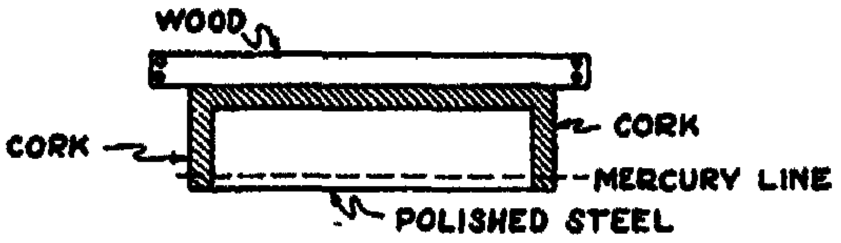

Fig. 2
Scraper

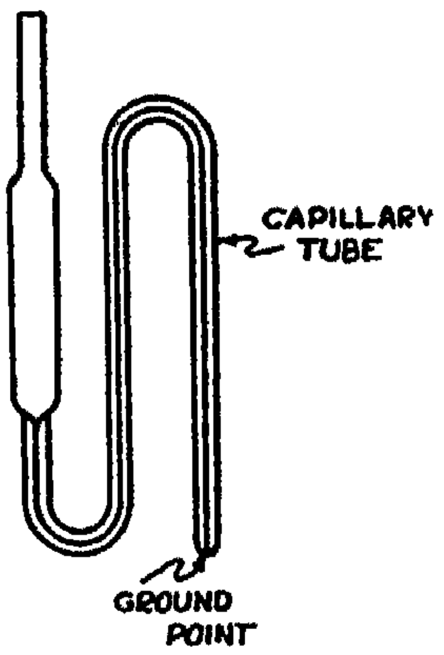

Fig. 3
Dropper

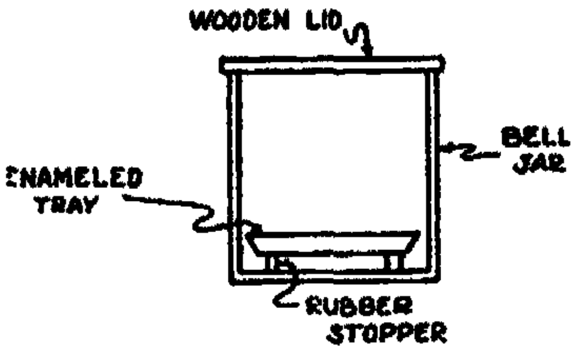

Fig. 4

Barton and Hunt[2] obtained colloidal films 10 to 20 Å.U. thick by allowing amyl-acetate solutions to spread on a clean water surface.

Fischer[3] spread certain oils on mercury and determined their thicknesses by the volume-area method. The outline of the film was determined by breathing upon the mercury surface. His results were in agreement with Langmuir's and Adam's.

Walcott[4] spread collodion, gelatin, and other such films on mercury for the purpose of studying phase shifts of light by reflection. His films were relatively thick.

Taylor[5] was successful in making celluloid films on mercury from 30 to 700 Å.U. thick for a vacuum-tight membrane. Celluloid spread on water did not give vacuum-tight membranes which was possibly due to an orientation effect. This effect was more or less absent when the celluloid was spread on mercury.

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[1] Dewhurst: Proc. Phys. Soc., 39, 39 (1926).
[2] Barton and Hunt: Nature, 114, 361 (1924).
[3] Fischer: Ann. der Physik, 68, 414 (1899).
[4] Wallbott: Ann. Physik, 68, 496 (1899).
[5] Taylor: J. Sci. Instr., 3, 400 (1926).

Preliminary Work

Observations on the behavior of these films on water indicated that water was not the ideal substance on which to do the work. Many of the best solvents for cellulose esters are soluble in water or are denser than water and tend to drag the cellulose esters below the surface. Consequently mercury was chosen. For some time, however, it appeared to be equally unsatisfactory.

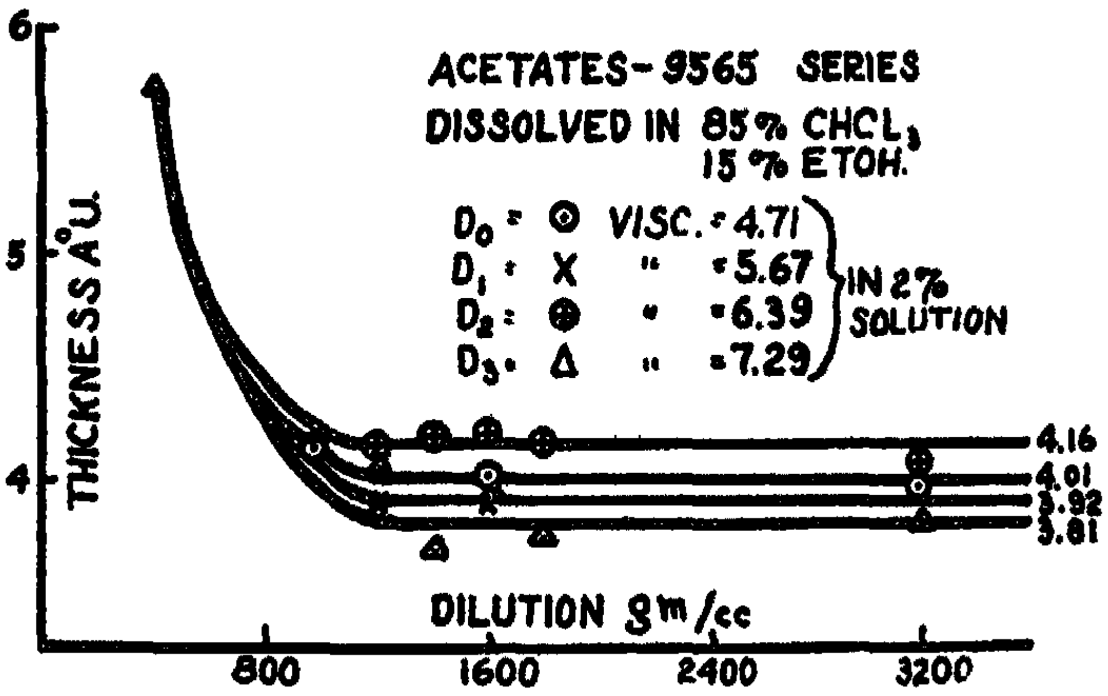

Fig. 5

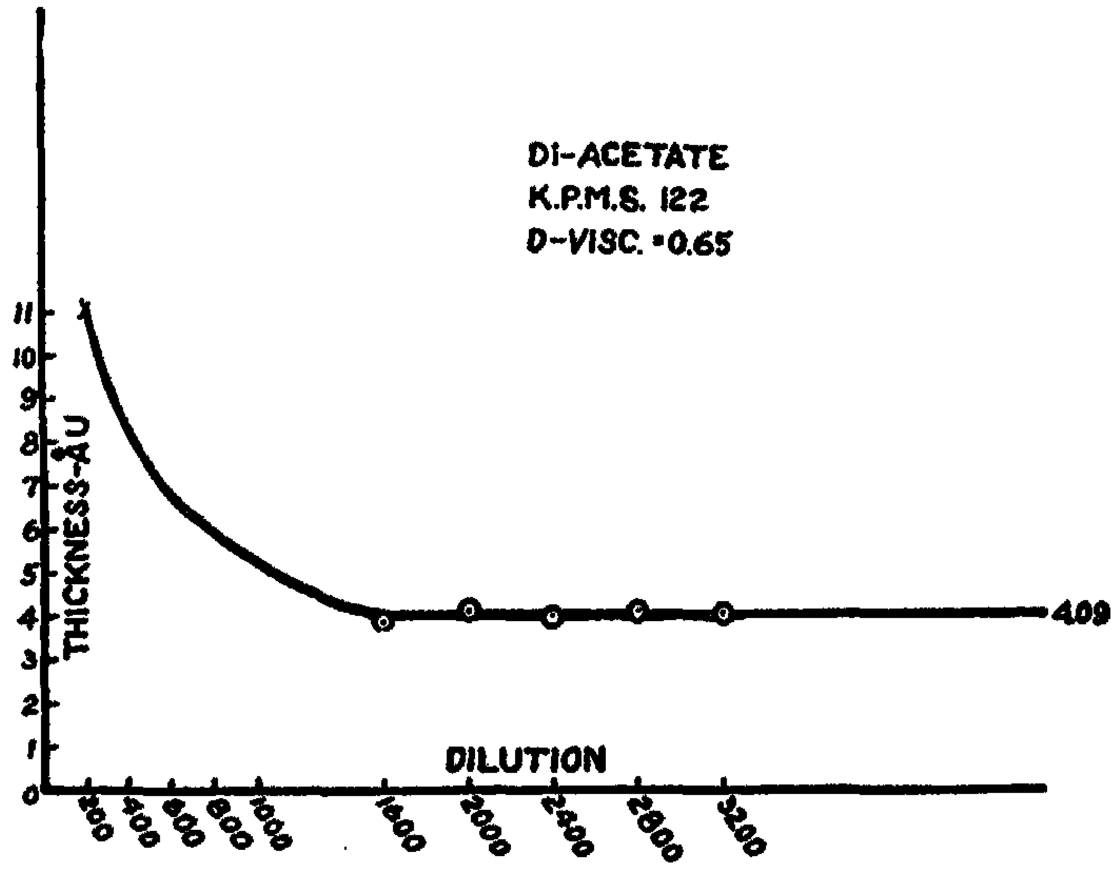

Fig. 6

Purification of the Mercury

The mercury was electrolyzed for three days by making it a cathode in a weak nitric acid solution. It was washed free from acid, dried, and distilled

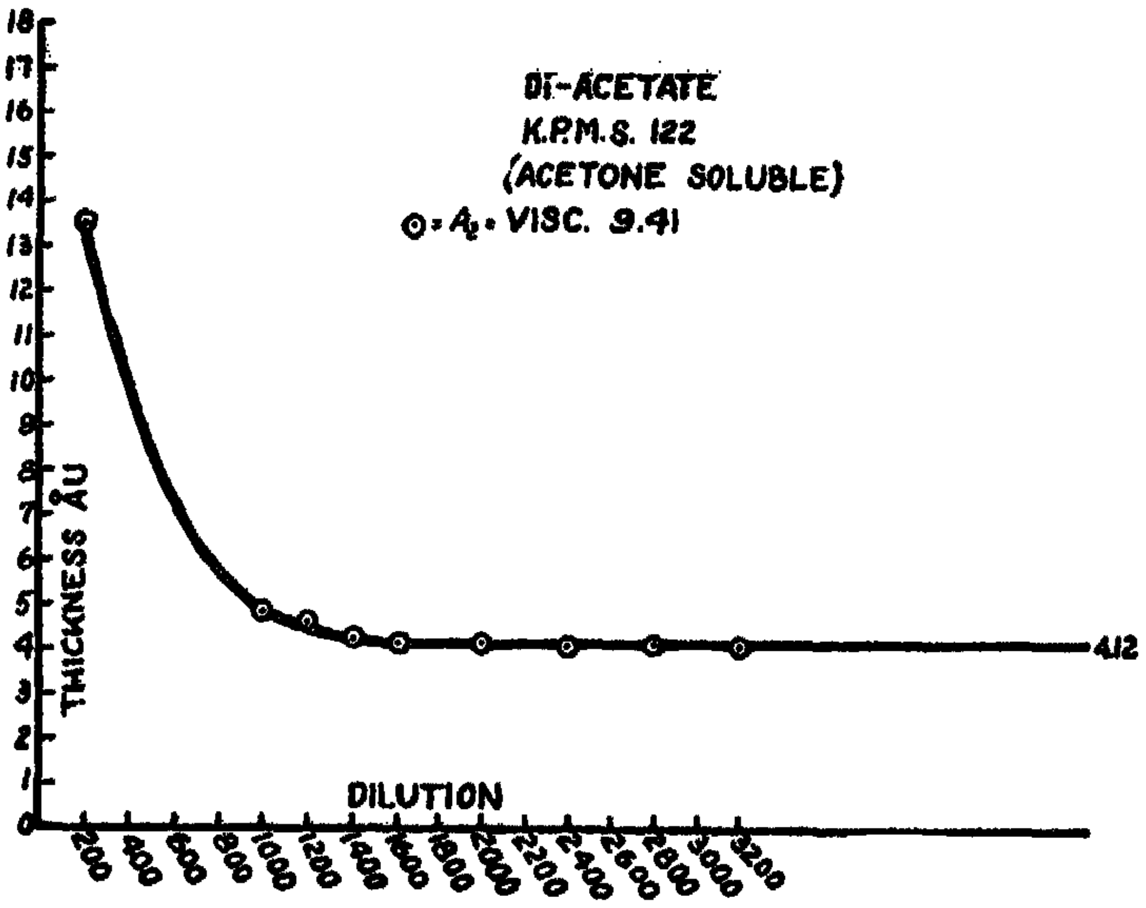
DI-ACETATE
K.P.M.S. 122
(ACETONE SOLUBLE)
⊙=A₂=VISC. 9.41
THICKNESS Å U
DILUTION
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000
3200
4.12

Fig. 7

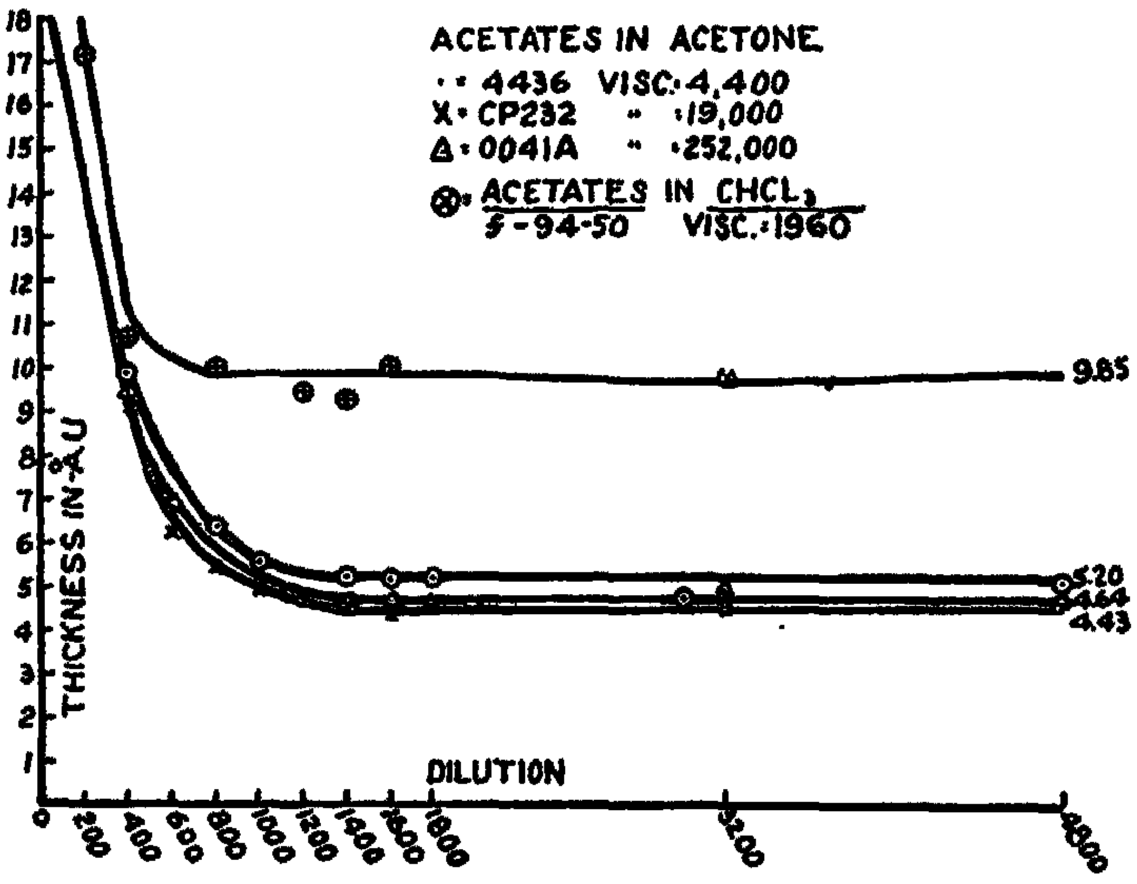
ACETATES IN ACETONE
· = 4436 VISC.=4,400
X = CP232 " =19,000
Δ = 0041A " =252,000
⊗ = ACETATES IN CHCL₃
§-94-50 VISC.=1960
THICKNESS IN Å U
DILUTION
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
200
400
600
800
1000
1200
1400
1600
1800
3200
4800
9.85
5.20
4.64
4.43

Fig. 8

three times in a vacuum, then placed in a photographic tray and covered with a thick film of cellulose acetate which was scraped off after some hours. It was found that the mercury improved steadily for several weeks after fresh films were coated on it and scraped off. At first, the films could not be formed by spreading but, as the surface became purer, spreading was finally accomplished. A thin film was always left on the surface when not in use. Thus a clean surface could easily be obtained by the scraping procedure.

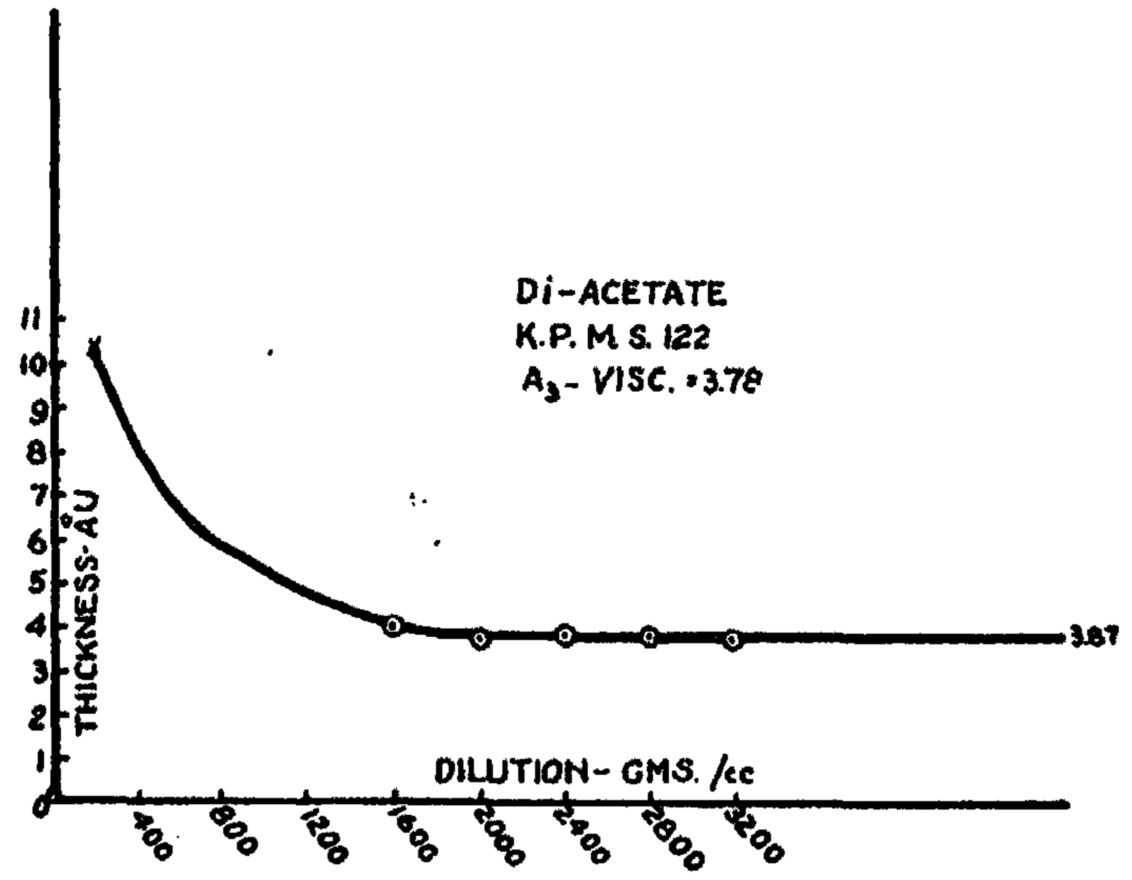

Fig. 9

Materials

The cellulose nitrates and acetates in the best state of purity were obtained in these laboratories. Solutions were made from solvents prepared at the Synthetic Organic Chemicals Department of the Eastman Kodak Co. and were of their purest stock.

The rubber was prepared by extracting pale crêpe with acetone to remove resins, and then diffusing it through a silk bolting cloth bag into petroleum ether, according to Feuchter's method.

The iso-electric gelatin was prepared by Mr. Hudson of these laboratories.

Description of the Apparatus

The apparatus consisted of an enameled photographic tray 4 cm. deep, 20 cm. wide, and 30 cm. long, which was placed in a bell jar fitted with a wooden cover to protect the mercury surface from air currents and to keep dust from settling on the mercury while standing over night (Fig. 4).

A scraper of flexible steel (Fig. 2) was made to fit tightly into the photographic tray by having strips of sheet cork at the ends. This scraper was allowed to dip a short distance into the surface of the mercury, which made it possible to scrape all surface impurities to one end of the tray.

The material was deposited on the mercury surface from a standardized dropper with a ground tip (Fig. 3). Only one drop of solution could be used for a given film. Drops falling after the first one do not touch the mercury surface but, instead, fall upon the solid film formed by the first drop, thereby preventing spreading. This was found to be true for those substances forming rigid (condensed) films.

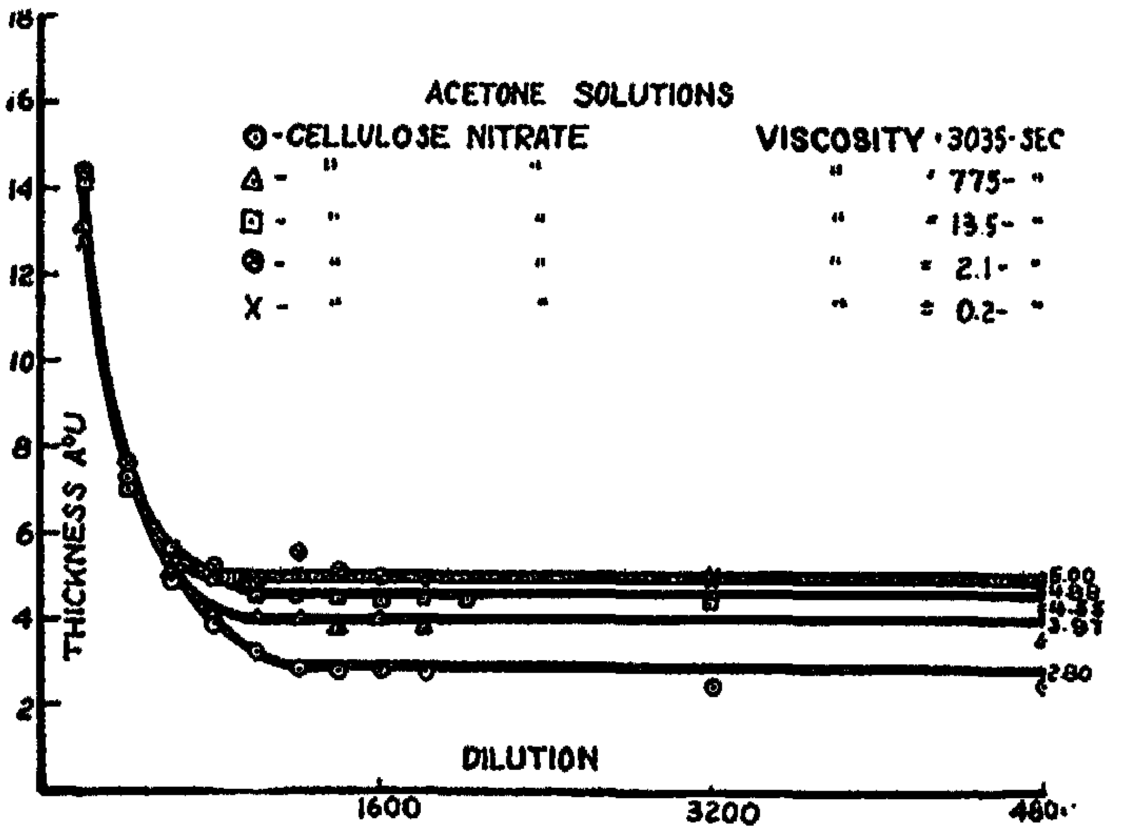

Fig. 10

A planimeter was used to measure the area of the film of which an outline had been traced on a glass plate (Fig. 1). The rigidity and irregularity of the film made direct area measurements impossible.

Experimental Procedure

A drop of solution containing a known amount of material was allowed to fall upon the scraped mercury. A film was obtained within a fraction of a second. The image of the film, developed with talc, was traced on a glass plate laid over the tray, and its area measured with a planimeter (Fig. 1). Several area measurements were made at each concentration (dilution). The dilutions were carried out to the point where the independent relation between thickness and dilution was well established. Solvent correction was made in each case where it was necessary.

In order to standardize the technique for working on mercury, several of the fatty acids were spread on mercury and the results compared with those recorded in the literature. These may be seen in Table I.

TABLE I

Compound	Formula	Solvent	T.Å.U.	T.Å.U.	Observers
Elaidic acid (isomer of oleic)	$C_{17}H_{33}COOH$	ether	12.2	11.2 (oleic)	Langmuir
Stearic acid	$C_{17}H_{35}COOH$	ether	21.9	21.8-25.0	Langmuir
Myristic "	$C_{13}H_{27}COOH$	acetone	22.5	21.1	Adams
N-Capric "	$C_9H_{19}COOH$	ether	13.6		

Discussion of Results

Figs. 5 to 10 show clearly that definite limit films of these bodies can be obtained on mercury. In the case of the cellulose esters and gelatin, an irregular, solid film was obtained (Fig. 11). At first, one might think that a drop of solution should spread in a circular fashion on a clean surface, but this is not the case.

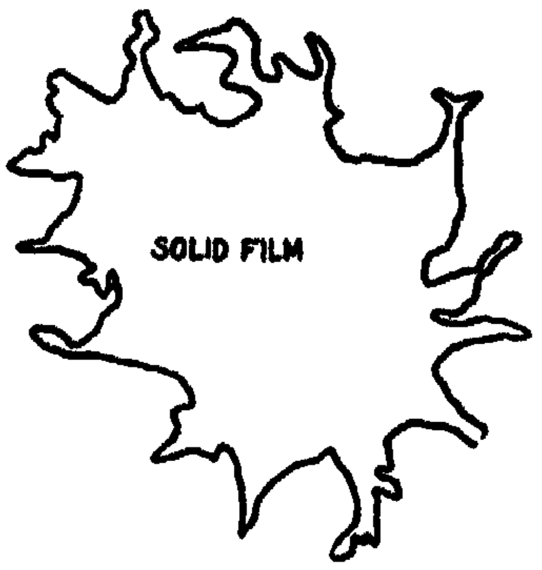

FIG. 11

When a drop of solution falls on mercury the surface forces cause spreading. The edge of the drop becomes thin, as it is forced out along the surface from the center, and the solvent evaporates, leaving a solid film of cellulose ester surrounding an island of solution. The surface forces continue to be effective, causing a squeezing out of more material from the center of the drop in order to reach its limit of spreading (monomolecular layer). To spread further, this solid film at the edge must break and let more solution out, pushing the thin solid rim to the side.

This causes a very irregular-shaped film, characteristic of the rigid films of this type.

Table II gives the comparative spreading and thickness relations between the cellulose esters at varying viscosities. The concentration 1 to 1600 was taken because all of the limit films could be noticed there as well as at higher dilutions and the 1 to 1600 concentration was more representative. The viscosities in column two are comparable in each series but not from one series to the next.

In the case of the nitrates an inverse relation between thickness and viscosity was found (Fig. 10).

A paper on "The Supermolecular State of Polymerized Substances in Relation to Thin Film and Interfaces"[1] contains a theoretical discussion on these thin films, from which the following conclusions are extracted.

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[1] Sheppard, Nietz, and Keenan: presented at the Symposium on Polymerization of the American Chemical Society Meeting, Swampscott, Mass., Sept., 1928, to be published shortly on *Ind. and Eng. Chemistry*.

TABLE II
Comparison Data

Cellulose Acetate Substance	Viscosity Centripoises	Concentration	Area sq. cm.	Thickness $\times 10^{-8}$ cm.	Remarks
F-94-50	1960	1–1600	53	9.85	$CHCl_3$ soluble Tri-acetate
C.P. 232	19,000	1–1600	241	4.43	
0041A	252,000	1–1600	230	4.64	Comb acetates
4436	4,400	1–1600	206	5.20	acetone soluble*
9565D_0	4.71	1–1600	142	4.01	85% $CHCl_3$ } soluble
9565D_1	5.67	1–1600	146	3.92	15% Et.OH }
9565D_2	6.39	1–1600	135	4.16	Hydrolyzed in
9565D_3	7.29	1–1600	145	3.81	suspension*
M.S. 122A_2	9.41	1–1600	257	4.12	Di-acetates
M.S. 122D	0.65	1–1600	273	4.09	Acetone soluble
M.S. 122A_3	3.78	1–1600	262	3.87	
Cellulose Nitrate	Viscosity Seconds				
T 59	3025	1–1600	296	2.80	
T 321	0.20	1–1600	168	5.00	
T 65	775	1–1600	202	3.97	Acetone soluble
T 64	13.5	1–1600	186	4.55	
T 322	2.10	1–1600	170	4.88	

*Approaching the di-acetates on acetyl contact.

These strikingly thin films seem to support the theory[1] that the cellulose bodies are composed of ribbons or chains of $C_6H_{10}O_5$ groups of an indefinite length, and a thickness amounting to approximately 2.5 Å.U. to 4.5 Å.U.

The iso-electric gelatin spread from water solutions on mercury (Fig. 12) gave values in good accord with the values obtained by E. Gortner and F. Grendel[2] for protein films on water.

The thinnest films obtained on mercury were those of rubber (Fig. 13). The thickness value (1.5 Å.U.) may possibly represent the value for the methyl group in Staudinger's isoprene chain.

Recently, H. Devaux[3] has described his work on the formation of thin films of sugars, starch, and albumen on mercury. His values also show extraordinarily thin films but his conclusions seem hardly necessary in view of the similarity between certain films formed on aqueous solutions and non-aqueous solutions.

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[1] Sponsler and Dore: Fourth Colloid Symposium Monograph, 174-202 (1925).

[2] E. Gortner and F. Grendel: Trans. Faraday Soc., 22, 477 (1926).

[3] H. Devaux: J. Phys. Radium, 9, 345 (1928). See also Sheppard and Keenan: Nature, June 23, 1928.

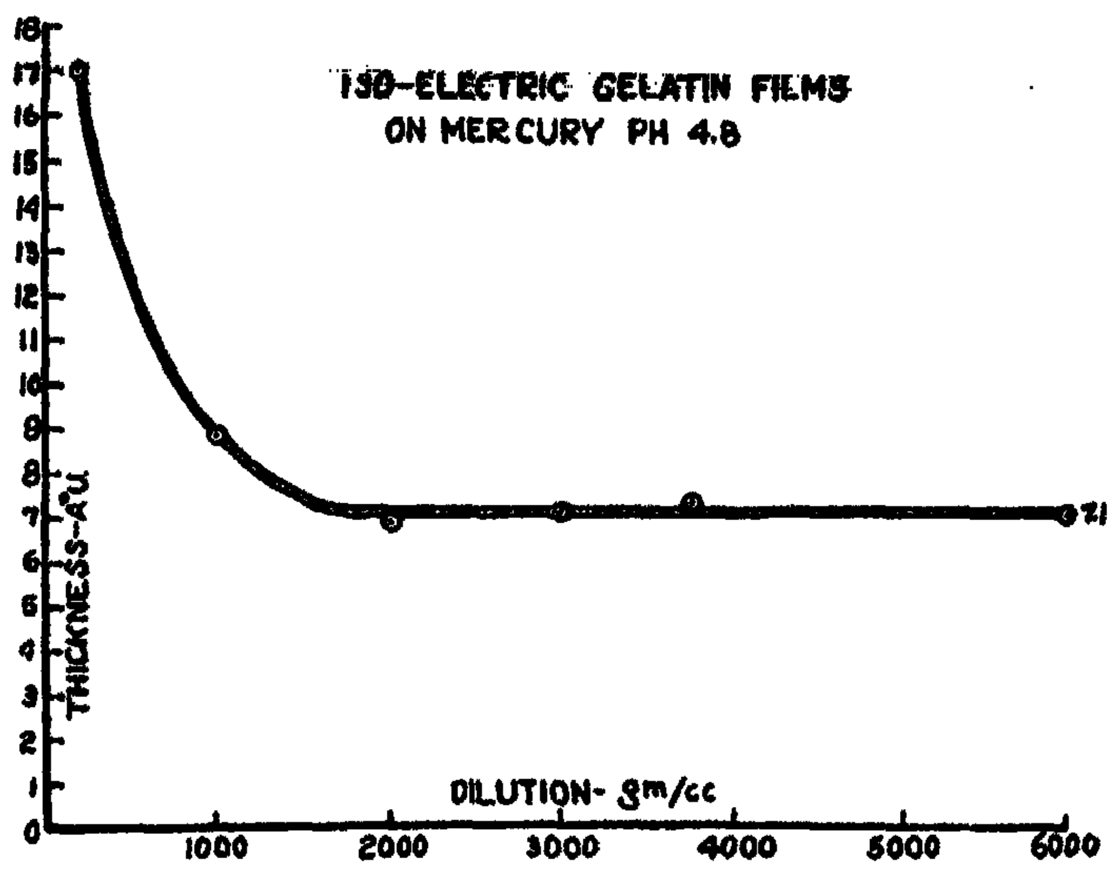
ISO-ELECTRIC GELATIN FILMS
ON MERCURY PH 4.8
THICKNESS-A°U.
DILUTION- g^m/cc
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
1000
2000
3000
4000
5000
6000
7.1

FIG. 12

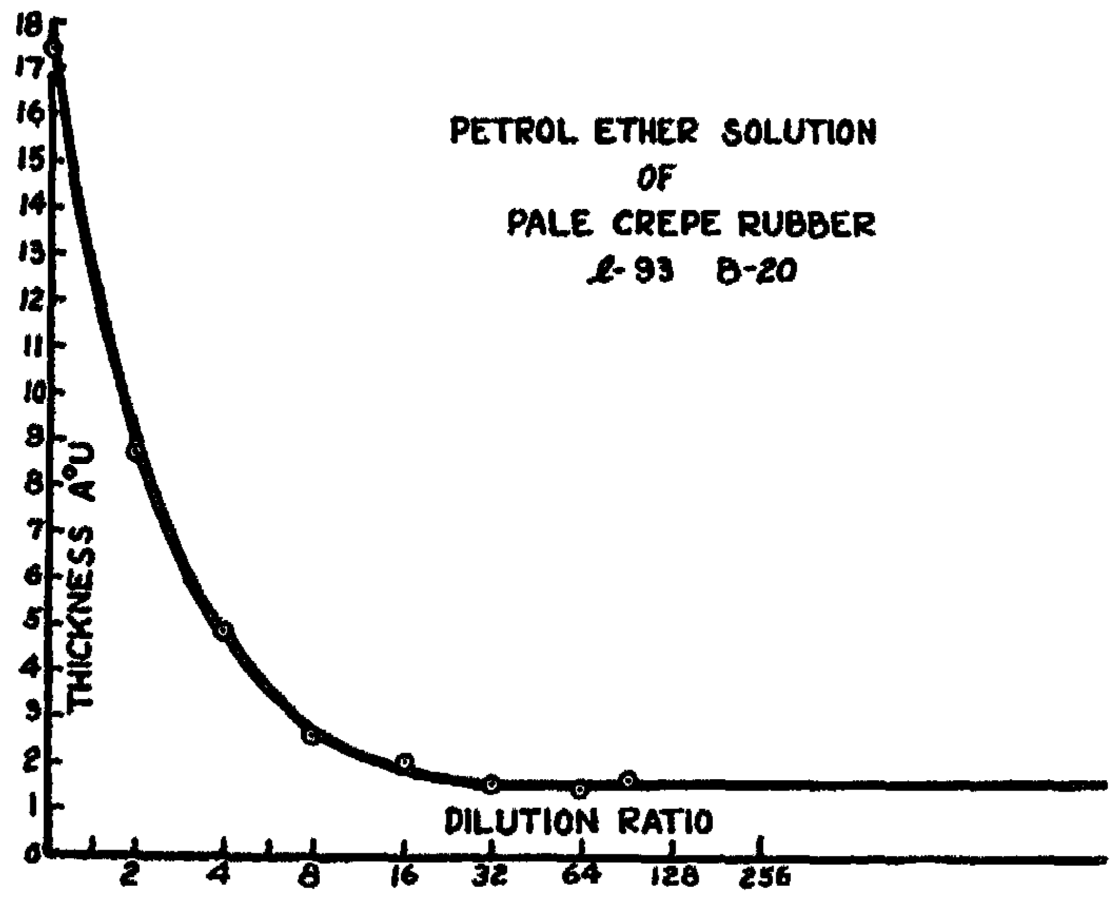
PETROL ETHER SOLUTION
OF
PALE CREPE RUBBER
ℓ-93 B-20
THICKNESS A°U
DILUTION RATIO
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
2
4
8
16
32
64
128
256

FIG. 13

If these films cannot be considered as a measure of one dimension of the molecule, then we must believe that they are not continuous, but consist essentially of a network structure. Work bearing on this phase is being started and it is hoped that the porosity, if it exists, may be determined.

Summary

1. A technique has been developed for obtaining thin films of organic colloids on mercury.
2. Several series of cellulose acetates, with varying viscosities and in different solvents, were used.
3. In the case of the cellulose nitrates, the limit film thickness varied in an inverse relation with the viscosity of the solutions.
4. Films of rubber and iso-electric gelatin were formed on mercury.
5. Films of the cellulose esters and gelatin were rigid, and condensed, while the rubber films were elastic.
6. The limit thickness increased with increasing complexity of the atom groups, as:—

Rubber	Cellulose	Gelatin
(C, H)	(C, H, O)	(C, H, O, N)
1.5 Å.U.	2.5. to 5.0 Å.U.	7.0 Å.U.

Conclusion

The results indicate that these films are composed of long chains or ribbon-like molecules lying flat upon the surface or of an open-work structure somewhat like a fish net.

The author wishes to express his appreciation for the valuable suggestions given by Dr. S. E. Sheppard and Dr. E. K. Carver of these laboratories.

IS HYDROGEN PEROXIDE FORMED IN ELECTROLYTIC GAS BY ALPHA RAYS?

BY BARNARD M. MARKS

The combination of hydrogen and oxygen at ordinary temperature has been produced in a variety of ways. The two modes of activation of immediate interest to the following experiments are activation by resonated mercury atoms and ionization by alpha particles from radon.

The first mode of activation has recently been used by Marshall[1] and by Bates and Taylor[2] who reported the formation of hydrogen peroxide by the use of resonated mercury atoms in mixtures of hydrogen and oxygen. They determined the amount of peroxide in their product by titration with permanganate. The hydrogen peroxide, as well as the water formed in the reaction, were removed together by condensation in a trap surrounded by a carbon dioxide-ether bath. They found that the amount of hydrogen peroxide produced was a function of the rate of flow as well as the ratio of oxygen to hydrogen.

The second method of activation was used in 1914 by O. Scheuer[3] who reported some extensive experiments on the interaction of hydrogen and oxygen under the influence of alpha-radiation from radon. He used the Lind[4] alpha-ray bulb as well as the system of Cameron and Ramsay[5]. The amount of reaction was determined by the change in pressure only. In order to account for the excess of hydrogen that he obtained on analysis of the initial and final systems over that required for the simple formation of water, he postulated the formation of hydrogen peroxide. In his conclusion he states: ". . . the analysis shows moreover the absence of ozone, or, since ozone cannot exist in the presence of hydrogen peroxide and mercury (as is the case in our experiments) . . ." This statement shows that in the system that he used there was mercury present. This will account for the disappearance of oxygen in excess of the proper quantity required for the formation of water.

Scheuer's experiments were carried out in a static system with no direct analysis for hydrogen peroxide; all of the excess of hydrogen in the residual gases being attributed to the formation of hydrogen peroxide. *It is evidently important to carry out the experiment under conditions where a direct analysis for hydrogen peroxide can be made.* In the present work such experiments were made in a flow system using alpha-particle ionization as shown in Fig. 1. The products of the reaction were collected in a liquid-air trap for a period of

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[1] A. L. Marshall: J. Phys. Chem., 30, 34 (1926); J. Am. Chem. Soc., 49, 2446 (1927).

[2] J. R. Bates and H. S. Taylor: J. Am. Chem. Soc., 49, 2763 (1927).

[3] O. Scheuer: Compt. rend., 159, 423 (1924).

[4] S. C. Lind: "Chemical Effects of Alpha-Particles and Electrons," 86 (1928).

[5] A. T. Cameron and Wm. Ramsay: J. Chem. Soc., 91, 931, 1266, 1593 (1907); 92, 966, 992 (1908).

72 hours so as to obtain a measurable concentration. The products were then allowed to distil into another liquid-air trap constructed so that it could be removed and weighed. During the distillation and the time required for the trap to warm sufficiently to remove it from the collection system, the exit gases were allowed to bubble through a solution of potassium iodide. If ozone is produced in the reaction its concentration must have been less than the vapor pressure of ozone at liquid air temperature as the above test gave no evidence of the presence of ozone. The receiver was stoppered immediately after it was removed from the collection system with a fitted stopper containing a plug of P_2O_5 to prevent loss of moisture. The whole was allowed to warm to room temperature and then weighed. Immediately after weighing, the receiver was added to an acid solution of the proper concentration for permanganate titration. The blank and sample were found to require the same amount.

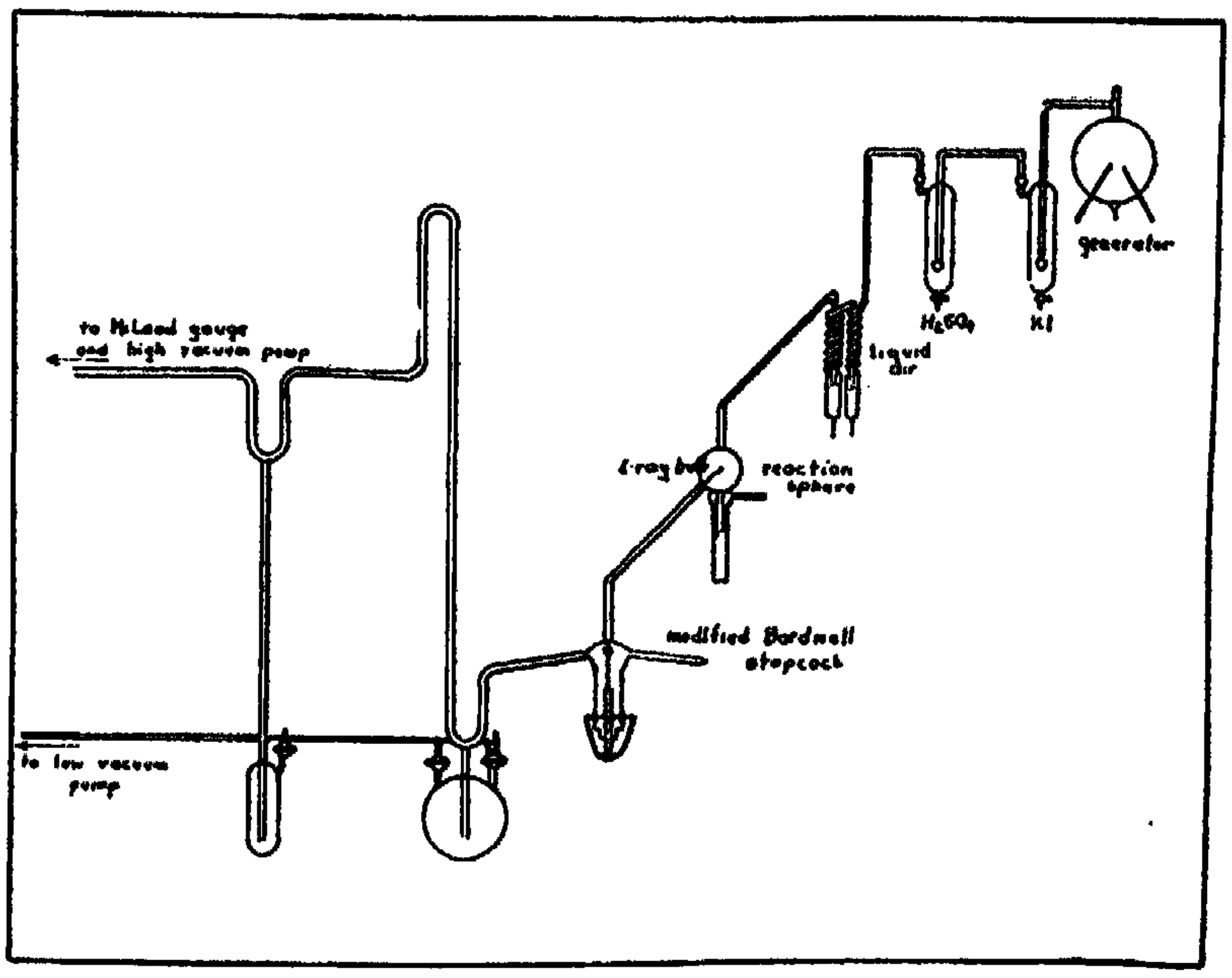

FIG. 1

In a second experiment the receiver was constructed so that it was immediately below the reaction chamber. This eliminated any possibility of loss due to the catalytic decomposition of the hydrogen peroxide due to the walls of the reaction vessel. A run of 92 hours was made during which time the receiver was immersed in liquid air. After that time, the receiver was warmed sufficiently to remove it and then placed in a desiccator as before. Immediately after weighing the contents of the receiver, the amount of peroxide was determined by adding a drop of 0.038 N permanganate solution. It was found that the amount of peroxide formed during that period was insufficient to affect the color. In an experiment to determine the sensitivity of the method used, it was found that 1.5×10^{-7} equivalents was sufficient to decolorize that amount of permanganate immediately.

In these experiments it was found that the amount of water collected in the traps was greater than the amount that would be predicted from the decrease of pressure in static experiments. This excess water was probably due to the liberation of occluded water from the walls of the reaction system. The results of the above experiments clearly indicate that the amount of peroxide formed in electrolytic gas by alpha rays, if any at all is formed, is very very small and the previously reported results obtained in a static system are in error probably due to the presence of mercury, which combined with part of the oxygen, leaving an excess of hydrogen, which was not evidence, however, of the formation of hydrogen peroxide.

Summary

No evidence of the formation of hydrogen peroxide by the action of alpha-particles on electrolytic gas has been obtained in experiments where a direct test was made for it.

The absence of ozone was also shown by direct test.

An explanation of the results of previous investigations, where the presence of hydrogen peroxide was claimed, is given.

The author wishes to express his appreciation to Dr. S. C. Lind who suggested the problem and under whom the work was carried out, and to Drs. R. S. Livingston and G. Glockler for their assistance.

University of Minnesota,
Minneapolis.

DISTRIBUTION OF ACETONE THROUGH A RUBBER MEMBRANE*

BY D. S. MORTON

Introductory

The law governing the distribution of a common solute between two liquid phases was worked out by Nernst[1] in 1891, and may be stated as follows: "If the molecular weight of the solute is the same in both solvents, the ratio in which it distributes itself between them is constant for a given temperature." That is,

$$c_1/c_2 = K$$

where c_1 is the concentration of the solute in the first phase, c_2 is the concentration in the second phase. K is called the distribution coefficient and depends upon the temperature and the nature of solute and solvent. The concentrations c_1 and c_2 correspond to solutions having equal partial pressures of the solute in the vapor phase, since both solutions are in equilibrium with the same vapor.

The distribution of iodine between water and carbon disulphide was investigated by Berthelot and Jungfleisch.[2] They obtained a constant distribution ratio when concentrations were expressed in grams solute per 10 cc. of solvent, that is, a constant ratio of the volume concentrations of the two phases.

A thorough investigation of the distribution of succinic acid between water and ether was carried out by Forbes and Coolidge.[3] This case was complicated by the mutual solubility of the ether and water. The distribution ratio was not a constant when volume concentrations were used, but did come out nearly constant when compositions were expressed as mol fractions.

It has been shown by Bell and Field[4] that solutions of ammonia in water and chloroform deviate considerably from the distribution law at high concentrations.

It is at once evident that in cases of unlimited solubility the ratio of the volume concentrations cannot remain constant as concentration increases, unless that ratio is unity. For, as we add solute to the system, the composition of each liquid phase approaches pure solute, and the limiting value of the distribution coefficient is equal to the ratio of the density of the solute to the density of the solute, or unity. But in general the distribution coefficient is

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* A thesis presented to the Faculty of the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Master of Arts. This paper is preliminary to the programme now being carried out at Cornell University under a grant to Professor Bancroft from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[1] Z. physik. Chem., 8, 110 (1891).

[2] Ann. Chim. Phys., (4) 26, 396 (1872).

[3] J. Am. Chem. Soc., 41, 15 (1919).

[4] J. Am. Chem. Soc., 33, 940 (1911).

not equal to unity, and hence the ratio of the volume concentrations is not a constant. A similar objection applies to expressing concentrations as mol fractions.

Professor Bancroft suggests that the distribution equilibrium is primarily a function of mass concentration (grams solute per gram solvent) rather than of volume concentration. A study of dilute solutions affords little evidence on this point because of the approximate proportionality between mass and volume concentration. It is the purpose of this thesis to investigate distribution equilibria between concentrated solutions and to find out if it is possible to derive a simple relation for the distribution in terms of mass concentrations.

A rubber membrane is readily permeable to acetone, much less permeable to methyl alcohol, and practically impermeable to water. Under ordinary conditions, methyl alcohol and water are miscible in all proportions; but they form a two-phase system when separated by an impermeable membrane. When acetone is added to the system, it should pass through the membrane and distribute itself between the two phases in a manner analogous to the distribution of a solute between immiscible solvents. The system will attain equilibrium when the concentrations of the two phases become adjusted so as to give the same partial pressure of the acetone in the vapor over each phase. We have here a unique opportunity to study distribution equilibria over the entire composition range from zero to 100 percent, and to determine whether or not the effects are primarily dependent on mass concentration.

One distinction between distribution through a semi-permeable membrane and the ordinary distribution between immiscible liquids should be noted. In the ordinary case both solvents, as well as the solute, are in equilibrium with the same vapor phase, whereas in the case of the membrane the solute only is in equilibrium in the vapor phase. This circumstance in no way affects the general validity of conclusions drawn from distribution through membranes; in both cases the equilibrium is actually determined by the partial pressure of the solute in the vapor.

Experimental

The first series of experiments is concerned with determining directly the distribution of acetone between methyl alcohol and water by dialysis with rubber membranes. The object of the second series of experiments is to check up on the results of the distribution experiments by means of measurements of the partial pressures of acetone over acetone-water and acetone-methyl alcohol solutions.

Materials. J. T. Baker's absolute methyl alcohol and Kahlbaum's acetone from bisulphite compound were employed. Specific gravity determinations indicated less than 0.1% water in the methyl alcohol. The acetone was redistilled before using; the specific gravity of the distillate indicated the presence of about 0.5% water.

Apparatus and method. The simple form of apparatus shown in Fig. 1 gave satisfactory results. An inverted thistle tube[1] A was supported by a cork stopper in the 100 cc wide-mouth bottle B. A rubber membrane cut from a toy balloon was fastened tightly across the bottom of the thistle tube. All membranes were tested for leaks before using. The thistle tube was corked at the top after introducing the solutions and the corks sealed with paraffine to preclude loss of vapor. About 5 cc of the acetone-water solution were placed inside the thistle tube, and about 50 cc of the acetone-methyl alcohol solution outside, in contact with the membrane. The purpose of using such unequal quantities of the two solutions was to allow for considerable gain or loss of acetone by the water solution without materially affecting the composition of the methyl alcohol phase.

Fig. 1

Due to slow permeation of the membrane by methyl alcohol, it was found impracticable to obtain an equilibrium simply by adding acetone to one of the phases and letting the concentrations adjust themselves. To locate the equilibrium point for a given acetone-water solution an adaptation of the method of Bancroft and Nugent[2] was adopted. An acetone-water solution of the desired composition was made up by weighing out and mixing the components. Portions of this solution were then placed in the distribution apparatus, in contact with a series of acetone-methyl solutions of regularly graded concentrations. Under these conditions the water solution would gain or lose acetone according as the methyl alcohol solution was more or less concentrated than the equilibrium value. The amount of acetone gained or lost by the water solution was determined by analyses. A good approximation of the concentration of the methyl alcohol phase that would exist in equilibrium with the water phase could then be obtained by interpolation between the highest observed concentration that gained acetone from the water and the lowest observed concentration that lost acetone to the water.

For instance, to determine the distribution for a 10 percent acetone-water solution, portions of the 10 percent solution were run against acetone-methyl alcohol solutions containing 1 percent, 10 percent, 20 percent and 50 percent acetone respectively. The water gained acetone from the 20 percent solution but lost acetone to the 10 percent. Hence the equilibrium point lay somewhere between 10 and 20 percent. The experiment was therefore repeated using 12, 14, 16, 18 and 20 percent acetone-methyl alcohol solutions. Acetone was gained from the 18 percent solution and lost to the 16 percent solution. By interpolation the equilibrium point was estimated to be about 16.5 percent acetone in the methyl alcohol solution.

The acetone in the water solution was determined by the Messinger method.[3] This method, which requires a sample containing about 0.01 g of

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[1] The draughtsman did not make a good thistle tube.

[2] Colloid Symposium Monograph, 5, 149 (1927).

[3] Goodwin: J. Am. Chem. Soc., 42, 39 (1920).

acetone, gave results which were consistent but invariably a little low. For this reason the original water solution was analyzed, although its composition was known accurately, in order to get a figure with which to compare results obtained after contact with the methyl alcohol solutions.

Acetone-methyl alcohol solutions were made up to the concentrations desired by measuring the liquids carefully out of calibrated burettes.

Experimental conditions. All work was done at room temperature, about 23°C ±1°. Solutions were allowed to remain in contact 24 hours, and were shaken thoroughly three or four times during the standing period.

Errors. The most annoying source of error was the tendency of the methyl alcohol to pass through the membrane into the water solution. The volume of the water solution phase would usually show a marked increase inside of a week and would continue to increase as long as the solutions remained in contact. In some instances an osmotic pressure sufficient to rupture the membrane or blow out the corks was developed.

Unfortunately there is no good method for determining small amounts of methyl alcohol in the presence of acetone. It is possible, however, to infer indirectly the effect of the methyl alcohol by analyzing solutions for acetone at frequent intervals. Results of such a series of analyses indicated that the equilibrium was approached in three stages:

(1) *Saturation of the rubber membrane with acetone.* All water solutions, whether more or less concentrated than the equilibrium composition, showed a small initial loss of acetone. This loss appeared to be due to absorption of the acetone by the rubber membrane, equilibrium being attained within five hours or less.

(2) *Osmosis of the acetone through the rubber membrane* from the water side to the methyl alcohol side, or vice versa, depending on the ratio of the acetone concentrations in the two phases. This flow of acetone proceeded fairly rapidly and gave an easily determinable concentration change within 24 hours. The direction of the osmosis, as has been pointed out, is an index of the position of the acetone-methyl alcohol solution with respect to the equilibrium point for the given acetone-water solution.

(3) *Slow osmosis of the methyl alcohol accompanied by acetone.* All acetone-water solutions, regardless of composition, began to gain acetone at the end of two days and continued to do so as long as observations were taken. This effect can be explained by assuming that methyl alcohol, especially in the presence of acetone, permeates the rubber membrane slowly and introduces methyl alcohol eventually into the water solution. Since the methyl alcohol solution always contains more acetone than the water solution in equilibrium with it, it seems reasonable to expect that as the concentration of the methyl alcohol increases in the water solution, the concentration of the acetone will increase correspondingly. The water solution is changing over into a methyl alcohol solution, so to speak, and is approaching the composition of the methyl alcohol solution on the other side of the membrane. This hypothesis

seems to be the only one that accounts for the observed continuous increase in the concentration of acetone in the water layer.

These three effects undoubtedly proceed more or less simultaneously. So far as could be determined from the results of the analyses, the second effect was the predominant one after a standing period of 24 hours; estimates of the equilibrium point were therefore based on analyses taken 24 hours after placing the solutions in contact. Values for the equilibrium concentration were thus obtained agreeing within 1 percent or less on the lower concentrations and 1 and 2 percent on the higher concentrations.

Check results obtained at different times indicated that the error introduced by variations in room temperature was slight compared with the error due to diffusion of the methyl alcohol.

The analytical method used gave results concordant to 1 part in 100 parts of acetone—a degree of accuracy entirely adequate for the purpose of these experiments.

An occasional extraordinary result was rejected as being due to a defective rubber membrane.

Results. The equilibria obtained for the various acetone-water solutions are shown in Table I. There is no evidence of constancy in the distribution ratio regardless of the mode of expressing concentration.

Curves. In order to determine whether the distribution equilibrium could be represented by any simple type of equation in terms of mass concentration,

TABLE I

Distribution of Acetone between Water and Methyl Alcohol at 23°

A = Gram percentage acetone in water solution
B = Gram percentage acetone in alcohol solution
C = Ratio of gram percentages = B/A
D = Mass concentration acetone in water solution = A/100 − A
E = Mass concentration acetone in alcohol solution = B/100 − B
F = Ratio of mass concentrations = E/D
G = Mol fraction acetone in water solution
H = Mol fraction acetone in alcohol solution
I = Ratio of mol fractions = H/G

A	B	C	D	E	F	G	H	I
0	0	—	0	0	—	0.000	0.000	—
10	17	1.70	0.111	0.205	1.85	0.033	0.102	3.05
20	32	1.60	0.250	0.471	1.88	0.072	0.206	2.86
30	46	1.53	0.429	0.852	1.99	0.119	0.319	2.68
40	59	1.47	0.666	1.44	2.16	0.171	0.443	2.59
50	69.5	1.39	1.00	2.28	2.28	0.239	0.557	2.40
60	77.5	1.29	1.50	3.44	2.30	0.318	0.655	2.06
70	85	1.21	2.34	5.66	2.42	0.420	0.757	1.80
100	100	1.00	∞	∞	∞	1.000	1.000	1.00

concentrations of the acetone-methyl alcohol solutions were plotted against corresponding concentrations of acetone-water solutions on logarithmic paper. The result is a very satisfactory straight line. This means that the data can be represented by $\log (G_{Ac}/G_{Alc}) - a \log (G'_{Ac}/G_W) = \log K$, as shown in Table II.

TABLE II

Distribution of Acetone between Water and Methyl Alcohol at 23°

$$\log \frac{G_{Ac}}{G_{Alc}} - 1.09 \log \frac{G'_{Ac}}{G_W} = \log K = 0.3502$$

% acetone in water solution	% acetone in alcohol solution	$\frac{G_{Ac}}{G_{Alc}}$	G_{Ac}/G_W found	calc.	log K calc.
10	17	0.205	0.111	0.111	0.3567
20	32	0.471	0.250	0.239	0.3303
30	46	0.852	0.429	0.412	0.3312
40	59	1.44	0.666	0.667	0.3508
50	69.5	2.28	1.00	1.017	0.3579
60	77.5	3.44	1.50	1.482	0.3446
70	85	5.66	2.34	2.341	0.3541

The agreement is satisfactory over the whole range covered by the experiments—up to seventy-six mol percent of acetone in the methyl alcohol solution. If the equation is to be tested further, some more exact method of measuring the distribution ratio at high concentrations must be devised.

Vapor Pressure Measurements

In any case of equilibrium of a solute between two liquid phases, the partial pressure of the solute in each phase must be the same. Therefore a distribution curve for the system acetone-water-methyl alcohol can be deduced from vapor pressure data, by plotting acetone-methyl alcohol solutions against acetone-water solutions having equal partial pressures of acetone in the vapor phase. In view of the possibility of error due to osmosis of the methyl alcohol in the membrane experiments, it seemed desirable to check up on the results by means of partial pressures.

Since up to the present writing there appear to be in the literature no accurate vapor pressure data on the system acetone-water, and none at all on acetone-methyl alcohol, it was necessary to obtain these data experimentally.

The partial pressure of a constituent of a vapor is equal to the product of the total vapor pressure and the mol fraction of the constituent, assuming validity of the gas laws and normal molecular weights. To compute the partial pressure we must determine in some manner both the composition and total pressure of the vapor.

The usual method of determining vapor compositions is to condense the vapor completely and analyze the condensate. Unless considerable care is taken, error will be introduced by refluxing during the vaporization and by incomplete condensation of the vapor. The composition of the original liquid may be measurably changed by the distillation, and if this occurs there is always some uncertainty as to what composition of residue corresponds with the observed composition of the distillate. Various ingenious methods have been devised to eliminate or reduce these causes of error.[1] By using special precautions and rather elaborate forms of apparatus it seems to be possible to secure results of a fair degree of accuracy by the isothermal distillation method.

A second method, that has received less attention, consists in measuring some physical property of the vapor which is a known function of its composition, such as refractive index. This method is theoretically the ideal one since it permits a direct analysis of the vapor phase under equilibrium conditions. Cunaeus[2] attempted to work out the system acetone-ether by analyzing the vapor phase with an interferometer, but got into difficulties which he attributed to condensation of vapor in the end of his tubes. More recently Hoover and Glassey[3] have used the interferometer to determine vapor compositions in systems of two volatile liquids, and report good agreement with Wrewsky's results for the systems ethyl alcohol-water and methyl alcohol-water.

A method similar to that of Cunaeus was adopted for the present investigation. The vapor in equilibrium with a given solution was admitted into the interferometer and its refractivity measured against air as a standard. Assuming refractivity to be a linear function of vapor composition, the vapor composition and the partial pressure of each component were obtained by a simple calculation.

The interferometer used was found incapable of compensating for the difference between the refractivity of air at atmospheric pressure and that of the vapors under their own vapor pressures. Hence in every case the pressure of the air was reduced in the interferometer chamber until its refractivity exactly equaled that of the vapor. In this way calibration of the instrument was avoided, temperature corrections applicable to difference in refractivity were eliminated, and calculations were greatly simplified.

Formulas. Following is a derivation of equations expressing refractivity and composition in terms of measured quantities.

Let R_A = refractivity of gas A at pressure pA, absolute temperature T_A
R_B = " " " B " pressure pB, absolute temperature T_B
R_C = " " " C " pressure pC, absolute temperature T_C
R_M = refractivity of mixture of A and B at pressure pM, temperature T_M
a = mol fraction of A in mixture
b = " " " B " "
$\overline{R}_A$, $\overline{R}_B$, $\overline{R}_C$, $\overline{R}_M$ = respective refractivities at 760 mm., 273°A.

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[1] Wrewsky: Z. physik. Chem., 81, 1 (1912); Sameshima: J. Am. Chem. Soc., 40, 1482 (1918).

[2] Cunaeus: Z. physik. Chem., 36, 232 (1901).

[3] Hoover and Glassey: Trans. Roy. Soc. Canada, III (3), 19, 35 (1925).

(1) By definition, $R = n - 1$

(2) By law of Gladstone and Dale[1]

$$\frac{n-1}{d} = \frac{R}{d} = r_1,$$

where d = density of gas,

r_1 = a constant called the specific refraction.

(3) Assuming validity of the gas laws,

$$d \propto p/T$$

$$\text{or } R = k(p/T)$$

(4) For $R_A = \overline{R}_A$, $k = \dfrac{273\,\overline{R}_A}{760}$

(5) Subs

$$R_A = \frac{273\,p_A}{760\,T_A}\,\overline{R}_A$$

$$R_B = \frac{273\,p_B}{760\,T_B}\,\overline{R}_B$$

(6) So far as is known the refractivity of a gas mixture is very nearly additive. Therefore

$R_M = aR_A + bR_B = aR_A + (1-a)\,R_B$[*]

(7) Solving for a,

$$a = \frac{R_M - R_B}{R_A - R_B} = \frac{R_M - \dfrac{273p_M}{760T_M}\,\overline{R}_B}{\dfrac{273p_M}{760T_M}(\overline{R}_A - \overline{R}_B)}$$

$$= \frac{\dfrac{760T_M}{273p_M}\,R_M - \overline{R}_B}{\overline{R}_A - \overline{R}_B} = \frac{\overline{R}_M - \overline{R}_B}{\overline{R}_A - \overline{R}_B}$$

(8) Under experimental conditions $R_M = R_C$, $T_M = T_C$

(9) But $\overline{R}_M = \dfrac{760T_M}{273p_M}\,R_M = \dfrac{760T_M}{273p_M}\,R_C$

$$= \frac{760T_M}{273p_M}\cdot\frac{273p_C}{760T_C}\,\overline{R}_C = \frac{p_C}{p_M}\,\overline{R}_C$$

(10) In these experiments C is dry air free from carbon dioxide, and $\overline{R}_C = .0002917$[2]

(11) Subs, $\overline{R}_M = \dfrac{p_C}{p_M}\,(.0002917)$

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[1] Phil. Trans. (1858).

[*] R_A, R_B, R_M for same temp. and pressure.

[2] Meggers and Peters: Bur. Standards Bull., 14, 698-740 (1918).

In the following experiments the zero refractivities of acetone, methyl alcohol, and water were first determined, and the values substituted in equation (7) for $\bar{R}_A$ and $\bar{R}_B$. The zero refractivities $\bar{R}_M$ of various mixed vapors were then determined by observing the vapor pressure of the solution p_M and the pressure p_C of air having equal refractivity, and applying equation (11). The mol fraction of acetone in the vapor could then be calculated by substituting for $\bar{R}_M$ in equation (7).

Apparatus. (Fig. 2.)

The solution under investigation is contained in the glass-stoppered flask F. This flask is provided with a side tube communicating with the right-hand gas chamber I_2 of the interferometer, and with the manometer M_2. There are also tubes connecting with a vacuum pump with stopcocks *c*, *d*, and *e* inserted as shown. The far end of the chamber I_2 is connected through a stopcock with tubes containing calcium chloride and soda-lime (not shown in the figure).

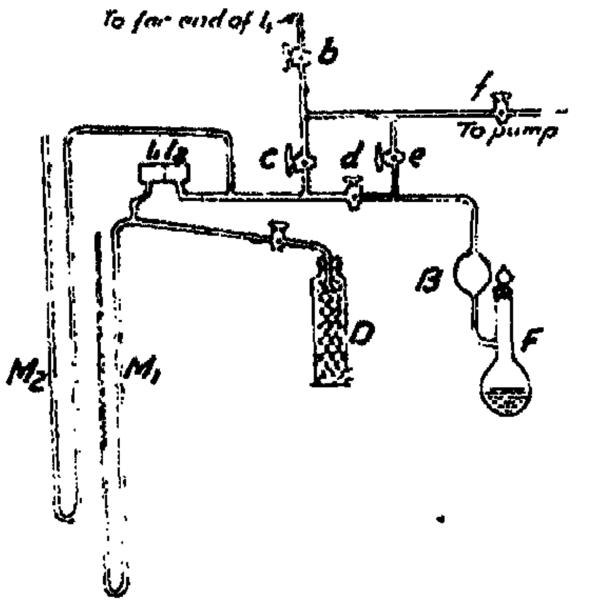

FIG. 2
Apparatus for determination of partial vapor pressures

A tube is run from the pump line to the remote end of the gas chamber I_1, with stopcock at *b*. The near end of chamber I_1 communicates with manometer M_1 and with the atmosphere through stopcock *a* and drying tower D, which is filled with calcium chloride and soda-lime.

Ordinary 7 mm. glass tubing was used for the manometers and connecting tubes. Stopcocks were of 2 mm. bore. Rubber connections were avoided as far as possible in those parts of the apparatus coming in contact with acetone vapor; it was necessary, however, to use two short lengths of rubber tubing to connect the glass tubing with the brass nipples on the extremities of the interferometer chamber.

The interferometer was of the Zeiss laboratory type, with gas chambers 100 cm. long. It was easily capable of measuring refractivities to 1×10^{-6}.

Experimental procedure. The liquid under investigation was introduced in flask F and the stopper inserted. The flask and its contents were then thoroughly cooled with carbon dioxide-alcohol mixture. With stopcocks *b*, *c*, and *d* closed and *e* and *f* open, the space over the solution was evacuated for an hour or more to remove the air. Little vapor was lost in the evacuation because of the low vapor pressure of the solution at the temperature of solid carbon dioxide. After the air had been pumped off, stopcock *e* was closed and the cooling bath removed. A water bath regulated at 20°C was put in contact with the flask F.

While waiting for the solution to warm up to 20° the interferometer was adjusted by drawing air at atmospheric pressure into both gas chambers and turning the compensator screw so as to bring the interference bands to the zero position. This was repeated two or three times, or until the setting was constant.

Stopcock *d* was then closed, *c* was opened, and the interferometer chamber I_2, manometer M_2, and connecting tubes evacuated to .1 mm. or less, when *c* was closed again. Stopcock *d* was opened to admit the vapor into the interferometer, flask F being shaken to hasten the equilibrium. At the same time the pressure of the air in chamber I_1 was slowly reduced, by opening *b* slightly and pumping, until the interference bands as viewed through the eyepiece of the interferometer were brought back to the zero position, when *b* was closed. The heights of the mercury columns in the two manometers were then observed. The difference between atmospheric pressure and the reading on M_2 was equal to p_M, the vapor pressure of the solution, while the difference between atmospheric pressure and the reading on M_1 gave the pressure p_a of air having the same refractivity as the vapor.

The refractivity as calculated from the first few readings generally came out too low, probably because of some residual air remaining in the solution. Therefore some of the vapor was pumped off through *e* and the observations repeated, until p_M and p_a became constant.

Some difficulty was experienced in establishing a state of equilibrium between the liquid and the vapor in remote parts of the apparatus. By jarring and shaking flask F persistently, however, one could usually succeed in bringing the interference bands to a fairly stable position. It would have been better to provide F with a magnetic stirrer.

A very gradual but steady displacement of the bands took place even after equilibrium appeared to be established; this may have resulted from slow vaporization of heavy impurities in the acetone. As a rule this effect was too slow to interfere much with the readings. Duplicate runs gave values of p_a checking to 1 mm. or less in most cases.

TABLE III

Vapor Pressures of Acetone-Water Solutions at 20°C

A Percent acetone in Solution	B Mass conc. $B = \frac{\text{acetone}}{100 - A}$	p_M Total vapor pressure mm	$\overline{R}_M$ Zero refract. of vapor	a Mol fraction of acetone in vapor $a = \frac{\overline{R}_M - 255}{877}$	p_A Partial pressure of acetone $p_A = ap_M$ mm	p_W Partial pressure of water $p_W = p_M - p_A$ mm
0.0	.000	17.1	255 $(10)^{-6}$	.000	0.0	17.1
10.3	.116	49.2	996	.845	41.2	8.0
20.0	.250	81.1	1051	.913	73.2	7.9
29.3	.414	103.3	1094	.956	98.5	4.8
39.0	.639	119.8	1100	.964	115.8	4.0
58.3	1.39	141.5	1112	.975	138.1	3.4
79.6	3.90	156.3	1113	.976	152.5	3.8
100.0		179.2	1132	1.00	179.2	0.0

All solutions were made up by weighing out the components. About 50 ml. of solution were used for a run. In the case of acetone-water solutions the specific gravity of each solution was determined after the experiment and the composition obtained from Young's[1] table. The results are given in Tables III and IV.

TABLE IV

Vapor Pressures of Acetone-Methyl Alcohol Solutions at 20°C

A Percent acetone in solution	B Mass conc. $B = \frac{\text{acetone}}{100-A}$	p_M Total vapor pressure mm	$\overline{R}_M$ Zero Refract. of vapor	a Mol fraction of acetone in vapor $a = \frac{R_M - 600}{534}$	p_A Partial pressure of acetone $p_A = ap_M$ mm	p_B Partial pressure of methyl alcohol $p_B = p_M - p_A$ mm
0.0	.000	96.0	600 $(10)^{-6}$	.000	0.0	96.0
10.0	.111	110.8	738	.258	28.6	82.2
24.2	.319	128.4	837	.444	57.0	67.4
30.0	.423	134.2	888	.540	72.4	61.8
40.0	.666	145.4	928	.614	89.2	56.2
49.8	.992	154.4	959	.672	103.8	50.6
60.0	1.50	162.9	989	.729	118.8	44.1
70.1	2.35	169.8	1014	.775	131.6	38.2
80.1	4.02	173.5	1044	.831	144.2	29.3
90.1	9.06	179.0	1082	.902	161.4	17.6
100.0		179.2	1132	1.000	179.2	0.0

Curves and discussion. In order to check up on the results of the membrane experiments partial pressures of acetone were plotted against percentage of acetone. Curve (1), Fig. 3, shows the relation for the system acetone-water, and curve (2) that for the system acetone-methyl alcohol.

The compositions required for equilibrium between the two solution phases are obtained by taking abscissae corresponding to the same partial pressure ordinate. Thus, the ordinate 41 mm. intersects the water solution curve at 10 percent and the methyl alcohol solution curve at 16 percent. Therefore a 10 percent acetone-water solution will exist in equilibrium with a 16 percent acetone-methyl alcohol solution.

Table V consists of corresponding abscissae read off the two curves:

TABLE V

Acetone-water % acetone	Acetone-methyl alcohol % acetone	Acetone-water % acetone	Acetone-methyl alcohol % acetone
0.0	0.0	40.0	59.4
10.0	16.1	50.0	69.0
20.0	30.5	60.0	76.2
30.0	46.6	70.0	81.5

---

[1] Young: "Distillation Principles and Processes," 261 (1922).

The curve corresponding to these values is shown in Fig. 4, (2). Curve (1) is the one obtained from the rubber-membrane experiments. The agreement between the two curves is fairly satisfactory when one considers that they were obtained by entirely independent methods, each involving more or less error. The primary object of this investigation has been to determine the form of the vapor pressure and distribution relationships in concentrated solutions, rather than to carry out measurements to a high degree of precision.

The fact that the distribution equilibria can be represented by a simple linear equation in terms of mass concentration suggests that a similar equation can be found for the partial vapor pressures. Professor Bancroft proposes the formula[1]

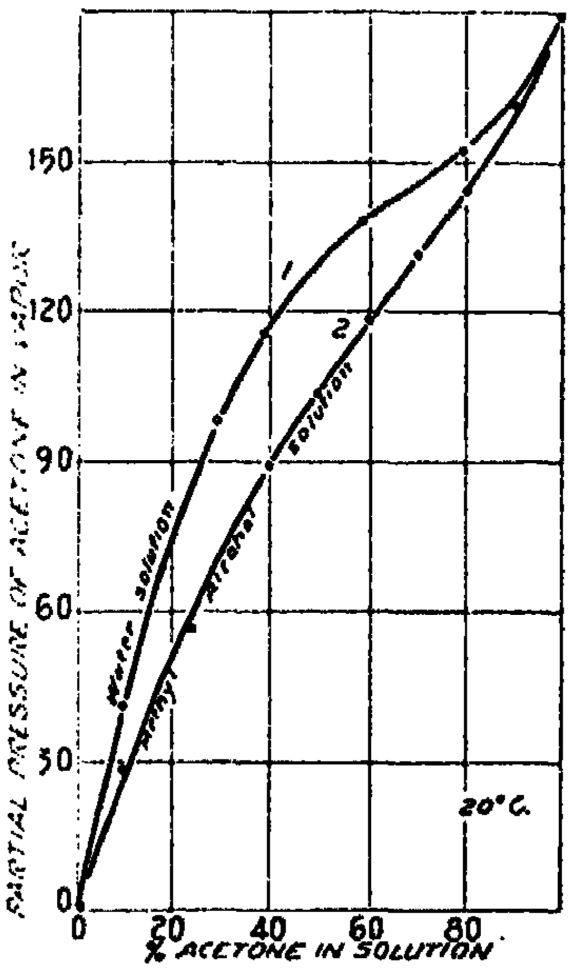

FIG. 3
Partial pressure of acetone in vapor over acetone-water and acetone-methyl alcohol solutions.

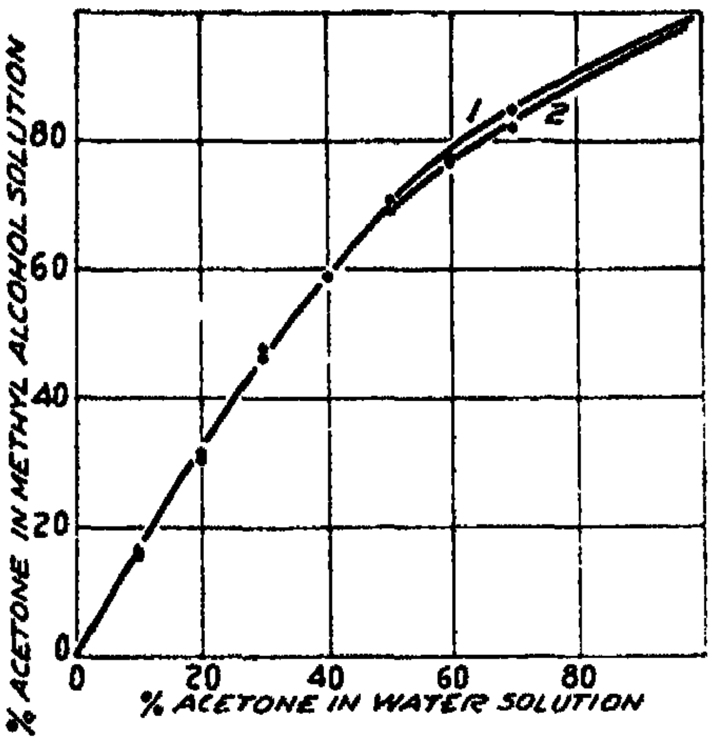

FIG. 4
Curve No. 2. Equilibria between acetone-methyl alcohol and acetone-water solutions
(1) By separation with rubber membranes
(2) From vapor pressure data.

$$\frac{p - p'}{p'} = K\,(G_S/G_A)^a, \qquad (1)$$

where p = the vapor pressure of pure acetone = 179.2 at 20°C, p′ = the partial pressure of acetone over a solution containing G_A grams of acetone and G_S grams of solute, and K and a are constants depending on the solvent and the temperature. This equation is equivalent to Raoult's law for a = 1 and $K = M_A/M_S$.

Taking logarithms on both sides, we get

$$\log\left(\frac{p - p'}{p'}\right) = \log K + a \log\,(G_S/G_A), \qquad (2)$$

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[1] Bancroft and Davis: J. Phys. Chem., 33, 361 (1929).

which is the equation for a straight line. The calculated data are given in Tables VI and VII. The agreement is quite satisfactory for acetone and methyl alcohol; but there is considerable discrepency for the acetone-water solutions at the highest and the lowest concentrations. It may be that the method of vapor analysis used is unsuitable for such readily condensable mixtures. It is hoped that this point may be cleared next year.

Table VI

Methyl Alcohol and Acetone at 20°

$$0.83 \log \frac{G_{Alc}}{G_{Ac}} - \log \frac{p_{Ac} - p'_{Ac}}{p'_{Ac}} = \log K_1 = 0.14$$

$$0.62 \log \frac{G_{Ac}}{G_{Alc}} - \log \frac{p_{Alc} - p'_{Alc}}{p'_{Alc}} = \log K_2 = 0.03$$

% acetone in liquid	log K_1 calc.	p′ acetone found mm	p′ acetone calc. mm	log K_2 calc.	p′ alcohol found mm	p′ alcohol calc. mm
0.0	——	0.	——	——	96.0	——
10.0	0.0710	28.6	32.7	0.1834	82.2	75.7
24.2	0.1235	57.0	62.5	0.0642	67.5	65.8
30.0	0.1361	72.4	73.8	0.0188	61.8	62.4
40.0	0.1419	89.2	88.8	0.0407	56.2	55.6
49.8	0.1416	103.8	103.6	0.0449	50.6	49.9
60.0	0.1475	118.8	118.1	0.0384	44.1	43.6
70.1	0.1337	131.6	132.1	0.0558	38.2	36.8
80.1	0.1118	144.2	146.0	0.0162	29.3	29.9
90.1	0.1625	161.4	160.6	1.9698	17.6	20.6
100.0	——	179.2	——	——	0.	——

Table VII

Water and Acetone at 20°

$$0.9 \log \frac{G_{w}}{G_{Ac}} - \log \frac{p_{Ac} - p'_{Ac}}{p'_{Ac}} = \log K_1 = 0.39$$

% acetone in liquid	log K_1 calc.	p'_{Ac} found mm	p'_{Ac} calc. mm
0	——	0.0	——
10.3	0.3210	41.2	46.5
20.0	0.3811	73.2	74.1
29.3	0.402	95.5	95.4
39.0	0.4274	115.8	113.8
58.3	0.3954	128.1	137.7
79.6	0.2245	152.5	160.1
100.	——	179.2	——

Summary

(1) The distribution of acetone through a rubber membrane between methyl alcohol and water has been measured by two independent methods over a composition range of 0 to 70 percent, and has been shown to agree with the equation

$$G_{Ac}/G_{Alc} = 2.24\ (G_{Ac}/G_{w})^{1.09}$$

(2) The partial pressure of acetone over acetone-methyl alcohol solutions at 20°C is represented fairly well by the expression

$$\left(\frac{G_{Alc}}{G_{Ac}}\right)^{0.83} = 1.38\,\frac{179.2 - p'}{p'}$$

(3) The partial pressure equation for acetone-water solutions as derived from the two preceeding equations is

$$2.655\,\frac{179.2 - p'}{p'} = \left(\frac{G_{w}}{G_{Ac}}\right)^{0.9}$$

This equation agrees with experimental values for intermediate concentrations, but not with those for high and low concentrations. It is possible that the discrepancies are due to experimental error.

(4) The results indicate that the distribution of a solute between two phases is primarily a function of mass concentrations.

Cornell University

DENSITY OF WOOD SUBSTANCE, ADSORPTION BY WOOD, AND PERMEABILITY OF WOOD

BY ALFRED J. STAMM[1]

A knowledge of the true density of wood substance and of its apparent densities in different liquids and gases is of considerable importance. Such information should help in giving some idea of the nature of the colloidal and the molecular dispersion of the materials making up the cell wall. It should give the relative permeability of the cell wall to different liquids, the extent to which compressive adsorption of the liquids takes place on the internal wood surfaces, and the adsorption of gases by wood. Values for the apparent densities of wood substances in various aqueous solutions together with adsorption measurements should give additional information as to the nature of the adsorption. The value for its true density is useful also in the calculation of the total void volume of wood or the average void cross section of thin sections of wood. All of these properties are important in the study of the flow of liquids through wood.[2]

Previous Density Determinations

Unfortunately most of the previous known determinations of the density of wood substance are based upon experimental methods that, with the advance in science, have become somewhat questionable. Though they give the correct order of magnitude and indicate that the variations in the values among the different species are slight, they fail to furnish all of the information that such experimental work should disclose.

Sachs[3] determined the density of wood substance, applying Archimedes' principle, by weighing thin wood sections both in air and in a liquid of known density, using in turn water and alcohol. He also found the densities of calcium nitrate and of zinc nitrate solutions in which thin wood sections were in approximate equilibrium, that is, sank very slowly. The first method gave 1.5 for pine with distilled water as the immersion liquid and 1.523 with alcohol, whereas the second one gave 1.54. Hartig,[4] using the second method, obtained 1.555 for the average of the densities of five different species. Dunlap,[5] also using the method of equilibrium in salt solutions, obtained values ranging from 1.4990 to 1.5639 for the seven species that he investigated.

Though the equilibrium method is simple in experimental manipulation and may give reproducible results, theoretically it is not entirely sound. It depends upon the erroneous assumption that the concentration of the salt

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[1] Chemist in Forest Products, U. S. Forest Products Laboratory, Madison, Wis.

[2] Stamm: J. Agr. Research 38, No. 2 (1929). "The Capillary Structure of Softwoods. I.—As indicated by Electroendosmotic Flow Studies."

[3] Arb. Bot. Inst., Würzburg, 2, 291 (1897).

[4] Untersuch. Forestbott. Inst., München, 2, 112 (1882).

[5] J. Agr. Research, 2, 423 (1914).

solution will be the same in the fine inner structure of the wood as in bulk. Adsorption, either positive or negative, or an osmotic or Donnan equilibrium effect resulting in a non-uniform distribution of the salt and solvent, or a change in the extent of penetration will affect the density. This fact is illustrated by some of the data presented in the present paper.

Richter[6] determined the density of wood substance using the pycnometric method with alcohol as the displacement liquid. Black spruce gave 1.512 for the heartwood and 1.516 for the sapwood, while white spruce gave the corresponding values 1.517 and 1.528. Previous extraction with ether and alcohol increased the values somewhat, the black spruce sapwood then giving 1.569. As will be seen later, the results using 95 per cent alcohol for the displacement liquid agree quite well with those in which water is similarly used.

The previous determinations of the density of cellulose alone have, in general, been more satisfactory than those for wood substance. De Mosenthal[7] determined the density of various celluloses by means of the pycnometric method using water for the displacement liquid. He obtained 1.607 for cotton cellulose, 1.575 for wood cellulose, 1.570 for ramie cellulose, and 1.548 for flax. Alcohol gave practically the same values, and bezene somewhat less. Richter[6] also determined the density of cellulose by the same method. He obtained 1.584 for cotton cellulose and 1.583 for filter paper, in alcohol. Lewis[8] made similar determinations on cotton cellulose using both water and toluene; the first medium gave 1.593 to 1.607 and the second 1.560 to 1.582. He also determined the effect of temperature on the density of the cellulose, from 20° to 50°C. In water the density decreased over this range from 1.612 to 1.590 in approximately a linear fashion. The effect of temperature upon the density in toluene was quite erratic, the general trend being towards an increase in density with an increase of temperature. This trend is diametrically opposed to the results of the following reference and the results of the investigation now reported.

After completing the experimental work of this investigation a recent publication by Davidson[9] came to the author's attention. This investigator determined the density of cotton cellulose pycnometrically, using water and several different organic liquids for displacement. He also determined the displacement by helium gas in a manner similar to that of the author's work. Davidson's measurements with the pycnometer at 20°C., using a soda-boiled cotton, gave 1.612 with water and 1.550 to 1.558 with six different non-polar organic liquids. Helium gas displacement gave 1.567. Cotton from different sources, soda-boiled and mercerized, viscose, cuprammonium, and nitro artificial silks, all gave practically the same density for each particular determination medium. Davidson further determined the effect of temperature from 0° to 80°C. for water and for toluene displacement. Both of these gave

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[6] Wochenbl. Papierfabr., **46**, 1529 (1915).

[7] J. Soc. Chem. Ind., **26**, 443 (1907).

[8] Cross and Dorée: "Researches on Cellulose," Vol. 4, p. 27 (1910-21).

[9] J. Textile Inst., **18**, T175 (1927).

a linear decrease in density with an increase in temperature. With water as the displacement liquid the density decreased from 1.615 to 1.575, and with toluene from 1.552 to 1.535.

Pycnometer Method for the Determination of the Apparent Densities of Wood Substance

Determinations of the apparent density of wood substance were made at 25°C., in 50 cc. Gay-Lussac pycnometers, on samples of wood meal. The measurements were made using distilled water, various organic liquids, and a series of aqueous solutions for the displacement media. The data necessary for the calculation of the density are the oven-dry weight of the wood (which has been dried to constant weight at 105°C.), m; the density of the displacement liquid, d_4^{25}; the weight of the pycnometer filled with the displacement liquid alone, $p + w_0$; and the weight of the pycnometer filled with the wood and the displacement liquid, $p + m + w_0$. The density D can then be determined from the equation,

$$D = \frac{m}{\frac{w_0 - w_1}{d}} = \frac{md}{m - [(p + m + w_1) - (p + w_0)]}$$

All weighings were made with a similar pycnometer serving as a weighing tare. 2.000 ± 0.001 grams of wood were used in each of the determinations.

In the preliminary experiments, in which distilled water and benzene were used in turn as the displacement liquids, two different procedures were tried to insure complete replacement of air by the liquid. (a) The dry wood meal in the pycnometers was first exposed to the vapors of the displacement liquid for several hours in order to obtain saturation of the fine structure. The moistened meal was then completely covered with the liquid and was gradually subjected to vapor treatment a second time by boiling the liquid nearly to dryness. The meal was again completely covered with the liquid and boiled for an hour. After standing for two days, being brought to the boiling point several times during this period, the final weighings were made to constant weight at 25°C. (b) The dry wood meal was immediately covered with the displacement liquid, was warmed slightly on the water bath, and was then subjected intermittently to a reduced pressure of a few centimeters of mercury in a vacuum desiccator. The application of suction was continued intermittently for from two days to two weeks. As the following data will show, these two procedures gave the same results, within the limits of experimental error; after learning this fact, procedure (b) was adopted for all subsequent measurements, since it is less limited in its experimental application than (a). In the measurements involving aqueous solutions, the weight was determined just before and just after heating and subjecting to the vacuum treatment, so that an appropriate correction could be made for the slight change in concentration caused by evaporation of the solvent.

Gas-Displacement Method for the Determination of the Density of Wood Substance

The essential parts of the gas-displacement apparatus used in this investigation are shown in Figure 1.[10] *A* is the displacement bulb of 135 cc. capacity in which the wood meal is placed; *B* is a 100 cc. gas burette with mercury leveling tube *L*; *M* is a mercury manometer of capillary bore; J, J_1, and J_2 are water jackets through which water is rapidly circulated from a water thermostat; tube *D* is connected to the purification train and source of gas used for displacement; tube *C* is connected to a phosphorus pentoxide drying tube, a mercury-vapor vacuum pump, a McLeod vacuum gauge, and a Cenco oil-immersed vacuum pump. All volume readings were made at 760 mm. of mercury pressure, a small temperature correction for the slight volume of the apparatus not held at constant temperature being taken into account.

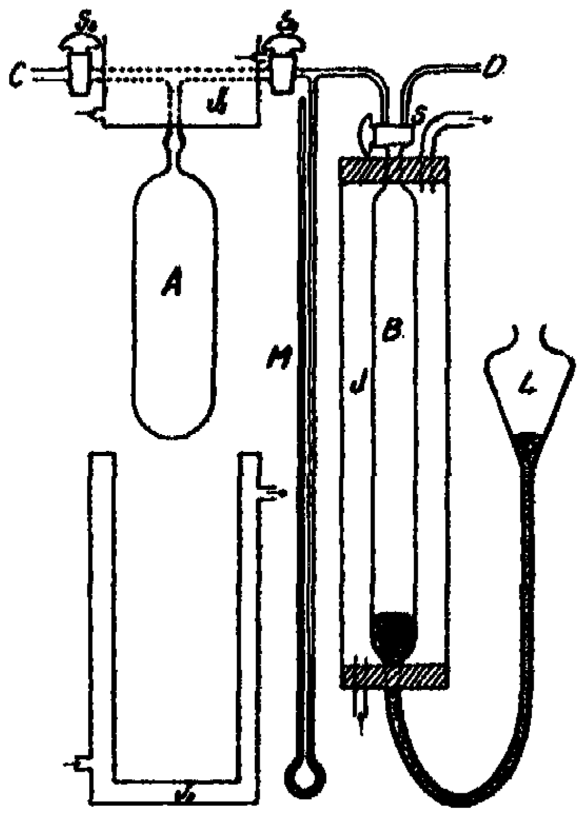

FIG. 1
Apparatus for the gas replacement method for the determination of the density of wood substance

In making the determinations, the gas burette *B* and connections were first flushed free from air by filling *B* several times with the displacement gas and discharging it through stop cock S_1. With the empty bulb *A* in place and S_1 closed, the bulb was evacuated with the oil-immersed pump and then with the mercury-vapor pump to from 10^{-4} to 10^{-5} mm. of mercury. To insure the removal of all water vapor, *A* was immersed in a beaker of boiling water during the latter stages of the evacuation. *B* was filled with gas from *D* and the 2-way stop cock *S* was then opened to the manometer *M*; at the same time *S* was closed to *D*. The volume of the gas in *B* was read after adjusting *L* so that the pressure reading was 760 mm. of mercury plus the correction. S_2 was closed and S_1 was gradually opened enough to allow about 60 cc. of gas to pass into A, after which S_1 was again closed and the volume taken from *B* was determined. The burette *B* was then refilled from *D* and the pressure and volume readings for it were taken as before. After again opening S_1, this time letting it stand open, the equilibrium volume of *A* and *B* was read with the pressure adjusted to 760 mm. of mercury plus the correction. This same procedure was followed when the bulb *A* was filled with wood meal except that a greater length of time was allowed after filling the bulb with gas

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[10] The author is indebted to Dr. T. G. Finzel of the Chemistry Department of the University of Wisconsin for the use of his adsorption apparatus, which suited admirably the requirements of this research.

before taking the final reading; equilibrium was in all cases obtained in less than an hour. The volume of the wood in A is then the difference in the volume of the bulb when empty and when filled with wood.

Materials for the Experimental Work

The heartwood of seven different softwoods and of two hardwoods was studied. All of the samples were ground to pass a mesh of either 20, 40, or 80 to the inch. Extractives were removed from the wood, only in the cases specified, by successive extractions with hot water, alcohol, and ether. The cotton cellulose used was sterile absorbent cotton manufactured by Bauer and Black. The wood cellulose was obtained from catalpa heartwood by chlorination and extraction of the lignin with sodium sulfite (the method of Cross and Bevan); it was then digested with boiling water for several hours to remove the readily hydrolyzable carbohydrates. The lignin was obtained by removing the cellulose and other carbohydrates from the heartwood of western yellow pine with 72 per cent sulfuric acid.

The organic liquids and salts used were of high commercial purity, so that no further purification was resorted to in any case. The helium gas used, which was obtained from the Bureau of Mines, contained a small amount of nitrogen, the removal of which was unnecessary, as the following results indicate. All of the gases used were dried by passing them through concentrated sulfuric acid and over solid potassium hydroxide, and traces of oxygen were removed from the other gases by passing them over hot metallic copper.

TABLE I

Apparent Densities of Wood Substances obtained by the Water Displacement Method, at 25°C.

Species of wood; heartwood only	Apparent density of wood substance	Size of particles in meshes to the inch	Treatment to secure complete penetration of the liquid*
Alaska cedar	1.545	20	(a)
Do.	1.549	20	(a)
Do.	1.551	20	(a)
Do.	1.547	20	(b)
Do.	1.546	20	(b)
Do.	1.547	20	Repetition of (b) on previous sample after evaporation to dryness
Sitka spruce	1.529	40	(b)
Do.	1.527	40	(b)
Do.	1.525	80	(b)
Do.	1.530	80	(b)
Do.	1.529	80	(b)

* (a) Vapor treatment followed by liquid treatment and boiling.

(b) Liquid treatment followed by warming and intermittent subjection to reduced pressure.

Experimental Work

Water displacement.

The effect of the method of treatment and of the size of the wood meal upon the apparent densities of wood substances as obtained by the pycnometric method with water as the displacement liquid are presented in Table I. The size of the wood meal showed no effect upon the densities obtained, indicating that the equilibrium penetration and the total surface are independent of the particle size. Check experiments in all cases showed a maximum observed deviation of 0.4 per cent from the mean density value.

Organic liquid displacement.

Table II shows the effect of the displacement liquid upon the apparent density of the wood substance. The liquids that were used are placed in the table approximately in the order of their increasing polarity. The apparent density appears to be dependent upon the polarity of the displacement liquid, an increase in polarity giving an increase in apparent density. The densities, viscosities, and compressibilities of the displacement liquids apparently have no effect. With very viscous liquids like "Stanolax," a heavy hydrocarbon oil, and glycerine a longer and more vigorous treatment is required to remove all of the air from the wood capillaries, but the equilibrium values, nevertheless, seem to be independent of the viscosity. The non-polar liquids seem also to show a smaller adhesion tension towards wood than the polar liquids and in consequence either less penetration of the wood, a lower degree of surface compression, or orientation of the adsorbed surface layers.

TABLE II

Apparent Densities of Alaska Cedar Wood Substance ground to pass 20 Meshes to the Inch, obtained by Displacement with Different Liquids at 25°C.

Displacement liquid	Density of liquid d^{5}_{4}	Number of determinations	Apparent density of wood substance; heartwood only
"Stanolax"	0.8694	1	1.460
Carbon disulfide	1.2562	2	1.474
Carbon tetrachloride	1.5840	3	1.474
Benzene	0.8727	7	1.476
Dimethyl aniline	0.9529	1	1.477
Nitrobenzene	1.2020	1	1.478
Chloroform	1.4716	2	1.478
n Butyl alcohol	0.8134	1	1.482
n Propyl alcohol	0.8023	2	1.481
Glycerine	1.2523	1	1.484
Ethyl alcohol (absolute)	0.7856	3	1.537
Ethyl alcohol (95 per cent)	0.8056	1	1.547
Water	0.9970	6	1.548

Whether the differences in apparent density are due to differences in penetration, in adsorption compression, or in both is a difficult question to answer. The same problem has arisen in the studies of the apparent densities of charcoal. Cude and Hulett[11] attribute such differences to differences in penetration, whereas Williams[12] and Harkins and Ewing[13] have evidence in favor of the adsorption-compression view. The latter investigators calculate from their data adsorption-compression pressures of 10,000 atmospheres and greater. Lowry [14] on the other hand shows no partiality to either of these views, believing that with the proper technique very similar values can be obtained with quite different displacement liquids.

It is desirable to call attention here to the fact that the degree of swelling of wood in itself has no effect upon the values obtained for the true density. Swelling, which affects the dispersion of the material in the cell wall, will of course make the internal structure more accessible to the displacement liquid and will thus increase the calculated value of the density. This effect, however, is identical with that caused by the differences in penetration of various liquids and thus need not be considered separately. Swelling cannot affect the true density of wood substance, because the true density is the value for the ultimate material that is impermeable to both liquids and gases.

Helium gas displacement

Because an accepted explanation of the deviations in their apparent densities in different liquids was lacking for other materials as well as for wood, measurements using helium gas for displacement were undertaken by the author in the hope of clarifying the situation. Howard and Hulett[15] had found that the adsorption of helium by charcoal was negligible at room temperatures. Since the adsorption of other gases by wood is much less than that by charcoal, the author assumed in carrying out his work that the adsorption of helium by wood is also negligible. Davidson[9] has assumed in a similar manner that the adsorption of helium gas by cotton is negligible; he further strengthened his assumption by showing that the densities obtained by making his measurements at different pressures of helium gas were the same.

Table III records the apparent densities of wood substance calculated from the displacement of gases on the basis of no adsorption of the gas, and also the adsorption of each gas (the increase in the observed volume of the wood caused by immersion in the gas) determined on the assumption that immersion in helium gave the true volume of the wood. The adsorption values for spruce are approximately one one-thousandth of the corresponding ones for charcoal.[16]

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[11] J. Am. Chem. Soc., 42, 391 (1920).

[12] Proc. Roy Soc, 98, 223 (1920).

[13] J. Am. Chem. Soc., 43, 1787 (1921).

[14] J. Am. Chem. Soc., 46, 824 (1924).

[15] J. Phys. Chem., 28, 1082 (1924).

[16] Hempel and Vater: Z. Elektrochemie, 18, 724 (1912).

TABLE III

Apparent Densities of Sitka Spruce Wood Substance, obtained by Displacement with Different Gases at 25°C., and the Volume of Gas adsorbed, assuming that Helium Gas gives the True Density

Displacement gas	Number of determinations	Apparent density of wood substance; heartwood only	CC. of gas adsorbed per gram of wood, at 760 mm. pressure
Helium	5	1.522	0.000
Hydrogen	2	1.553	0.013
Nitrogen	3	1.570	0.020
Oxygen	2	1.626	0.042

The density measurements using helium gas, a volumetric method, could not be checked with quite the accuracy of the pycnometric measurements, which were obtained by weighing, the maximum observed deviation from the mean being 0.7 per cent. As in the case of the pycnometric measurements, the density value obtained is not affected by the size of the wood particles.

Comparison of densities in different media.

Table IV compares the densities obtained with helium gas, water, and benzene as the displacement media for several different species of wood. The values obtained with helium gas are intermediate to those for water and for benzene displacement.

TABLE IV

Summary of the Apparent Densities of Wood Substance at 25°C. for Different Species, determined with the Three Types of Displacement Media

Species of wood; heartwood *only*	Density with helium gas		Apparent density with water		Difference between water and helium values	Apparent density with benzene	
	Number of determinations	Value	Number of determinations	Value		Number of determinations	Value
Alaska cedar	2	1.536	6	1.548	+0.012	7	1.476
Sitka spruce	5	1.522	5	1.528	+0.006	1	1.471
Western yellow pine	2	1.520	2	1.529	+0.009	–	———
Yellow poplar	2	1.508	2	1.516	+0.008	–	———
Red fir	2	1.518	4	1.533	+0.015	–	———
Western red cedar	3	1.503	2	1.521	+0.018	–	———
Redwood (extracted)	3	1.495	2	1.511	+0.016	–	———
Redwood (not extracted)	4	1.484	2	1.506	+0.022	–	———
Loblolly pine	–	———	3	1.531	———	1	1.466
White oak	–	———	5	1.540	———	1	1.473

Assuming that the helium gas displacement gives the true density of wood substance, which would be the case if penetration were complete and there were no adsorption, the results indicate that the difference between the values obtained by water and by benzene displacement is due to both an adsorption compression effect with water and to lack of complete penetration by benzene.

The mean compression in the adsorbed water film can be calculated approximately by assuming that the difference between the specific volumes of wood substance in water and in helium gas are due to a compression that takes place entirely within the volume of water that is adsorbed by the wood in securing equilibrium with 100 per cent relative humidity. For Alaska cedar this volume is about 0.285 cc. per gram of wood. The resulting compression amounts to 0.0195 cc. per gram of wood. Dividing this figure by the compressibility of water per atmosphere of applied pressure a mean adsorption compression pressure of 433 atmospheres is obtained. The force of adhesion between wood and water must be equal to or greater than the cohesion of water itself because of the fact that wood can be completely wetted by water. The cohesion of water has been determined by Edser[17] to be about 12,450 atmospheres. If, for purposes of calculation, it is assumed that the adhesion between wood and water is just equal to the cohesion of water, and that the attractive force varies as the fifth power of the distance from the surface, as was found to be the case by Edser,[17] then the film that shows a mean compression of 433 atmospheres will have an effective thickness of 30 molecular diameters or 9.2 mμ. This value for the mean thickness of the adsorbed water film on wood is of the same order of magnitude as values obtained by other investigators for other materials. McHaffie and Lenher[18] found the thickness of the adsorbed film of water on glass, quartz, and platinum plates in equilibrium with saturated vapor to exceed 100 molecular diameters. Calculations from the data given by Edser[17] indicate that an adsorbed film 600 molecules thick can be held against gravity. It is natural that the value obtained for the mean thickness of the adsorbed film of water on wood should be less than these two values since the thickness of a large part of the adsorbed water is limited by the fine closed capillary structure.

Another interesting approximate calculation can be made. Dividing the volume of the adsorbed water by the mean thickness of the adsorbed film gives 310,000 sq. cm. total adsorbing surface per gram of wood substance. The total surface of the microscopically visible structure can be estimated from some previous results of the author's.[19] A square centimeter of a transverse section of Alaska cedar contains about 135,000 cell cavities of 0.002 cm. average diameter. Since the internal surface of all the cell cavities in a cubic centimeter of such wood is substantially equal to that of 135,000 tubes of the same diameter and of uniform bore and 1 cm. long, the total internal area of a cubic centimeter is 850 sq. cm. Per gram of wood the surface will

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[17] "Fourth Report on Colloids," British Association for Advancement of Science, pp. 40-114 (1922).

[18] J. Chem. Soc., 127, 1559 (1925), 128, 1785 (1926).

[19] J. Agr. Research 38, No. 2 (1929). "The Capillary Structure of Softwoods. II.—As indicated by Hydrostatic Flow Studies."

be above the value divided by the bulk density of the wood, or 1930 sq. cm. Thus, only about 0.6 per cent of the total adsorbing surface is visible under the microscope.

Though the adsorption compression effect with water accounts for part of the difference between density values of the same wood substance as determined with water and with non-polar organic liquids, the effect of incomplete penetration of the organic liquids presumably is responsible for the major part of each difference.

The figures of Tables II and IV indicate that if accurate values for the absolute density of wood substance are required, the determinations should be made with helium gas. For ordinary purposes, however, the apparent densities determined by water displacement should suffice.

Temperature coefficient.

The effect of temperature upon the densities of wood substance as obtained with the three different displacement media is given in Table V. The temperature coefficients for each of the media are the same, each showing a linear decrease in density, at the same rate, with an increase in temperature. Davidson[9] found practically the same temperature coefficient for the density of cotton cellulose in water. His temperature coefficient for toluene displacement, however, was somewhat smaller. The fact that the three different media give the same coefficient is a strong indication that neither the equilibrium penetration for benzene nor the adsorption compression film for water is appreciably affected by temperature, over the range investigated. The thermal coefficient of cubical expansion of Sitka spruce wood substance calculated from these data is 3.7×10^{-4} per degree centigrade. The measured external cubical expansion of a block of wood caused by heat will be less than the value calculated by means of this coefficient, because part of the expansion of each cell wall will be relieved inward, in the internal capillary structure, in the same way that swelling caused by a liquid is partially relieved. Measurements on blocks of Sitka spruce with radial and tangential dimensions of 5 by 5 centimeters and a length of 0.7 centimeter gave a coefficient of

TABLE V

Effect of Temperature on the Density of Sitka Spruce Wood Substance; Heartwood only

Temperature °C.	Density with helium gas		Apparent Density with water		Apparent Density with benzene	
	Number of determinations	Value	Number of determinations	Value	Number of determinations	Value
10.0	2	1.533	2	1.536	1	1.479
25.0	5	1.522	5	1.528	1	1.471
40.0	2	1.514	2	1.519	2	1.462

Density at t°C. = Density at 0°C. $(1 - 0.00037\ t)$.

cubical expansion of 1.0×10^{-4} per degree centigrade. Villars[20] reported values ranging from 0.72×10^{-4} to 1.25×10^{-4} per degree centigrade for different species of wood. According to these figures only about one-third of the thermal expansion manifests itself in a change in the external dimensions. Roth,[21] by microscopical measurements, found that same fractional part of the swelling due to adsorption of water by the cell wall to be transmitted externally.

Densities of wood constituents.

Table VI gives the densities of cotton cellulose as determined by water displacement and by displacement with different organic liquids. The same increase in density with an increase in polarity of the liquid used for displacement that was shown in Table II for Alaska cedar wood substance exists here. The densities of cotton cellulose, however, are definitely higher than those of wood substance. Cross and Bevan wood cellulose gave values similar to those obtained with cotton cellulose. Lignin isolated from wood by dissolving the cellulose in 72 per cent sulfuric acid gave a considerably lower density.

Wood is made up of from 50 to 60 per cent of cellulose, 20 to 35 per cent of lignin, and smaller amounts of pentosans and other carbohydrates together with extractives. The data for redwood (Table IV) show that the density of

TABLE VI

Apparent Densities of the Constituents of Wood Substance, at 25°C.

Material	Displacement liquid	Number of determinations	Apparent density
Cellulose			
Cotton, sterile absorbent	Water	1	1.598
Same, benzene-washed	Do.	1	1.600
Same, alcohol-washed	Do.	1	1.597
Cotton, sterile absorbent	Benzene	2	1.574
Do.	Carbon disulfide	1	1.576
Do.	Chloroform	1	1.577
Do.	Propyl-alcohol	1	1.583
Do.	Ethyl alcohol (absolute)	1	1.590
Wood cellulose, Cross and Bevan			
Catalpa heartwood	Water	1	1.594
Do.	Benzene	1	1.571
Lignin, insoluble in 72 per cent H_2SO_4			
Western yellow pine heartwood	Water	1	1.451
Do.	Benzene	1	1.436

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[20] Pogg. Ann., 133, 400 (1868).

[21] Z. Botan., 52, 217 (1894).

the extractives is less than that of the wood substance, for removing the extractives increases the density. Richter[6] made this same observation with black and with white spruce. Assuming 60 per cent of the wood to be made up of cellulose (density 1.594) and the remaining 40 per cent to be made up of lignin (density 1.451), together with materials of similar density, the calculated density of wood substance would be 1.538. This agrees satisfactorily with the values for the density of different wood substances listed in Table IV. Even if the densities of all of the isolated constituents could be accounted for, exact agreement between observed and built-up total values could hardly be expected, since lignin undoubtedly is changed in the process of isolation. The deviations in the densities of wood substance for the different species can also be accounted for in a general way by the slight variations in composition. For example, a sample of western yellow pine containing 57 per cent of cellulose and 27 per cent of lignin has a higher density than a sample of redwood that is made up of only 48 per cent cellulose and 34 per cent lignin.

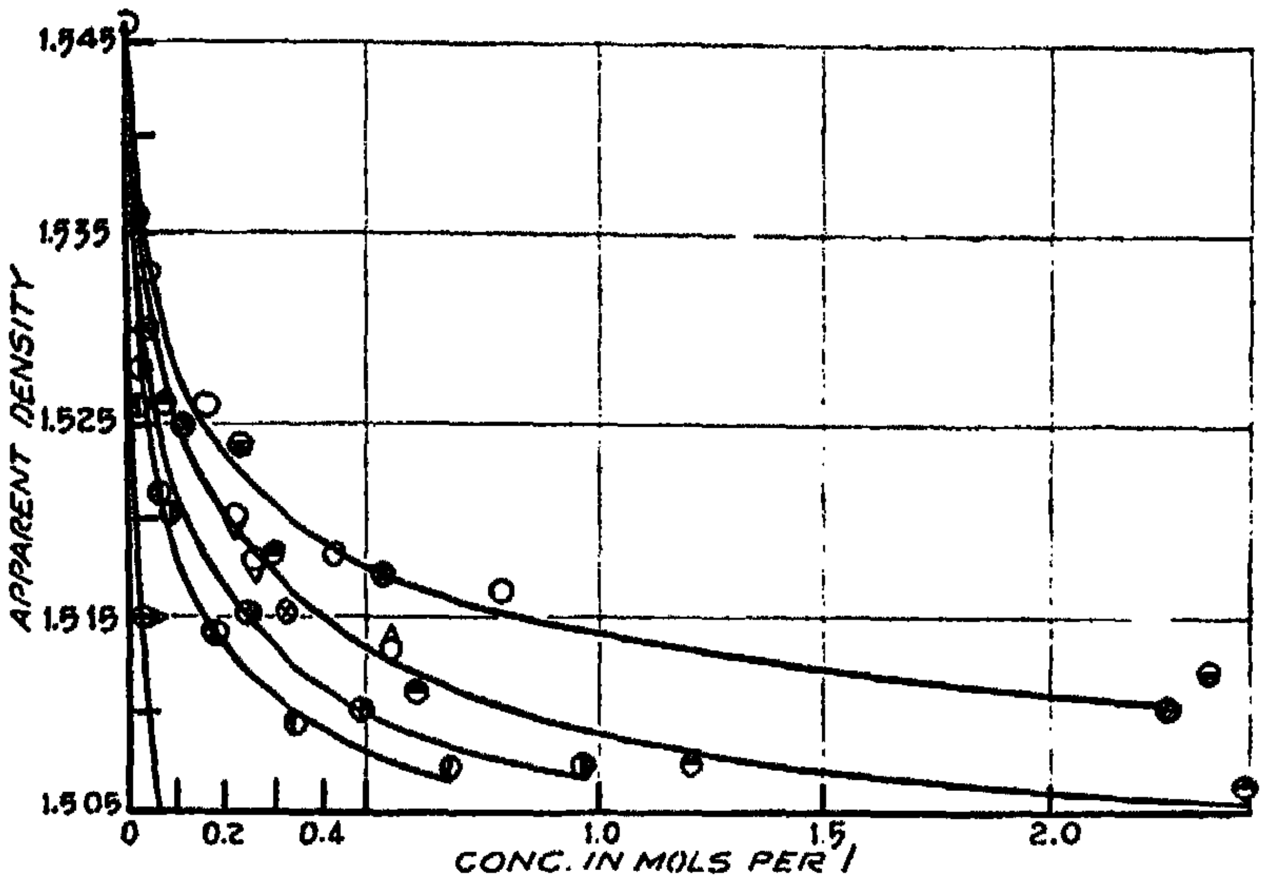

FIG. 2

Effect of solutes upon the apparent density of wood substance:

○ Glucose
● Glycerine
◒ Acetic Acid
◓ NaCl
♀ HCl
○> KOH
◑ $BaCl_2$
⊘ H_2SO_4
◐ K_3PO_4
ô H_3PO_4

Displacement of various aqueous solutions.

Table VII gives the apparent density of Alaska cedar wood substance as determined in different aqueous solutions at various concentrations. In Figure 2 the apparent densities are plotted against the concentration in mols. per liter. In all cases there is a decided drop in apparent density with an increase in concentration. All of the curves are definitely parabolic. The non-electrolytes, glucose and glycerine, depress the apparent density to the same extent with an increase in molal concentration. The weak electrolyte, acetic acid, shows a similar depression. The strong electrolyte, sodium chloride, on the other hand gives the same depression of apparent density with about half as great a molal concentration. Barium chloride does it for one-third the concentration and potassium phosphate for one-fourth. These facts make the drop appear like a vapor-pressure depression or an osmotic-pressure phenomenon, that is, the depression in apparent density seems to be proportional to the total number of ions plus undissociated molecules making up the solution. Though the dissociation of these salts is by no means complete, it is approximately so within the accuracy of these determinations. Sulfuric acid is not so greatly dissociated as the tri-ion salt, barium chloride; thus a greater concentration of the acid is required to give the same depression in apparent density. The same is true of phosphoric acid but to a considerably greater extent; a concentration of the acid twice that of the corresponding salt is required to give the same depression in apparent density. The degree of dissociation of the salt is likewise about twice that of the acid.

TABLE VII

Effect of Aqueous Solutions upon the Apparent Density of Alaska Cedar Wood Substance at 25°C.

Solute	Concentration mols. per liter	pH	Apparent density of wood substance; heartwood only
Glycerine	0.0223		1.536
Do.	0.1115		1.524
Do.	0.535		1.517
Do.	2.230		1.510
Glucose	0.0406		1.533
Do.	0.164		1.526
Do.	0.420		1.518
Do.	0.793		1.516
Acetic acid	0.233	2.5	1.524
Do.	2.33	1.7	1.512
NaCl	0.075		1.526
Do.	0.300		1.518
Do.	0.600		1.511
Do.	1.200		1.507
Do.	2.400		1.506
HCl	0.035	1.5	1.528
Do.	0.223	0.7	1.520
Do.	0.270	0.6	1.518

TABLE VII (Continued)

$BaCl_2$	0.0240		1.527
Do.	0.0961		1.520
Do.	0.2402		1.515
Do.	0.4805		1.509
Do.	0.9610		1.508
H_2SO_4	0.0077	2.5	1.530
Do.	0.270	0.5	1.515
K_3PO_4	0.0171		1.526
Do.	0.0683		1.521
Do.	0.1708		1.514
Do.	0.3415		1.508
Do.	0.6830		1.507
H_3PO_4	0.550	1.0	1.513
Water	———	5.6	1.548
KOH	———	7.1	1.541
Do.	0.00001	9.2	1.523
Do.	0.101	13.0	1.498 (1)
Do.	1.013	13.9	1.484 (2)
Water	———	5.6	1.541 (3)*
Do.	———	5.6	1.533 (4)*

* (3) is the water-displacement value of the apparent density for the wood sample of (1), after the sample had been washed free from alkali. (4) is the similar value for (2).

One marked exception to the preceding generalization, that the relative depression of the apparent density is proportional to the combined ionic and molecular concentration of the solution used for displacement, was found, namely, strong alkalies. Potassium hydroxide depressed the apparent density to a far greater extent than would be expected from the other results.

Adsorption

The decrease in the apparent density of wood substance with increase in concentration of the solution employed can be more readily explained after studying the adsorption of solutes by wood. Table VIII gives the results of a series of adsorption experiments. To respective samples of 2.000 ± 0.001 grams of oven-dry Alaska cedar meal 25 or 50 cc. of each of the aqueous solutions was added. The concentrations given are with respect to the ion indicated. The determinations of the cations and anions were not made on the same solution, hence the difference in their concentrations. The samples of the adsorption systems were sealed in weighing bottles for at least 12 hours before the analysis was made in order to insure the attainment of equilibrium. Blank determinations were made in each case and any slight necessary correction was applied.

TABLE VIII

Adsorption of Salts by Alaska Cedar Heartwood at 25°C.

Salt	Ion determined	Mols. per liter concentration Originally	Mols. per liter concentration After adsorption	Volume of solution Cc.	Mols. adsorption per gm. of wood
KOH	OH^-	1.0130	0.9180	50	+0.002375
KOH	OH^-	0.1013	0.05670	50	+0.00112
HCl	H^+	1.1130	1.11323	50	−0.000006
NaCl	Cl^-	0.21002	0.21125	25	−0.000015
$BaCl_2$	Cl^-	0.22215	0.22310	25	−0.000012
$BaCl_2$	Ba^{++}	0.19948	0.19902	50	+0.000012
$AlCl_3$	Cl^-	0.30703	0.30760	25	−0.000007
$AlCl_3$	Al^{+++}	0.2914	0.2906	50	+0.000020

Potassium hydroxide alone showed a considerable positive adsorption as determined by the change in alkalinity. Hydrochloric acid on the other hand showed a slight negative adsorption from the change in acidity. The mono-, di-, and trivalent cation salts all gave a slight negative adsorption with respect to the chloride ion and a slight positive adsorption with respect to the cation. This indicates that the adsorption of salts is hydrolytic in character. Barium and aluminum hydroxides presumably are selectively adsorbed as a result of a surface hydrolysis of the salts, thus leaving the solution acid. The potassium hydroxide is adsorbed as such. In this case the extent of adsorption is not limited by the increasing counter tendency of the acid formed during the hydrolysis to cause a reversal of the reaction. The existence of such hydrolytic adsorption has been recently confirmed by Miller,[22] through the use of ash-free charcoal. Though the wood used in the wood-density experiments had an ash content of 0.1 per cent, this content was almost entirely insoluble and siliceous in character. Hence the chances of the adsorption being an exchange adsorption are not great.

Vignon[23] obtained a positive adsorption of sodium hydroxide and barium hydroxide on cotton cellulose, of the same order of magnitude as that of potassium hydroxide on wood. He further found a negligible adsorption of sulfuric acid.

The selective and hydrolytic adsorption of OH^- ions and hydroxides obtained in the investigation reported here further agrees with the author's[24] findings on the effect of electrolytes upon the contact potential of wood with respect to water.

Not only is the adsorption by wood of electrolytes other than hydroxides very small, but that of nonelectrolytes is also. Some unpublished experiments by Salzberg of the Forest Products Laboratory indicate through optical

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[22] "Colloid Symposium Monograph," 5, 55 (1927).

[23] Compt. rend., 143, 550 (1906).

[24] "Colloid Symposium Monograph," 5, 361 (1927).

rotation measurements that glucose shows a slight negative adsorption on wood. Moreover, wood appears to show a selective adsorption of water from non-electrolyte solutions, and a selective adsorption of OH⁻ ions from electrolyte solutions.

Discussion of Results

The absence of any appreciable positive adsorption for all of the solutes listed in Tables VII and VIII, with the exception of potassium hydroxide, eliminates the possibility of the depression in apparent density of wood substance with increase in molal concentration being due to a positive adsorption, that is, to the solute being removed from solution with an increase in volume of the entire system. The increase in the volume of the system caused by the salt leaving the solution, however, may show a slight effect upon the apparent density of wood substance in the case of potassium hydroxide solutions.

The decrease in the apparent density of wood substance with an increase in concentration of the solute presumably must then be due to a decrease in the surface adsorption compression of the negatively adsorbed water, a decrease in the penetration of the solution, or both. The first possibility cannot entirely account for the phenomenon since the decrease in density is greater than that which would result if the adsorption compression were reduced to zero. There must then be a decrease in penetration of solution into the fine wood structure with a resulting increase in concentration. A sort of osmotic equilibrium may be set up with the wood substance acting as a kind of semi-permeable membrane, the fine structure being permeable to water but not to the solute. Such a condition would tend to prevent water from entering part of the internal structure, and the extent of this effect would be dependent upon the total ionic and molecular concentrations of the solute.

To determine whether the abnormal effect of the potassium hydroxide was not due to a chemical action on the wood, the densities of wood substance determined in water after removing the alkali by washing are given at the end of Table VII. These show that the action of potassium hydroxide of appreciable concentration causes a permanent reduction in the density of wood substance, which increases with an increase in the concentration of the alkali used to treat the wood. Other investigators have found mercerization of cellulose to decrease its density permanently[23] as well as to change its X-ray crystal lattice diagram. This permanent effect of alkalies seems to manifest itself appreciably only in higher concentrations. It is well illustrated by the effect of alkalies on electroendosmose through wood membranes.[24] The so-called hydration of pure cellulose and of wood by alkali appears then to cause a distention of the crystal lattice of the wood. Such a distention would have to more than compensate for any presumed increase in surface, which would cause an increase in the extent of the surface compression film, in order to account for the decrease in apparent density of wood substance that was observed.

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[23] Herzog: Pulp and Paper Magazine of Canada, 24, No. 24, June 17 (1926); Naturwissenschaften, 12, 955 (1924).

A similar distention of the crystal lattice of the material making up the cell wall of wood may also result from the addition of other electrolytes, but to a degree less marked than with alkalies. Since the alkalies alone are strongly positively adsorbed and alone show a definite effect upon the crystal lattice, however, such distention of the crystal lattice for the other solutes is not probable.

Summary

The apparent density of wood substance in water, in organic liquids, and in various aqueous solutions has been determined, as well as its actual density in helium gas. The size of the wood particles has no effect upon the density.

The densities obtained by means of helium gas displacement are slightly less than the apparent densities obtained by displacement with water, and are larger than the values obtained by displacement with non-polar organic liquids. The adsorption compression for water calculated from the various data is about 433 atmospheres, which corresponds to an average thickness of the adsorbed film of 30 molecular diameters and a total adsorption surface per gram of wood of 310,000 sq. cm. The microscopically visible surface is about 0.6 per cent of this value.

The effect of variations in temperature upon the density of wood substance was determined and the coefficient of cubical thermal expansion of wood substance was found to be 3.7×10^{-4} per degree centigrade. This is about three times the expansion transmitted to the external dimensions of a block of wood.

The density of wood substance varies slightly among species as a result of variation in the chemical composition of the substance. The density of isolated wood cellulose is similar to that of cotton cellulose and is somwhat greater than that of wood substance in entirety. The density of isolated lignin is correspondingly less than that of wood substance.

The presence of a solute in the aqueous displacing media causes a decrease in the apparent density of wood substance, in a parabolic fashion, with an increase in concentration. The depression seems to be a function of the total number of ions and undissociated molecules in the displacing solution. Alkalies bring about abnormally great depression of the apparent density, and cause a slight permanent depression of it even after removal of the alkali; this is shown by subsequent water displacement.

Of the materials studied, gases are but very slightly adsorbed by wood. Aqueous non-electrolyte solutions are negatively adsorbed, while aqueous electrolyte solutions show a selective and hydrolytic adsorption. Alkalies show a considerable positive adsorption and acids a negative one. The hydroxides are hydrolytically adsorbed to a slight extent from their salt solutions.

The values for the apparent density of wood substance, obtained by using different liquids for displacement, indicate that the finer structure of wood is not permeable to non-polar organic liquids. The permeability of this structure increased with an increase in polarity of the displacement liquid.

STUDIES ON THE PHYSICAL AND CHEMICAL PROPERTIES OF THE PLATINOCYANIDES. I

The Hydrates of Lithium Platinocyanide*

BY FRANK E. E. GERMANN AND O. B. MUENCH

Potassium platinocyanide, or Gmelin's Salt, the first of the platinocyanides known, was discovered by v. Ittner. Under the heading of double cyanides, Berzelius[1] says in part: "The ability of iron to combine prussic acid with bases was long thought to be a property possessed by this metal only, and Porret and Robiquet claimed that iron is thereby combined with the constituents of prussic acid, to a new acid. In the meantime v. Ittner showed that this property of iron is shared by gold, silver, platinum and copper, whose cyanides (or iron-free prussic acid salts) are dissolved by the cyanide of potassium, among others, to real double cyanides or double prussic acid salts. These properties are shared according to Leopold Gmelin[2] by palladium, mercury, zinc and cobalt, and according to Woehler, by nickel. Gmelin described a new method for preparing the double cyanides of platinum. The older method consisted in mixing platinic chloride with potassium ferrocyanide, and evaporating to crystallization. Gmelin's method consists in mixing platinum sponge obtained from ammonium chlorplatinate, with an equal part of potassium ferrocyanide, and heating just up to incandescence, but no more. By this process a part of the iron is replaced by platinum, and a mixture of both salts is obtained. The double cyanide of potassium and platinum can be crystallized from the saturated water solution of the above salt mixture, and can be purified by repeated crystallization."

It would appear from the above that v. Ittner prepared potassium platinocyanide by the following reaction:

$$K_4Fe(CN)_6 + PtCl_4 = K_2Pt(CN)_4 + 2KCl + FeCl_2 + (CN)_2$$

However, the simplified reaction which usually bears v. Ittner's name does not involve iron, and is written as follows:

$$6\ KCN + PtCl_4 = K_2Pt(CN)_4 + 4KCl + (CN)_2$$

Gmelin's method,[3] involving the use of platinum sponge can be represented by the following equilibrium reaction:

$$K_4Fe(CN)_6 + Pt \rightleftharpoons K_2Pt(CN)_4 + 2KCN + Fe.$$

We have, at present, at least five distinct methods for the preparation of the various platinocyanides which may be tabulated as follows:

1. By neutralizing the free acid with the base of the desired salt as indicated by the following equation:

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* Contribution from the Department of Chemistry of the University of Colorado.

[1] Berzelius Jahresber., 3, 95 (1824).

[2] Gmelin: J. Chem. Physik, (2) 6, 230 (1822).

[3] Gmelin: l.c. See also Gmelin: Handbuch, 1st ed., p. 1456.

$$H_2Pt(CN)_4 + 2KOH = K_2Pt(CN)_4 + 2H_2O.$$

2. By double decomposition of the metallic sulphate with barium platinocyanide in solution as follows:

$$BaPt(CN)_4 + K_2SO_4 = K_2Pt(CN)_4 + BaSO_4.$$

3. The metallic platinocyanides, when insoluble in water may be formed by the following reaction:

$$K_2Pt(CN)_4 + CuSO_4 = CuPt(CN)_4 + K_2SO_4$$

4. The alkali or alkaline earth cyanide solutions may be warmed with platinum salts, when the following reaction proceeds:

$$6\ KCN + PtCl_4 = K_2Pt(CN)_4 + 4KCl + (CN)_2$$

5. The most recent method consists in passing an alternating electric current through platinum electrodes immersed in aqueous solutions of the cyanides of the alkali or alkaline earth metals, and is probably represented by the following equation:

$$Pt + 4KCN + 2H_2O = K_2Pt(CN)_4 + 2KOH + H_2.$$

Lithium platinocyanide seems first to have been described by Schabus,[1] and has received but little attention since that time. Weselsky[2] claimed to have converted lithium platinocyanide to lithium platinicyanide, but his work was proved to be in error by Hadow[3] and later by Levy.[4] He does not, however, describe lithium platinocyanide, nor tell how he obtained it. Martius[5] passes over the salt with the following brief statement: "Lithium platincyanür (LiCy;PtCy + 3HO) erhielt ich beim Fällen von Barium platincyanür mit schwefelsaurem Lithon als ein leicht krystallisirendes Salz von milchweisser Farbe und blauen Flächenschiller."

Sir James Dewar[6] made certain observations on the color changes which he had observed when a salt, which had been supplied to the Laboratory of the Royal Institution as "Lithium platinocyanide," was cooled in liquid air. Dewar gave J. Emerson Reynolds[7] some of the salt with which he had worked. Reynolds refers to the salt as "this nearly white crystallized substance" and later states that "Chemical examination of the Royal Institution specimen led to the conclusion that it was a mixture of the hydrated chloride, cyanide and sulfate of lithium with a platin-cyanogen salt of lithium, and that the proportion of the latter salt was small.—Hence the percentage of platinum *compound* present could not exceed 5 per cent of the mixture of salts.—I prepared afresh some pure lithium platinocyanide and obtained the salt in fine grass-green crystals when fully hydrated. On completely analysing these crystals they gave data agreeing well with the formula $Li_2Pt(CN)_4$, $5H_2O$."

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[1] Schabus: "Bestimmung der Krystallgestalten in chemischen Laboratorien erzeugter Produkte," page 43 (1855).

[2] Weselsky: Sitz. Akad. Wiss. Wien., **20**, 282 (1856); J. prakt. Chem., **69**, 276 (1856).

[3] Hadow: J. Chem. Soc., **13**, 106 (1861).

[4] Levy: J. Chem. Soc., **101**, 1081 (1912).

[5] Martius: "Ueber die Cyanverbindungen der Platinmetalle," Inaug. Diss., Göttingen, page 45 (1860).

[6] Dewar: Proc. Roy. Inst., **1895**, 667.

[7] Reynolds: Proc. Roy. Soc., **82A**, 380 (1909).

Levy[1] converted lithium platinocyanide to lithium platinicyanide, but states nothing of the preparation or properties of the former salt.

Terry and Jolly[2] state that Baumhauer[3] described lithium platinocyanide, but this is not true, since the original article deals only with double salts of lithium platinocyanide with potassium platinocyanide and rubidium platinocyanide.

From this small amount of experimental work, the various chemical dictionaries have obtained their data. Many errors have crept in, so that we find the degree of hydration for what is apparently the same hydrate given as $3H_2O$, $3?H_2O$, $5H_2O$ and xH_2O. Some state that the salt is *slightly soluble* in water, while others state that it is *very soluble*. The color of the crystals is given as grass green, greenish yellow, rose red, blue, and milk white. In view of the above chaos, it was thought desirable to subject the salt to a systematic revision.

Experimental

Barium platinocyanide. A very high grade of barium platinocyanide can be obtained on the market, which can readily be made more pure by several re-crystallizations. Accordingly, the second method, which involves the double decomposition of barium platinocyanide and lithium sulfate, was used in the preparation of the lithium platinocyanide.

Lithium sulfate. The highest grade lithium sulfate obtainable was spectroscopically free of potassium salts, but showed traces of sodium. For its further purification, advantage was taken of the fact that the solubility of lithium sulfate[4] decreases about 10% in heating from 20 to 95°C. Accordingly a saturated solution was made at room temperature and heated to boiling and the precipitated salt filtered off while hot. In order to keep down the sodium content, it was necessary to use Pyrex in all the operations. Even with its use, the sodium content in the lithium sulfate was decreased with one precipitation, but increased if several precipitations were used.

Lithium platinocyanide. A slight excess of lithium sulfate solution was added to one gram of barium platinocyanide in seventy-five c.c. of hot conductivity water. After standing on the hot plate over night, the barium sulfate was filtered off. The clear filtrate gave negative tests for both sodium and barium. The filtrate was evaporated almost to dryness and the lithium platinocyanide allowed to crystallize. The crystals were then re-crystallized four times from alcohol and finally from conductivity water, to insure the absence of alcohol of crystallization. All operations were carried out in Pyrex with the result that the final product showed only traces of sodium as evidenced by the faintness of the D line.

The hydrate thus prepared crystallized in long pointed needles having a grass green appearance. Parallel to the long axis (probably the C-axis)

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[1] Levy: J. Chem. Soc., **101**, 1091 (1912).

[2] Terry and Jolly: J. Chem. Soc., **123**, 2217 (1923).

[3] Baumhauer: Z. Kryst. Min., **49**, 113 (1911).

[4] Etard: Ann. Chim. Phys. (7), **2**, 547 (1894).

the crystals are bluish-green in appearance, while perpendicular to this axis the color appears to be more of a canary yellow with a slight tinge of green. It is very soluble in water.

Determination of the Hydrates

Thin films of the saturated solution of lithium platinocyanide were painted on microscope cover glasses by means of a rubber policeman. These samples were put in desiccators over the following per cents of sulfuric acid; (10, 20, 30, 40, 50, 60, 70, 80). A sample of the dehydrated salt was also put in each one of these desiccators. These were allowed to stand at 25°C., and observed from time to time. It was soon evident that the samples over the 10, 20 and 30 per cent acid were in solution, while the rest seemed to form stable salts. The samples over 80% acid appeared to be anhydrous. (Determinations had been made over concentrated sulfuric acid and phosphorus pentoxide, and it was found that each of these readily and completely dehydrated the salt). The anhydrous salt had a bright canary yellow color. This then gave a rough qualitative determination of approximately the concentration of sulfuric acid over which certain forms of the salt are stable. More than this, after standing a while over the acids, there were certain color changes in the samples, which were proved to take place without decomposition. Whenever the anhydrous salt is but momentarily exposed to the air, or over a lower concentration of acid (70% or less), the color immediately changes to tan. The grass green hydrate also begins to change to the tan after a few days, especially when over 60%-70% acid. When the tan hydrate is left a week or more, over the 70% acid, it changes to a dark green and finally becomes almost black with a purple metallic sheen. There was no abrupt change from one color to another over certain strengths of acid.

To determine the hydrates quantitatively, use was made of the micro method devised by the authors[1] of this paper and was found especially suitable for the determination of the hydrates of lithium platinocyanide.

The densities of the sulfuric acid solutions which were used, were determined by means of accurate hydrometers, and after each determination the density was checked by means of a sensitive Westphal chainomatic balance. This latter was necessary because of the change in density due to the acid taking up water from the salt and from the air. The percentages and vapor pressures of the acid solutions were obtained from the results of careful determinations by various experimenters.[2] After equilibrium conditions had been reached, for example, in a desiccator or the balance case, some of the acid was taken out and checked by means of the Westphal balance at the time a determination was finished. All the quantitative work reported in this paper was carried out at 25°C.

Concentrated sulfuric acid completely dehydrated lithium platinocyanide. Several determinations leave no doubt on this point. The fact that the salt

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[1] Germann and Muench: J. Phys. Chem., 32, 1380 (1928).

[2] Landolt-Börnstein-Roth: "Tabellen," p. 265 (1912); R. E. Wilson: J. Am. Chem. Soc., 43, 721 (1921); J. Ind. Eng. Chem., 13, 326 (1921).

is readily dehydrated over concentrated sulfuric acid, gives us a convenient starting and also reference point for the calculations of the amount of hydration of the hydrates after a constant weight has been reached.

$Li_2Pt(CN)_4.4H_2O$, Hydrate (a). The tan salt is readily obtained by exposure of the anhydrous (canary yellow) salt to the air, or a low concentration of acid. When this experiment is performed in the balance, the color change is seen to be accompanied by an increase in weight until equilibrium conditions are reached.

A saturated solution of lithium platinocyanide was painted in thin films on carefully weighed microscope cover glasses. These were dehydrated over concentrated sulfuric acid and the weights taken.

The acid in the balance was then changed to 40% sulfuric acid (later 50%, 60% and 70% were tried with the same result). One sample of the anhydrous salt was put in the balance in turn with each of the above concentrations of acid and after equilibrium had been nearly established, was weighed, and re-weighed until constant weight was obtained.

The detailed record of each of these weighings will not be recorded in this paper, but below is given a summary in the form of a table, of a few of the results and the calculations made from the weight of the anhydrous salt and the hydrate in question. On each side of it are given the weights that would have been obtained if the compound had consisted of a hydrate containing three and five molecules of water. This shows that the tan hydrate is the tetrahydrate. In the determination of each experimental figure, the procedure outlined above was followed.

TABLE I

Weights in milligrams

No.	Wt. of Anhydrous Salt	Wt. of Tan Hydrate	Calculated to $4H_2O$	Calculated to $3H_2O$	Calculated to $5H_2O$
1.	9.40	11.50	11.56	11.02	12.10
2.	10.60	13.10	13.04	12.42	13.64
3.	14.05	17.19	17.28	16.47	18.08
4.	4.35	5.34	5.35	5.10	5.60
5.	3.70	4.60	4.55	4.34	4.76
6.	14.05	17.25	17.28	16.47	18.08
7.	14.04	17.26	17.27	16.45	18.06
8.	15.42	18.90	18.87	18.07	19.84
9.	14.25	17.50	17.53	16.70	18.34
10.	13.14	16.10	16.16	15.40	16.91

The conclusion drawn form the above summary of the this work is that the tan hydrate is:

$$Li_2Pt(CN)_4.4\ H_2O.\ (tan)$$

No record of a tan hydrate can be found in the literature.

$Li_2Pt(CN)_4.4H_2O$, hydrate (b).—In working with the tan hydrate, it was observed that the color gradually became darker and some samples became almost black. By putting samples of the tan hydrate into the series of desiccators, it was seen that a concentration of about 70% acid favored the most rapid formation of the black modification. The change was gradual, taking almost two weeks for completion. Over 55% acid, it was obvious that transformation to the black was taking place after two months, but it was by no means complete. The transformation was so gradual that no definite strength of acid could be considered as the limit of the change.

The formation of the dark salt would indicate either decomposition, the formation of another hydrate, or another modification of the same hydrate. Quantitative determinations showed that there was no change in weight and that we were again dealing with a salt with four molecules of water of crystallization. That there was no decomposition was shown by transferring a black sample to a desiccator containing 30% acid and allowing it to take up moisture to form a solution, and then putting it over 40% acid. Under these conditions the green salt reappeared, which even under the microscope showed no traces of impurities. The weight of the green crystals obtained was identical to that of the original black form.

Since the change to the dark hydrate is very slow, even over 70% acid, attempts were made to accelerate the change, or to find a catalyst that would speed up the transformation. Levy[1] has shown that hydrogen, hydroxyl and cyanide ions are influential in producing such changes, when these ions are in contact with the solution from which the crystals are coming. In the present work it was found that the vapor from concentrated hydrochloric acid caused a rapid darkening, but there was also a change in weight. When 70% sulfuric acid containing four ten-thousandths of one per cent of hydrochloric acid was used the rate of change to the dark salt was about double that when pure 70% sulfuric acid was used. In this case there was no change in weight. A slightly greater increase in speed was obtained when a small lump of potassium cyanide was dropped into the 70% sulfuric acid. The HCN thus generated was volatile and was responsible for the change. Here again there was no change in weight. Hydrochloric acid added to 40% sulfuric had no effect, the tan going directly to the light green just as in the case of 40% sulfuric acid alone.

A drop of piperidine or of ammonium hydroxide placed near the dark modification brought about decomposition with increase in weight. The samples could not be restored to their original weights by heating and subsequently placing over lower concentrations of acid.

Solutions of sodium hydroxide having the same vapor tension as 70% sulfuric acid produced effects identical to those of 70% acid. Since this is non-volatile, the effect is one of pressure and not of OH ions.

When the tan hydrate was placed in the presence of 70% acid and exposed to bright sunlight, darkening was very rapid, a decided green appearing in the

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[1] Levy: loc. cit.

course of fifteen minutes. Ultraviolet light produced in the laboratory also had a very rapid effect.

It would, therefore, appear that there are several factors which control the formation of the black modification from the tan. Light when allowed to strike the salt in the presence of a low pressure of water vapor causes a rapid change. Light in the presence of high vapor pressure of water has little or no effect. Hydrogen and cyanide ions seem to accelerate the change.

The dark hydrate has a purple metallic sheen by reflected light. It seemed amorphous under the microscope. Its composition is:

$Li_2Pt(CN)_4.4H_2O$ (black).

$Li_2Pt(CN)_4.4H_2O$, Hydrate (c).—This is the very soluble grass green hydrate which is obtained by allowing solutions of lithium platinocyanide to crystallize from an aqueous solution of the salt.

In order to find the highest vapor pressure over which it is stable, a systematic process of elimination was used, and it was found that at 25°C, the grass green crystals formed and remained stable over 38.6% sulfuric acid, while over 38.5% acid, the sample remained liquid. From these facts, the vapor pressure at equilibrium of the system saturated solution-green hydrate at 25°C can readily be established.

According to Wilson[1] the vapor pressure of a 40% sulfuric acid solution is 13.46 mm. Hg. The vapor pressure of 37.87% acid is 14.47 mm. Hg. Then the calculated vapor pressure for 38.5% acid is 14.17 mm. Hg., and for 38.6% acid is 14.12 mm. Therefore at 25°C, the vapor pressure of the system saturated solution of lithium platinocyanide-green crystals is between 14.12 mm. and 14.17 mm. The most probable value, the average is 14.14 mm. Hg. This, then at 25°C, is the upper limit of vapor pressure at which the grass-green hydrate is stable, and is the vapor tension of the saturated solution at 25°C.

The lower limit of vapor pressure at which the green hydrate is stable is arrived at in much the same general way. At 25°C in the presence of acid of a concentration greater than 73.4%, the sample lost weight, while over 73.2% acid it was stable. This makes the vapor pressure of the system green hydrate-anhydrous salt at 25°C, 1.02 mm. Hg. This is generally called the vapor pressure of the grass green hydrate.

Determination of the Composition of the Grass Green Hydrate.—Using the same method as before, it was found that over 40% sulfuric acid the green salt crystallized and came to constant weight. This weight showed the hydrate to have four molecules of water of hydration. This strange result was at first doubted, for the tan hydrate was definitely found to be the tetrahydrate. The same plan of procedure was followed as in the case of the tan hydrate, only in this case most of the samples were also taken to the tan hydrate, and the weight found to check with that of the green hydrate. The general plan was this: a sample from the saturated solution was painted on the cover glass and this immediately put in the balance over 40% sulfuric acid, and allowed to come to equilibrium, the loss in weight being followed

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[1] Wilson: J. Am. Chem. Soc., 43, 721 (1921).

from time to time till constant weight was obtained. To be absolutely certain that there would be no further loss over this strength of acid, many of the samples were left in the balance for several days after constant weight had been obtained, and it was found that they neither gained, nor lost weight by as much as one-hundredth of a milligram.

This same green hydrate was then dehydrated over concentrated sulfuric acid, and with concentrated acid in the balance, the weight of the anhydrous salt obtained. This anhydrous salt was then allowed to take up moisture, in some cases from the air, in others over (40%, 50%, 60%) sulfuric acid, again to constant weight producing the tan hydrate. Thus nearly every sample was carried thru these three stages (grass green, anhydrous and tan) and in that way a weight of each modification obtained.

Again, only a summary of a few of the experimental results of the work are given in Table II. While the table gives a few more values confirming the formula for the tan hydrate, its chief interest is in the fact that the weight of the green hydrate is identical (within the limits of experimental error) with the tan hydrate. Mixtures of the two modifications of the tetrahydrate, forming on the cover glass in the balance under certain conditions, also show the same weight as either the green or the tan salt.

TABLE II

Weight in Milligrams

No.	Wt. of Anhydrous Salt	Wt. of Grass-green Hydrate	Wt. of Tan Hydrate $4H_2O$	Calculated to $4H_2O$
1.	11.02	13.52	13.52	13.55
2.	11.50	14.28	14.18	14.14
3.	13.50	16.60	16.55	16.60
4.	17.34	21.32	21.30	21.33
5.	14.60	17.96	17.98	17.96
6.	12.00	14.78	14.76	14.76
7.	19.65	24.19	24.17	24.17
8.	20.42	25.16	25.16	25.12
9.	15.54	19.12	19.10	19.11
10.	18.60	22.88	22.90	22.88

The conclusion drawn from the work summarized in the above table is, that the green as well as the tan salts are tetrahydrates, having the same general formula:

$$Li_2Pt(CN)_4.4H_2O \text{ (grass green)}$$

This is the well known hydrate which has been assigned various amounts of water of crystallization. Strangely enough, no one has given it the value of four molecules, which the above results warrant.

Summary

1. The early history of the platinocyanides is traced and a summary of the methods which have been used in their production is given.

2. A complete bibliography of all work done on lithium platinocyanide is collected and critically reviewed.

3. Pure lithium platinocyanide has been prepared and its hydrates studied by means of a vapor tension method.

4. Anhydrous lithium platinocyanide is formed at 25°C when the pressure of water vapor is less than 1.02 mm. Hg. It has a canary yellow color.

5. Lithium platinocyanide tetrahydrate is tan when formed at 25°C from the anhydrous salt by exposure to a pressure of water vapor greater than 1.02 mm. Hg.

6. Lithium platinocyanide tetrahydrate in a black modification is produced when the tan salt is exposed to bright sunlight, ultraviolet light, or is kept in contact with water vapor at very low pressures, but above 1.02 mm. Hg. Light alone will not cause this change if the pressure of water vapor is high. Hydrogen and cyanide ions catalyzed the change.

7. Lithium platinocyanide tetrahydrate of a grass green color is the familiar salt which crystallizes from water solutions. It crystallizes in needles, whose structure could not be determined even when grown under the microscope. The equilibrium pressure of the water vapor of the system lithium platinocyanide tetrahydrate-saturated solution at 25°C was found to be 14.14 mm. Hg.

8. It has been proved that lithium platinocyanide may be obtained as the anhydrous salt or with four molecules of water of crystallization. The other hydrates which have been reported do not exist.

THE OXIDATION POTENTIALS OF SOME HYPOCHLORITE SOLUTIONS*

BY V. H. REMINGTON AND H. M. TRIMBLE

Berthollet,[1] as early as 1785, showed that solutions of chlorine in caustic potash do not weaken linen fabrics as do its aqueous solutions. Crossley[2] found that the hydrogen ion concentration of a solution has an important effect upon the oxidizing properties of hypochlorites toward cellulose, non-cellulose impurities in fibers of vegetable origin, and certain dyes. Weissenbach and Mestrezat[3] found that the effectiveness of Dakin-Daufresne hypochlorite solution in killing certain bacteria was much increased by rendering it slightly acid. Dunstan and his coworkers[4] have found that the secret of success in the use of hypochlorites in refining certain petroleum products lies in controlling the alkalinity of the hypochlorite solutions within rather narrow limits. Schwalbe and Wenzl[5] found that, in the course of bleaching with alkaline hypochlorites, the bicarbonates which form retard the reaction, and may even bring it to a standstill. It seems clear from these few examples that hypochlorites possess different oxidizing powers in different media; but our knowledge of their relative activities under various conditions is distinctly limited.

An oxidizing material is, in general, characterized by its power to yield oxygen, either directly or indirectly. This power may not extend to visible evolution of gas but, in any case, the oxidizing power of an oxidizing agent is greater the greater its tendency to yield oxygen. According to a theory which was first proposed by Nernst,[6] an electrode which is not attacked, when immersed in a solution of an oxidizing agent, adsorbs oxygen from it and acquires a charge. The potential so set up, then, is directly proportional to the osmotic pressure of oxygen in the solution, and so also to the oxidizing power of the solution. This theory accounts satisfactorily for the setting up of a potential under these circumstances. It seemed to us that it should be possible to get a measure of the oxidizing powers of solutions of hypochlorites by determining their oxidation potentials.

A survey of the literature shows that but little work has been done upon the oxidation potentials of hypochlorite solutions, and that this work has given only disconnected and fragmentary data.

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*Contribution from the Chemistry Department of the Oklahoma Agricultural and Mechanical College.

[1] Mellor: "Treatise on Inorganic and Theoretical Chemistry," 2, 243 (1922).

[2] A. W. Crossley: Pharm. J. 115, 693-5 (1925).

[3] R. J. Weissenbach and Mestrezat: Compt. rend. soc. Biol., 81, 93-6 (1918).

[4] A. E. Dunstan: J. Inst. Petroleum Tech., 10, 201-15 (1924).

[5] C. G. Schwalbe and H. Wenzl: Z. angew. Chem., 36, 302-4 (1923).

[6] W. Nernst: "Theoretical Chemistry," Fourth Ed., p. 731 (1903).

Apparatus and Reagents

The apparatus used in measuring the potentials consisted of an ordinary student potentiometer with the usual accessories. A tenth normal calomel electrode prepared according to directions given by Clark[1] was used as reference electrode. Electrodes of smooth platinum were used in this work. Measurements were standardized by means of a certified standard Weston cell. All pipettes, volumetric flasks and burettes used in the research were calibrated and the necessary corrections were applied. A special type of electrode vessel, shown in Fig. 1, was developed for this work.

Zonite, a commercial preparation of sodium hypochlorite, was used in some of the earlier experiments. All other chemicals were of the best C. P. grade. The conductivity water used in making up all solutions was prepared by redistilling a good quality of distilled water from alkaline permanganate.

The hypochlorous acid which was used in most of the work was prepared in the following manner. Chlorine from a cylinder was passed into a suspension of mercuric oxide, yielding a mixture of salts of mercury and hypochlorous acid. This solution was diluted so as to contain about one percent of hypochlorous acid, and then distilled under the reduced pressure produced by a filter pump. A slow current of air was drawn through the solution during the distillation. To secure a product yet more nearly free from hydrochloric acid the solution was distilled a second time in the same manner. The final product was then analyzed by adding a known quantity of the solution to an acidified potassium iodide solution, and titrating the iodine which was set free with standardized sodium thiosulphate solution. The solutions were then diluted to approximately the concentration desired for our experiments with conductivity water and kept in brown glass bottles in a cool place until needed. Hypochlorous acid thus prepared contained only a very small trace of chloride. No solution more than two days old was ever used. The hypochlorous acid solutions were always analyzed just before they were used in experiments, and adjusted to the exact concentration which was wanted.

The Experiments

A large part of this investigation was of necessity given over to a study of the use of platinum electrodes in determining the oxidation potentials of hypochlorites in solution since it seems that this problem has never been satisfactorily solved. We have been unable to get any consistent results with platinized electrodes. We believe that they take up, either in preparation or while being used, impurities which act as "poisons," and which cannot be removed by any method of treatment which we have tried. It was found that when an untreated electrode of smooth platinum, is put in contact with a solution of hypochlorite the potential usually changes regularly but it shows no indication of ever reaching any equilibrium value. Results with a given electrode are rarely or never twice the same. The potentials tend to fall lower and lower in successive experiments. Different electrodes seem to

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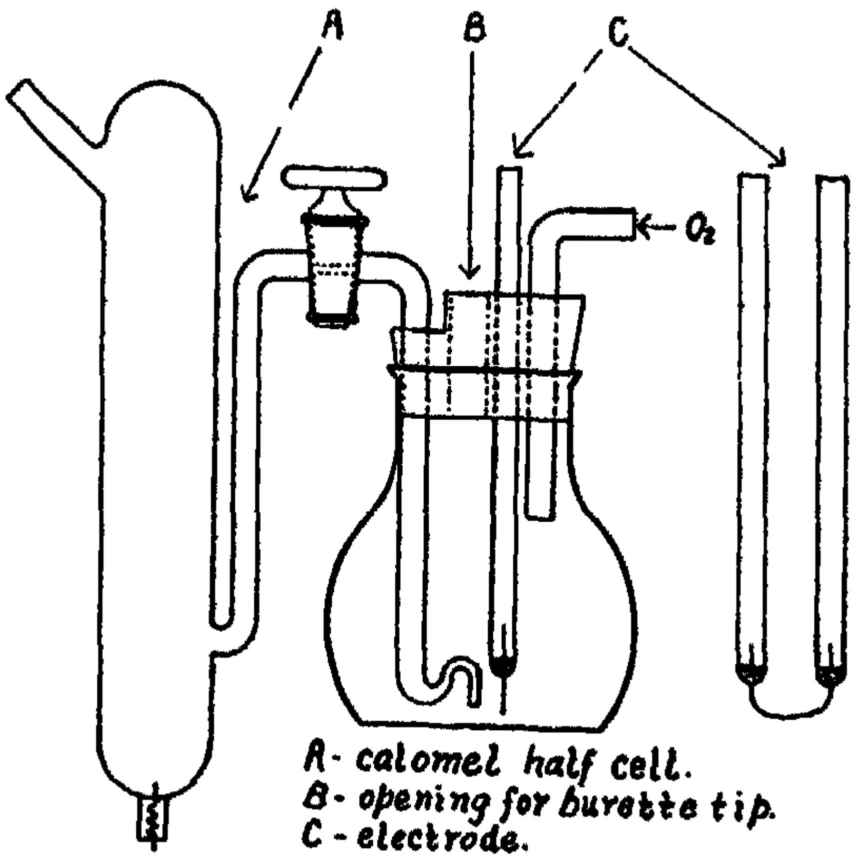
[1] W. M. Clark: "The Determination of Hydrogen Ions," 2nd Ed., Chap. XVII (1925).

behave quite differently. The electrodes were treated at different times with chromic acid, concentrated and fuming nitric acid, solutions of caustic alkalies and alkaline solutions of potassium permanganate, followed by washing with conductivity water, without improving their performance. Treatments with alkaline solutions followed by concentrated nitric acid gave no better results. Evidently these treatments failed to clean the electrodes.

If we accept Nernst's theory as to the setting up of an oxidation potential in these experiments, it follows that any foreign substance which may be present upon the electrode at the start may hinder the adsorption of oxygen



A- calomel half cell.
B- opening for burette tip.
C - electrode.

FIG. 1
Electrode Vessel

and so retard the establishing of a final equilibrium and cause the results to be irregular. Acting upon this suggestion, we cleaned an electrode by immersing it for some time in concentrated nitric acid, washed it thoroughly with conductivity water and heated it to a cherry red in the flame of a bunsen burner. It was allowed to cool for an instant and then immersed in the solution, and readings were taken at once. The results were much better than previously. An approximate equilibrium was soon reached and results in successive experiments were fairly consistent. The beneficial effects of degassing the electrodes each time before using them were obvious.

When an electrode is heated in the flame of a bunsen burner it may become contaminated by the gases of the flame. Then, too, the glass inseal which holds it is often cracked in the process. To overcome these difficulties we constructed an electrode which could be heated by passing an electric current through it. This consisted simply of a loop of platinum wire about 0.4 millimeter in diameter the ends of which were sealed through the ends of glass tubes as shown in C of Fig. 1. Wire larger than 0.4 mm. in diameter proved unsuitable, as it cracked the glass seal which held it when it was heated. At first copper wires were fused to the ends of the platinum wire and extended up the tubes, serving as leads. We found, that a potential was set up at the copper-platinum contact surface, and that, this contact potential varied by some millivolts from time to time. This difficulty was removed by using platinum wire connections welded to the wire of the loop. We found, however, that making contact with the loop by means of a column of mercury which filled the tube gave the same potential as did connections which were all of platinum, provided that the mercury was clean. This method of making the contact was used in all our careful measurements.

A detailed account of all our efforts to evolve a standard method to use in treating our electrodes cannot be given at this point. As the result of much study, however, we found the following procedure to give satisfactory results.

1. Place the electrode in hot, but not boiling, concentrated nitric acid for ten to fifteen minutes.

2. Wash thoroughly with conductivity water after cooling and then dry the glass shank of the electrode with a clean lintless towel.

3. Heat the platinum wire to dull redness for one or two minutes by passing a suitable electric current through it.

4. After cooling, place it at once in the solution.

The necessity for careful preparation of the electrode before each experiment, holding rigidly to the same routine method each time, cannot be too forcibly emphasized.

Even with such treatment the useful life of an electrode is limited. It was found in many cases that when electrodes began to give erratic results the tips of the lead glass inseals had cracked. A very tiny crack, which apparently did not reach through to the mercury was sufficient to cause the trouble. Whenever a crack appeared the electrode was useless for further work. We believe that these cracks took up nitric acid during the treatment of the electrode and later yielded it to the solution at the electrode surface, thus causing the potential as measured to be abnormal and inconstant.

It was found that electrodes made from new platinum wire were usually much better than those made from wire which had been used previously. We at first believed that this might be due to pitting of the wire by the hypochlorite solution, but careful examination under the microscope failed to reveal any apparent difference between new and used wire. The alteration in the surface which occurred in service, if any, was certainly very slight. New wire only was used in making up electrodes for our careful experiments.

Results were accepted as trustworthy in this work only when they had been secured with electrodes which (a) were free from mechanical defects, (b) which came to equilibrium normally and regularly as shown by measured potentials and (c) which had never given results which were erratic or abnormal. We believe that these are safe criteria to employ.

Our first experiments with zonite solutions exposed to the air, using our best electrodes, never gave an equilibrium potential even in six to ten hours, though the potential rose only slowly after about thirty minutes. This constant rise in potential was not due to a conversion of hypochlorite to chlorate, for some experiments showed that solutions of sodium chlorate at concentions comparable to those which might result from our solutions showed much lower potentials than those given by zonite. It was found that solutions fresh from the original container always had a lower potential than those which had been in contact with the atmosphere. It seemed probable that this effect might be due to reaction of carbon dioxide of the air with the sodium hypochlorite to liberate hypochlorous acid. To test this matter an apparatus such as is shown in Fig. 1 was used. A stream of oxygen was first passed through a soda-lime tube to free it from carbon dioxide and then it was led into the cell over the solution. A fresh solution of zonite showed a slow rise in potential at first, and the potential became constant after about 14 minutes. At the end of 24 minutes, a current of CO_2 was substituted for the oxygen, and the potential rose 0.219 volts in the next 8.5 minutes. Carbon dioxide-free oxygen was then again passed, and the potential came to a halt almost at once. The results of this experiment are shown graphically in Fig. 2. Merely interrupting the stream of oxygen after equilibrium had been reached, and breathing into the vessel caused the potential to rise abruptly by as much as 0.05 to 0.1 volt in several experiments. The necessity for excluding carbon dioxide from our alkaline solutions was apparent.

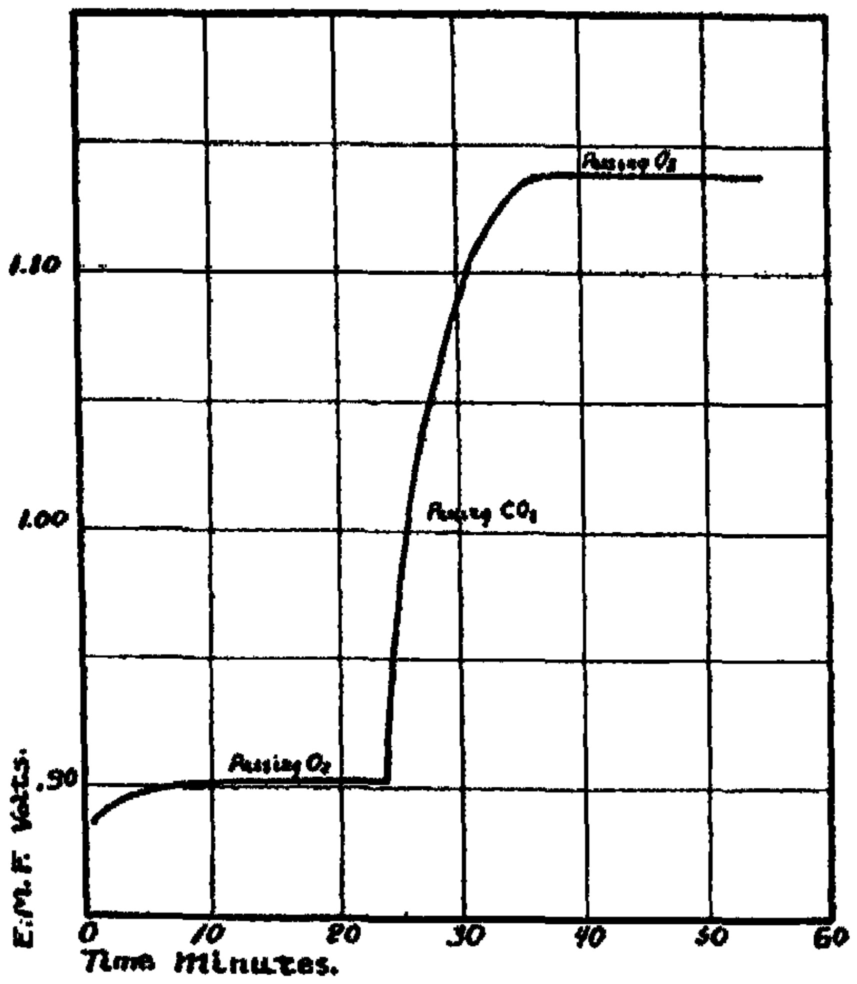


FIG. 2
Effect of eliminating CO_2 from above Alkaline Hypochlorite Solutions

Effect of adding a Base or an Acid to Hypochlorite Solutions

With the technique in hand, we first studied in a qualitative way the effect of progressively adding a base to a solution of hypochlorous acid, and then, reversing the process, the effect of progressively adding an acid to a solution of sodium hypochlorite.

Twnety-five cubic centimeters of hypochlorous acid containing only a trace of hydrochloric acid were placed in the flask. A burette, filled with 0.50 N. NaOH was placed so that its tip entered the cell through a hole in the stopper as shown in Fig. 1, B. Carbon dioxide-free oxygen was passed during these experiments. Potential readings of the cell were taken every few minutes and after the lapse of ten minutes when approximate constancy had been attained a final reading was taken and recorded. Without removing either electrode from the cell, a measured quantity of base was admitted and the cell was swirled as much as connections would permit in order to facilitate mixing. Ten minutes later when approximate equilibrium had been reached another reading was taken and more alkali added as before. These operations were repeated until several cubic centimeters of base had been added in excess of the amount calculated as necessary to just neutralize the hypochlorous acid present. At this point a burette containing 0.50 N. HCl was substituted for that containing alkali. The cell was not otherwise disturbed.

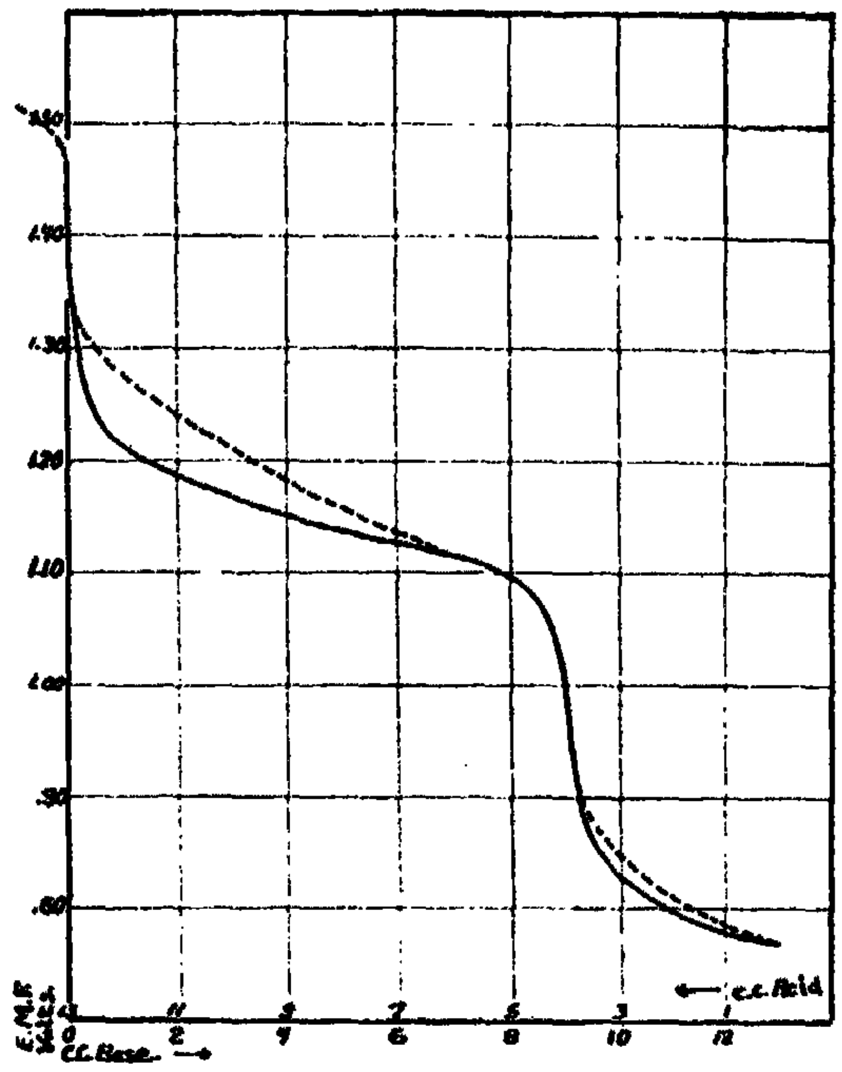


Fig. 3
Relation of Oxidation Potential to Acid or Base added

Hydrochloric acid was then added step by step to acidify the solution, employing the same routine method of addition as was used with the alkali, and the potentials corresponding to various quantities of acid added were determined.

The results of the above experiments are shown graphically in Fig. 3. Since the curves have been carefully drawn to scale, tables giving the data will not be included. The graph is representative of several experiments which checked fairly well. The lower curve indicates the changes during the addition of alkali; the upper, those found during the addition of acid.

The two "breaks" in these curves, we find, occur respectively at the points where free hydrochloric acid and hypochlorous acid are just neutralized when adding the base; or first introduced when adding the acid. We have carried out similar titrations using tenth normal reagents and find that electrometric titrations of hypochlorite solutions to determine their hypochlorite content and the amount of added acid or base can be carried out using our technique. The process is tedious, because it is necessary to wait for ten minutes before taking the final readings, and somewhat inconvenient because of the necessity for excluding carbon dioxide; but it is fairly accurate. We hope to study it in greater detail in the near future.

Experiments in Buffer Solutions

This set of experiments was, of course, qualitative rather than quantitative in nature, so far as a coordination between oxidation potential and hydrogen ion concentration is concerned. We next measured the oxidation potentials in buffer solutions, keeping the concentration of hypochlorite constant.

A few experiments were first tried using a buffer mixture made up with KCl and HCl solutions. The maximum oxidation potential of HOCl in such mixtures was reached within a very few minutes, five or six at the most, and remained constant over a period of thirty minutes or more. Although these experiments were very satisfactory from that standpoint, Cl_2O and Cl_2 were evolved quite vigorously. The concentration of HOCl necessarily diminishes rather rapidly under these conditions and the gases evolved have a serious destructive action upon the apparatus used. Solutions so buffered were, therefore, not investigated further. It seemd best to work with solutions which are more stable and, which correspond more closely to those which are cómmonly used in a commercial way.

Phosphate buffer solutions were prepared after the manner outlined by Sörensen.[1] He made up his buffer mixtures using fifteenth molal phosphate solutions. In our case, however, it was necessary to prepare more concentrated solutions so that after mixing with the HOCl solution the phosphates present would have the concentration specified by him. Therefore, we used fifth molal solutions of Na_2HPO_4 and KH_2PO_4 which were standardized by precipitating and weighing the phosphate as ammonium phosphomolybdate. Table I presents information concerning the composition of the

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[1] W. M. Clark: "The Determination of Hydrogen Ions," p. 114.

mixtures used. Column 2 gives the pH to be established; columns 3 and 4 give the amounts of .2 M. KH_2PO_4 and Na_2HPO_4 respectively, to be taken; and column 6 gives the amount of water necessary to bring the volume of the solution to 50 c.c., the constant volume to which all solutions were diluted. For example, in making up buffer mixture No. 1, we mixed 5 cc. of HOCl solution, 0.41 cc. of Na_2HPO_4, 16.25 cc. of KH_2PO_4 and 28.34 cc. of water. This final solution is of the same concentration in buffer agents as the first given by Sörensen and has a pH of 5.29. Walbum[1] states that the alteration of pH with temperature is for the most part negligible for phosphate buffer mixtures. Our experiments were carried out at room temperatures, which averaged about 24°C.

Table I
Composition of Mixtures following
Sörensen's Table

Solutions mixed.

HOCl Cont.	.0102 gm. per cc.
Na_2HPO_4	.200 molal
KH_2PO_4	.200 molal

No.	pH	c.c. Na_2HPO_4	c.c. KH_2PO_4	c.c. HOCl	c.c. H_2O
1.	5.29	0.41	16.25	5.00	28.34
2.	5.59	0.83	15.83	5.00	28.34
3.	6.24	3.33	13.33	5.00	28.34
4.	7.16	11.68	5.00	5.00	28.34
5.	7.73	15.00	1.66	5.00	28.34
6.	8.04	15.83	0.83	5.00	28.34

Table II
Composition of Mixtures following Auerbach and Pick's Table

Solutions mixed.

HOCl cont.	.0102 gm. per cc.
Na_2CO_3	.400 molal
$NaHCO_3$	.400 molal

No.	pH	c.c. Na_2CO_3	c.c. $NaHCO_3$	c.c. HOCl	c.c. H_2O
7.	8.35	0.00	25.00	5.00	20.00
8.	8.90	1.25	23.75	5.00	20.00
9.	9.15	2.50	22.50	5.00	20.00
10.	10.10	12.50	12.50	5.00	20.00
11.	10.65	20.00	5.00	5.00	20.00
12.	11.59	25.00	0.00	5.00	20.00

To cover a more alkaline range of pH, Auerbach and Pick[2] used buffer solutions consisting of mixtures of sodium carbonate and sodium bicarbonate. We prepared .4 molal solutions of Na_2CO_3 and $NaHCO_3$ and from them made

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[1] W. M. Clark: "The Determination of Hydrogen Ions," p. 116.

[2] W. M. Clark: "Determination of Hydrogen Ions," p. 323.

up solutions of the concentrations given by Auerbach and Pick. Table II, similar to that on the phosphates, furnishes information concerning the composition of each of our solutions for the pH values given. The method which we used in making up these solutions has been given above.

In these buffered solutions the normality of the hypochlorous acid was about 0.02, while the combined molal concentration of the salts of the buffer mixtures was 0.2 M in the carbonate, and 0.067 M. in the phosphate buffer mixtures.

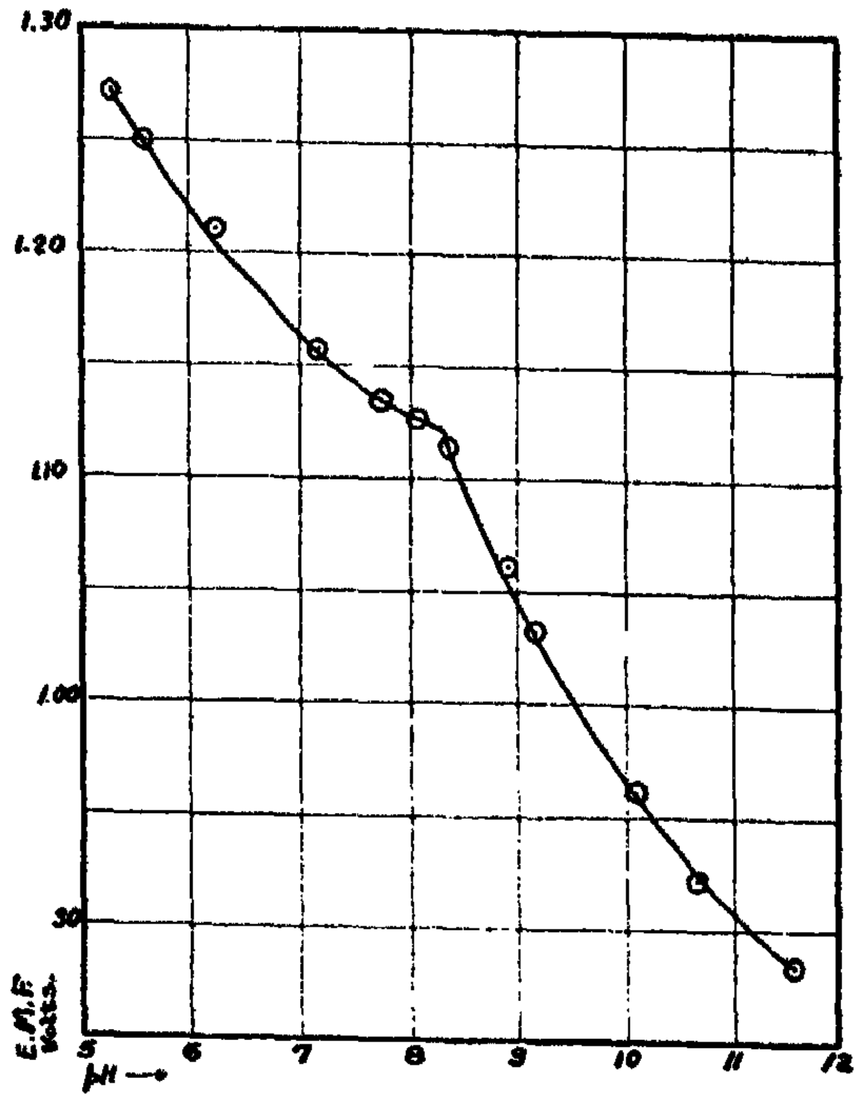

FIG. 4
Oxidation Potentials of Hypochlorite at Various Hydrogen Ion Concentrations

Now hypochlorous acid is a very weak acid. Noyes and Wilson[1] find that its ionization constant in .001 normal solution is 6.79×10^{-10}. Sand[2] found the value 3.7×10^{-8}. Results by other workers are in substantial agreement with these. Since the free hydrochloric acid present in our stock solutions was never more than sufficient in amount to give a very faint opalescence when silver nitrate solution was mixed with the solution of hypochlorous acid, it seems safe to assume that the concentration of hydrogen ion in them was very small. We believe, therefore, that the hydrogen ion concentrations in the solutions whose oxidation potentials were determined were not sensibly different from the hydrogen ion concentrations characteristic for the buffer mixtures themselves.

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[1] W. A. Noyes and Thomas A. Wilson: J. Am. Chem. Soc., 44, 1634 (1922).

[2] J. Sand: Z. physik. Chem., 48, 610 (1904).

The usual course of the building up of a potential with hypochlorite in a buffer solution, using an electrode prepared as previously described, may be set forth at this point. A rapid rise of 0.01 volt, or a little more, took place in the first few minutes, and the potential approached constancy after 8 or 9 minutes. The next five minutes showed an increase of only 1 or 2 millivolts. At the end of this time there was no further change in potential in most cases. In some instances a further rise occurred, but this rise was never more than one millivolt in the ensuing 15 minutes. We therefore, took the potential at the end of fifteen minutes as the equilibrium potential for the solution which was being examined.

In this work we did not depend upon results found with any one electrode or set of electrodes, but we used several in rotation, cleaning them carefully between determinations, and we always repeated the measurements two or three times with different sets of newly constructed electrodes.

The results of our work with buffer solutions are given in the Tables III and IV and shown graphically in Fig. 4. Each value is the mean of those found in many determinations. The potentials as measured differed from these values in every case by not more than ±.004 volts. The concentration of HOCl in these buffered solutions was in every case .00102 grams per cubic centimeter.

TABLE III

Variation of Potential with pH with Sörensen's Phosphate Mixtures

pH	Cell Potential	Oxidation Potential	pH	Cell Potential	Oxidation Potential
5.29	0.934	1.272	7.16	0.820	1.158
5.59	0.912	1.250	7.73	0.798	1.135
6.24	0.873	1.211	8.04	0.790	1.127

TABLE IV

Variation of Potential with pH with Auerbach and Pick's Carbonate Mixtures

pH	Cell Potential	Oxidation Potential	pH	Cell Potential	Oxidation Potential
8.35	0.777	1.115	10.10	0.623	0.961
8.90	0.723	1.061	10.65	0.584	0.922
9.15	0.695	1.033	11.59	0.546	0.884

We are at a loss to explain adequately the discontinuity of the curves as found with phosphate and with carbonate buffer mixtures. Certainly the small quantity of hypochlorous acid added could not shift the hydrogen ion concentrations of the buffer mixtures in such manner as to give these discrepancies. We believe that the reason for this failure to give a continuous curve lies in some intrinsic difference in the actions of phosphate and carbonate buffer mixtures;—that is, in a specific "salt effect."

Other buffer solutions cover the range which we have investigated, but those whose pH values are well established contain organic components and so could not be used in conjunction with hypochlorites.

It was planned to repeat these experiments with buffered solutions, using sodium hypochlorite, but lack of time prevented. A few preliminary experiments, however, showed that solutions of sodium hypochlorite and hypochlorous acid at the same concentration, in terms of available chlorine, gave nearly the same potentials in a solution of given pH, those with sodium hypochlorite being, in general, slightly lower.

Our results, though they only partially cover the field, show, we believe, that the oxidizing power of hypochlorite solutions increases as one passes from alkaline to acid solutions. This is in agreement with the information upon this subject which is now available in the literature.

This work seems to indicate, in a rough way, that the oxidizing power of a hypochlorite solution is directly proportional to its hydrogen ion concentration.

Summary

The oxidation potentials of hypochlorous acid and sodium hypochlorite in various solutions have been determined. A great part of the work was given over to a study of the method of measuring these potentials at platinum electrodes, and an apparatus for their measurement has been evolved. A method of treating the electrodes which gives reproducible potentials has been worked out. The oxidizing power of hypochlorites in solution as measured indirectly by potentiometric methods increases with acidity, that is, with increase in hydrogen ion concentration. It has been found possible to determine roughly the hypochlorite content and the amount of added acid or base in hypochlorite solutions by electrometric titration. Buffered solutions of the hypochlorites are more stable and give much more readily reproducible potentials than do unbuffered solutions. Slightly alkaline solutions of the hypochlorites are very readily decomposed by action of CO_2 of the air, with a marked increase in oxidizing power.

Stillwater, Oklahoma.
September 4, 1928.

THE EFFECT OF ELECTROLYTES UPON EMULSIONS. PRELIMINARY PAPER

BY H. V. TARTAR, C. W. DUNCAN, T. F. SHEA AND W. K. FERRIER

Introduction

The object of this investigation was to gain further knowledge regarding the influence of electrolytes on emulsions. Except in some preliminary experiments, use was made of materials of definite composition which could be prepared in quite pure form; most of the emulsions made therefore were definite and reproducible systems and the work may be duplicated by other investigators. One regrettable feature of much of the previous experimental work on emulsions is that at least part of the materials employed, have been of indefinite composition (mixtures) and further careful studies of the exact systems cannot be made. The presence of both univalent and multivalent metal cations in the same system has been avoided in the work reported in this paper.

There exists a dearth of information regarding the behavior of emulsions in the presence of electrolytes. Considerable work has been done which deals with the inversion of oil-in-water emulsions. In most instances, the inversion has been effected by the addition of salts yielding bivalent or trivalent cations, in sufficient amount that metathesis has taken place with the soaps of univalent metals used as emulsifying agents. It is unnecessary to give here any extensive review of the literature on emulsions and reference will be made only to those investigations having a direct bearing on the work reported herein.

Robertson[1] studied the effect of adding different amounts of sodium hydroxide on an emulsion of water with varying volumes of olive oil containing a small, but not accurately known, amount of free oleic acid. He concluded that when sodium hydroxide was used in sufficient quantity to convert to soap enough of the free fatty acid to cover with a protecting film a large volume of oil dispersed as globules, then an oil-in-water emulsion was formed; and when the quantity of alkali was not great enough to form the required concentration of soap, it might still be sufficient to yield an amount of soap which could surround the smaller volume of water present if it were dispersed as globules, and so a water-in-oil emulsion is formed in this case. The value of this work is minimized by the fact, that the concentration of the oleic acid, and consequently the concentration of the soap formed and of the excess of alkali was unknown.

Newman[2] states that the water-in-oil emulsion reported by Robertson was in reality not an emulsion at all but a cracked oil-in-water emulsion in which the appearance of the oil was changed by the presence of solid sodium oleate.

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[1] Robertson: Kolloid-Z., 7, 7 (1910).

[2] Newman: J. Phys. Chem., 18, 34 (1914).

Newman also investigated the two types of emulsions obtained with benzene and water. He found that when sodium oleate was the emulsifying agent, water was always the external phase regardless of the relative volumes of water and benzene used. With magnesium oleate he obtained emulsions of water in benzene. He also found that emulsions of water in benzene stabilized with magnesium oleate were inverted by adding sufficient sodium oleate.

Bancroft[1] with the work of Newman and of Donnan[2] as a background, developed a general theory of emulsion formation. He considered that the emulsifying agent is adsorbed into the surface separating the two liquids thus forming a separate phase and is wetted by both liquids but to a different extent by each. Consequently, there is a difference in surface tensions on the two sides of the interfacial film. As a result, the side with the higher surface tension becomes concave and so tends to envelop the liquid on that side. He states: "If the surface tension between liquid A and the emulsifying agent is lower than the surface tension between liquid B and the emulsifying agent, liquid A will be the dispersing and liquid B the disperse phase."

Clowes studied the inversion of emulsions and after considerable experimental work, agreed with Bancroft. Clowes[3] states: "The soaps tend to concentrate at the interface between water and oil and to form a coherent film. Soaps of monovalent cations, being readily dispersed in water, but not in oil, form a film or diaphragm which is wetted more readily by water than by oil; consequently the surface tension is lower on the water side than on the oil side. Since the area of the inside face of a film surrounding a sphere is obviously smaller than that of the outside face, the film tends to curve so that it encloses globules of oil in water, in this manner reducing the area of the side of higher surface tension to a minimum as compared with that of lower surface tension. On the other hand, a film composed of soaps of divalent or trivalent cations, being freely dispersed in oil, but not in water, is wetted more readily by the oil than by the water, the surface tension is lower on the oil than on the water side, and the film tends to curve in such a manner as to enclose the globules of water in an outer or continuous oil phase." Clowes found that sodium chloride and potassium chloride in small amounts in sodium hydroxide solution greatly increased the drop number obtained by dropping the electrolyte solution into oleic acid, which indicated that these salts promoted oil-in-water emulsions. Calcium salts had an opposite effect. He considered that equilibrium in an emulsion depended on the relative proportions of positive and negative ions adsorbed by the film around the globules, negative ions in excess favoring oil-in-water, and positive ions in excess promoting water-in-oil emulsions.

Briggs[4] using hydrous ferric oxide as the emulsifying agent, did not find that sodium chloride promoted benzene-in-water emulsions.

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[1] Bancroft: J. Phys. Chem., 17, 501 (1913); 19; 275 (1915).

[2] Donnan: Z. physik. Chem., 47, 188 (1904); Donnan and Potts: Kolloid-Z., 4, 208 (1910).

[3] Clowes: J. Phys. Chem., 20, 407 (1916).

[4] Briggs: J. Ind. Eng. Chem., 13, 1008 (1916).

Bhatnagar[1] prepared emulsions by adding increasing volumes of olive oil containing 0.5 per cent of oleic acid to 25 c.c. of approximately 0.01 normal potassium hydroxide, and tested for type by determining the conductivity of the resulting emulsion. He found that when the concentration of the oil phase was increased to 85 c.c. the conductivity fell to a very low value indicating that oil was the external phase. Paraffin oil containing 0.5 per cent of oleic acid gave similar results but the water-in-oil emulsion was very unstable.

Whether a certain mixture is or is not an emulsion is important, involving as it does the entire subject of methods for determining the existence and type of emulsions. Bhatnagar considers that he had a water-in-oil emulsion even though it existed not over two minutes.

In a later paper[2] Bhatnagar reported more work on the inversion of phases by electrolytes. He recognized that the use of alkaline solutions and free fatty acids in oils—as used by Clowes and by Bhatnagar in his earlier work—was unsatisfactory and complicated because either free fatty acid or free alkali may be present in excess. Therefore, he used soaps instead of alkali plus free fatty acid. His emulsions contained 10 c.c. of oil phase (paraffin oil, B.P.) and 10 c.c. of aqueous phase which contained a known amount of soap and known amounts of electrolytes. The soaps used as emulsifying agents were sodium oleate, lithium stearate and potassium stearate; and the electrolytes were barium nitrate, strontium nitrate, lead nitrate, nickel nitrate, aluminum sulfate and chromium sulfate. Inspection of Bhatnagar's results show that the amount of electrolyte required to invert an emulsion closely approximated the amount needed to convert the sodium oleate to the corresponding soap of the di- or trivalent cation. When this conversion took place the system no longer contained sodium oleate but contained oleates of barium, or other di- or trivalent cations which have been shown by the work of Bancroft, Newman, Clowes, and others to promote water-in-oil emulsions. This stoichiometric relationship seems to have been overlooked by Bhatnagar. It must be admitted, however, that this simple relationship does not apply when sodium linoleate was the emulsifying agent nor does it explain why more multivalent electrolyte is required to bring about reversal of phase when the external phase is diluted without changing the absolute amount of sodium oleate present.

Later Bhatnagar[3] has stated that "it is difficult to draw hard and fast lines between the effects of univalent electrolytes and bi- and ter-valent electrolytes on soap solutions, as both of these are adsorption phenomena. On the solubility hypothesis sodium chloride ought to be capable of changing the type of emulsion as well as barium chloride. This is, however, contrary to all experience and the multi-valent ions alone are known to cause reversal of type." He concludes that the two vital factors governing the process of emulsification are: (1) the nature of the charge on the emulsifying agent and

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[1] Bhatnagar: J. Chem. Soc., **117**, 542 (1920).
[2] Bhatnagar: J. Chem Soc., **119**, 61 (1921).
[3] Bhatnagar: J. Chem. Soc., **119**, 1766 (1921).

(2) the interfacial tension relations of the emulsifying agent with the two phases. All the data on reversal of type, he states, are in agreement with the empirical rule "that all emulsifying agents having an excess of negative ions adsorbed on them and wetted by water will yield oil-in-water emulsions, whilst those having an excess of adsorbed positive ions and wetted by oil will give water-in-oil emulsions."

Langmuir[1] and Harkins[2] investigated the structure of liquid surfaces and the nature of surface tension. The fundamental idea as stated by Harkins is, "that surface tension phenomena in general are dependent upon the orientation and packing of molecules in surface layers, and that the forces involved in this action are related to those involved in solution and adsorption." He also pointed out that "at any surface or interface the change which occurs is such as to make the transition to the adjacent phase less abrupt." Harkins, Davies, and Clark[3] conclude that the type of emulsion produced is related to the number of fatty acid radicles in the molecules of soap used. They consider that the soap is adsorbed into the interface largely as a unimolecular film and that droplets of the disperse phase would be stable whenever the molecules together with the adsorbed ions, etc., in the interface fit the curvature of the drop. Langmuir suggests that "the size of the colloidal particles is determined by the difference in size between the two ends of the molecules, just as the size of an arch is dependent upon the relative sizes of the two ends of the stones of which the arch is constructed."

Finkel, Draper and Hildebrand[4] have submitted data in support of the idea that the size of the droplets and the stability of the emulsions vary with the diameter of the polar end of the molecules of the soap molecules used as an emulsifying agent.

By counting the droplets in a given volume of emulsion and computing their total surface, Griffin[5] has shown that the reduction in concentration of the soap in the aqueous phase corresponded to an adsorbed film of soap of unimolecular dimension surrounding the droplets.

The data reported herein were obtained from the initial experiments of an investigation of emulsions which one of the authors (T) contemplates continuing much further. While the investigation has not yet reached the status to justify conclusions regarding some of the important factors of emulsification, the authors deem it advisable to offer at this time a preliminary paper giving experimental results. The discussion of the bearing of these data on the various theories of emulsification, will be reserved for future publication.

Preparation of Materials

Oleic acid was purified[6] by adding lead acetate solution to U.S.P. oleic acid. The lead oleate was washed free from excess of lead acetate and then

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[1] Langmuir: J. Am. Chem. Soc., 39, 1848 (1917).
[2] Harkins: J. Am. Chem. Soc., 39, 354, 541 (1917).
[3] Harkins, Davies and Clark: J. Am. Chem. Soc., 39, 581 (1917).
[4] Finkel, Draper and Hildebrand: J. Am. Chem. Soc., 45, 2780 (1923).
[5] Griffin: J. Am. Chem. Soc., 45, 1648 (1923).
[6] Harkins and Zollman: J. Am. Chem. Soc., 48, 69 (1926).

extracted by refluxing with ether. The lead oleate solution was treated with hydrochloric acid liberating the oleic acid. The ether was distilled under reduced pressure and in an atmosphere of carbon dioxide. The oleic acid thus obtained was probably somewhat impure; apparently very pure oleic acid has never been prepared.[1]

Sodium oleate was prepared by the method used by Harkins and Zollman.

Potassium stearate was prepared from U.S.P. stearic acid by refluxing with a solution of potassium hydroxide in absolute alcohol. The resulting solution was filtered and cooled, the potassium stearate separating out upon cooling. The precipitate so obtained was filtered, washed with absolute alcohol and ether and then dried. Two grams of this soap when dissolved in 100 cc of warm, distilled water gave a clear solution. Upon cooling below 30° an opaque gel was formed. It was found necessary to warm the solution to about 30° each time it was used.

The benzene, aniline, toluene, xylene, nitrobenzene, dimethyl aniline and ortho-toluidine were "C.P. Analyzed" and sponsored by a reliable manufacturer. They were distilled before using, the boiling points being used as tests for purity.

The sodium and potassium hydroxides were of the "C.P. Analyzed" grade, purified by alcohol and containing some carbonate.

Preparation of Emulsions

The emulsions were made in glass vials (eight drachm capacity) which had been carefully cleaned. The total volume of the liquids used in some emulsions was 16 cc., 12 cc. of one phase and 4 cc. of the other; in other emulsions one-half these volumes were used. This ratio of the phases was used because it approximates the composition of the most stable emulsions.[2]

In the preparation of part of the emulsions reported in Table I (by Shea) the "oil" phase was added from a burette in 2 cc. portions and, after each addition, the system was shaken by hand fifty times in sets of ten shakes with about five seconds interval between each set. Briggs[3] first noted the efficiency of this intermittent shaking method. In the preparation of the other emulsions, the materials were placed in the vials and then shaken in a mechanical shaker for a definite length of time—usually fifteen minutes. The shaking machine gave approximately three hundred oscillations per minute; and had a vertical amplitude of two inches and a horizontal amplitude at one end only of the vial holder of two inches.

Preliminary Experiments on the Effect of Acid and Base on the Stability of Benzene-Water Emulsions stabilized by Sodium Oleate

Because of the marked effect of hydrogen and hydroxyl ions on the stability of colloids, some preliminary experiments were made using electrolytes yielding these ions. The influence of hydrochloric, acetic, and oxalic acids on

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[1] Lapworth, Pearson and Mottram: Biochem. J., 19. 7 (1925).

[2] Pickering: J. Chem. Soc., 91. 2002 (1907); Hatschek: Brit. Ass. Colloid Reports, 2, 17 (1918).

[3] Briggs: J. Phys. Chem., 24, 120 (1920).

emulsions was studied by making up a series of emulsions each of which consisted of twelve c.c. of benzene, two cc. of 2 per cent aqueous sodium oleate solution, and two c.c. of acid. An emulsion of benzene in water was obtained whenever the amount of acid present was just insufficient completely to destroy the soap. Emulsions to which sufficient acid had been added to decompose half the sodium oleate, were in good condition after two months' standing.

The effect of oleic acid was next studied. The use of this acid eliminates some of the complexity introduced when an acid such as hydrochloric is added to an emulsion. The oleic acid does not decompose the sodium oleate nor does it serve as an emulsifying agent. Emulsions were prepared by adding to 4 c.c. of 1 per cent sodium oleate, a measured amount of oleic acid and sufficient benzene in small increments to make a total of 12 c.c. of "oil" phase and shaking by hand. It was determined that when a relatively high amount of oleic acid was used the usual oil-in-water emulsion was inverted to a water-in-oil emulsion. This emulsion was quite mobile and was tested thoroughly for type; although unstable it proved to be a water-in-oil emulsion. The results are recorded in Table I.

TABLE I

Effect of Oleic Acid on Emulsions stabilized by Sodium Oleate

Benzene c.c.	10.0	9.0	8.0	7.0	6.0
Oleic Acid c.c.	2.0	3.0	4.0	5.0	6.0
Type	O–W	O–W	O–W	Broke	W–O (unstable)

O–W indicates oil-in-water emulsion.
W–O indicates water-in-oil emulsion.

Emulsions were made using kerosene instead of benzene. Seven c.c. of kerosene with 5 c.c. of oleic acid emulsified easily in 4 c.c. of one per cent sodium oleate, giving a more stable W-O emulsion.

A series of emulsions consisting of 12 c.c. of oil, 2 c.c. of 2 per cent sodium oleate, and 2 c.c. of sodium hydroxide solution was prepared. The oils used were benzene, kerosene, olive oil, and a paraffin oil (Squibbs' Liquid Petrolatum). In all cases, the stability of the emulsions was decreased as the concentration of the sodium hydroxide was increased.

Influence of Sodium Chloride on the Type of Emulsion

To study the effect of sodium chloride, emulsions were prepared containing 12 c.c. of benzene and 4 c.c. of aqueous phase. The aqueous phase was always one per cent sodium oleate and held varying concentrations of sodium hydroxide and sodium chloride. A series of emulsions were made by two different workers one year apart, each without knowledge of the results obtained by the other. The data obtained are reported in Table II. In all of the tables, the concentrations of electrolyte given, are for the final aqueous phase of the emulsion.

TABLE II

The Effect of Sodium Chloride on Emulsions containing Benzene, Water, Sodium Oleate, and Sodium Hydroxide

First worker (Shea)

Normality of Sodium Hydroxide	Normality of Sodium Chloride 0.20	0.25	0.30	0.35	0.40	0.45	0.50
0.000—	O-W	O-W	O-W	O-W	I	W-O	W-O
0.0002	O-W	O-W	O-W	O-W	I	W-O	W-O
0.001	O-W	O-W	O-W	I	I	W-O	W-O
0.005	O-W	O-W	O-W	I	W-O	W-O	W-O
0.01	O-W	O-W	O-W	I	W-O	W-O	W-O
0.05	O-W	O-W	O-W	I	W-O	W-O	W-O
0.10	O-W	I	I	I	W-O	W-O	W-O

Second Worker (Ferrier)

	0.15	0.20	0.25	0.30	0.35	0.40	0.45
0.00	O-W	O-W	O-W	I	Broke	Broke	W-O
0.0002	O-W	O-W	O-W	I	Broke	Broke	W-O
0.001	O-W	O-W	O-W	I	I	Broke	W-O
0.002	O-W	O-W	O-W	I	I	W-O	W-O
0.01	O-W	O-W	O-W	I	I	W-O	W-O
0.05	O-W	O-W	Broke	Broke	I	W-O	W-O

I indicates the inversion point.

The data of the first worker were somewhat more carefully checked by repetition of the series. The normality of the sodium chloride required to produce a given result varied somewhat in the different series. The system called "inversion point" was made up of three layers, an upper layer of oil (about 12 c.c.), a shallow, intermediate, creamy, oil-in-water emulsion, and a slightly yellow watery layer (about 4 c.c.) on the bottom. On standing, an appreciably thick disc of solid formed on top of the intermediate layer. This may have been sodium oleate salted out by the salt. In the "W-O" type a yellowish white emulsion, about 4 c.c. in volume is formed at the bottom of the tube. When the sodium chloride was added to the sodium hydroxide solution of sodium oleate, a precipitate was usually formed. This precipitate soon disappeared from the tubes containing a small concentration of sodium chloride. The presence of this precipitate did not inhibit the formation of oil-in-water emulsions in all cases. In most cases it had disappeared from the vials which yielded the inversion type system before the benzene was added It was always present at the time of emulsification of the mixtures which formed the "W-O" type. The precipitate was undoubtedly sodium oleate.

The nature of the "W-O" layer was investigated. Tests by the drop-dilution method of Briggs gave rather unsatisfactory results in certain instances, although on the whole, they clearly indicated a water-in-oil emulsion.

Robertson's indicator method (using potassium permanganate instead of Sudan III) also indicated a water-in-oil emulsion. This finding was confirmed by Palmer's internal phase method.[1]

A similar series of emulsions using toluene and xylene were next prepared. The data are presented in Tables III and IV.

TABLE III

The Effect of Sodium Chloride on Emulsions containing Toluene, Water, Sodium Oleate and Sodium Hydroxide

Composition of Emulsion

12 c.c. toluene
2 c.c. 2 per cent sodium oleate solution
1 c.c. sodium chloride solution
1 c.c. sodium hydroxide solution

Normality of Sodium Hydroxide	Normality of Sodium Chloride							
	0.00	0.15	0.20	0.25	0.30	0.35	0.40	0.45
0.05	O-W	O-W	O-W	Broke	Broke	I	W-O	W-O
0.01	O-W	O-W	O-W	Broke	Broke	I	W-O	W-O
0.002	O-W	O-W	O-W	Broke	Broke	I	W-O	W-O
0.001	O-W	O-W	O-W	Broke	Broke	Broke	W-O	W-O
0.0002	O-W	O-W	O-W	O-W	Broke	I	W-O	W-O
0.00	O-W	O-W	O-W	O-W	Broke	I	W-O	W-O
0.00	O-W							

TABLE IV

The Effect of Sodium Chloride on Emulsions containing Xylene, Water, Sodium Oleate and Sodium Hydroxide

Composition of Emulsion

6 c.c. xylene
0.5 c.c. sodium chloride solution
1 c.c. 2% sodium oleate solution
0.5 c.c. sodium hydroxide solution

Normality of Sodium Hydroxide	Normality of Sodium Chloride							
	0.00	0.15	0.20	0.25	0.30	0.35	0.40	0.45
0.05	O-W	O-W	O-W	Broke	Broke	Broke	I	W-O
0.01	O-W	O-W	O-W	O-W	O-W	I	I	W-O
0.002	O-W	O-W	O-W	O-W	O-W	I	I	W-O
0.001	O-W	O-W	O-W	O-W	O-W	I	I	W-O
0.0002	O-W	O-W	O-W	O-W	O-W	I	I	W-O
0.00	O-W	O-W	O-W	O-W	O-W	Broke	I	W-O

With the toluene and xylene emulsions, the inversion point remains at approximately the same concentration of sodium chloride regardless of the concentration of the sodium hydroxide.

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[1] Palmer: "Biochemical Laboratory Methods," 22 (1927).

The writers believe this to be the first time that emulsions of benzene and water, toluene and water and xylene and water containing univalent cations only, have been inverted to water-in-oil emulsions by the use of sodium chloride.

Other Experiments with Emulsions using Different Emulsifying Agents or "Oil" Phases

The effect of potassium chloride upon emulsions stabilized by potassium stearate was next investigated. The concentrations of the solutions were the same as for the emulsions previously discussed. Emulsions were prepared from benzene, toluene, and xylene with water, potassium stearate, potassium chloride and potassium hydroxide. In all cases a permanent, white oil-in-water type of emulsion was obtained and in no case was there a sign of inversion due to the addition of potassium chloride. The emulsions were more easily prepared and were more stable than when sodium oleate was used. It would seem possible from data given in Tables II, III and IV that inversion could be obtained by using *a greater concentration of the electrolyte*. This was not done however.

Other "oils" were investigated for inversion of type both with sodium oleate and potassium stearate as the emulsifier. The investigation of aniline revealed that no emulsions were obtainable when even a very small amount of either sodium chloride or potassium chloride was present. Permanent emulsions were obtained with all concentrations of sodium hydroxide (0.0002N to 0.05N). Aniline emulsions stabilized with potassium stearate were very sensitive to potassium hydroxide—no permanent emulsion could be formed when the concentration exceeded 0.01 N. The emulsions of aniline and potassium stearate; aniline, potassium stearate and potassium hydroxide were more difficult to prepare than those with sodium oleate.

The emulsions of aniline when first taken from the shaker had the appearance of a permanent white emulsion filled with shiny, finely-divided crystals. This phenomenon became intensified as the concentration of sodium chloride increased. It was not so noticeable, however, in the case of potassium chloride. Upon standing a few minutes, the higher concentrations of salt caused the aniline to separate into large globules, 2 to 4 mm. in diameter. This effect persisted for hours, the smaller globules gradually coalescing with others to form larger ones; after twenty-four hours complete separation had taken place.

Emulsions were prepared with ortho-toluidine stabilized with sodium oleate and with potassium stearate which gave stable oil-in-water type. However, no emulsions could be prepared with the above components when even very small amounts of sodium hydroxide, potassium hydroxide, sodium chloride or potassium chloride were present.

The emulsions with nitrobenzene formed readily and were very stable. The data are given in Table V. The oil-in-water type of emulsion was obtained with all concentrations of sodium chloride used. Between the sodium hydroxide concentrations of 0.002N and 0.001N a marked difference in color of

TABLE V

The Effect of Sodium Chloride on Emulsions containing Nitrobenzene, Water, Sodium Oleate and Sodium Hydroxide

Composition of Emulsion

12 cc. nitrobezene
1 c.c. sodium chloride solution
2 c.c. 2% sodium oleate solution
1 c.c. sodium hydroxide solution

Normality of Sodium Hydroxide	Normality of Sodium Chloride							
	0.00	0.15	0.20	0.25	0.30	0.35	0.40	0.45
0.05	O-W	O-W	O-W	O-W	O-W	O-W	O-W	Broke
0.01	O-W	O-W	O-W	O-W	O-W	O-W	O-W	O-W
0.002	O-W	O-W	O-W	O-W	O-W	Broke	Broke	Broke
0.001	O-W	O-W	O-W	O-W	Broke	Broke	Broke	Broke
0.0002	O-W	O-W	O-W	O-W	Broke	Broke		
0.00	O-W	O-W	Broke	Broke	Broke	Broke		

the nitrobenzene layer was noticed. Emulsions with 0.001N sodium hydroxide or less displayed a well defined orange tint in the nitrobenzene layer. With concentrations of sodium hydroxide above 0.001N the nitrobenzene layer was a characteristic yellow. This effect may have been due to the repression of hydrolysis of the sodium oleate by concentrations of sodium hydroxide greater then 0.001N.

The effect of potassium chloride on nitrobenzene emulsions stabilized with potassium stearate was next studied. In all cases, very stable emulsions of oil-in-water type were formed and no signs of inversion or breaking were noticed with the concentrations of electrolytes used.

TABLE VI

The Effect of Sodium Chloride on Emulsions containing Dimethylaniline, Water, Sodium Oleate and Sodium Hydroxide

Composition of Emulsion

6 c.c. dimethylaniline
0.5 c.c. sodium chloride solution
1 c.c. 2% sodium oleate solution
0.5 c.c. sodium hydroxide solution

Normality of Sodium Hydroxide	Normality of Sodium Chloride							
	0.00	0.15	0.20	0.25	0.30	0.35	0.40	0.45
0.05	O-W	O-W	O-W	O-W	O-W	Broke	Broke	Broke
0.01	O-W	O-W	O-W	O-W	O-W	O-W	O-W	Broke
0.002	O-W	O-W	O-W	O-W	O-W	O-W	O-W	O-W*
0.001	O-W	O-W	O-W	O-W	O-W	O-W	Broke	O-W*
0.0002	O-W	O-W	O-W	O-W	O-W	O-W	Broke	O-W*
0.00	O-W	O-W	O-W	O-W	O-W	O-W	O-W	Broke

Dimethylaniline (See Table VI) emulsified very readily, with low concentrations of sodium chloride (0.0N to 0.20N); they formed stable, permanent white emulsions within five minutes. As the concentrations of sodium chloride increased, the time of shaking increased to fifteen minutes. The emulsions formed however were very viscous and stable. Emulsions containing 0.45N sodium chloride did not form when shaken fifteen minutes. Upon being shaken one hour, the three indicated with an asterisk were exceedingly viscous, tan in color, and very stable.

The effect of potassium chloride on emulsions of dimethylaniline, stabilized with potassium stearate was then studied. The emulsions formed readily and, in all cases, the foam from the emulsion filled the entire bottle. The type was oil-in-water and no signs of inversion or breaking were apparent. Upon standing twenty-four hours or longer, a thin layer of the aqueous phase settled out. In an attempt to find a "breaking point" more electrolyte was added to a new set of emulsions. Two c.c. of potassium chloride of the following concentrations: 1.0N, 1.4N, 1.6N, 1.8N, were placed in separate bottles of dimethylaniline and potassium stearate. They were shaken fifteen minutes in the mechanical shaker, allowed to stand for six hours and examined. All the emulsions were stable except the one containing two c.c. of 1.8N potassium chloride which showed signs of breaking.

Conclusions and Summary

1. Emulsions of benzene and water with sodium oleate as the emulsifying agent are destroyed by acids when approximately enough acid is added to effect the decomposition of the soap.

2. Benzene-water-sodium oleate emulsions of the oil-in-water type have been inverted by adding oleic acid to the benzene phase.

3. Sodium hydroxide does not increase the stability of emulsions using sodium oleate as the emulsifying agent.

4. The type of emulsion has been changed by the use of univalent electrolytes yielding the same cation as the soap.

5. Emulsions of benzene, toluene, or xylene with water and sodium oleate, show a well-defined zone of instability between sodium chloride concentrations of 0.25N to 0.45N with benzene; the inversion point shifted somewhat as the concentration of the sodium hydroxide was increased; with toulene and xylene the inversion point is not markedly influenced by the sodium hydroxide concentration.

6. With the water and "oil" phase used, potassium stearate was found to be superior to sodium oleate as an emulsifying agent; the emulsions were prepared more easily and had a greater stability.

7. All of the emulsions produced by the use of potassium stearate were of the oil-in-water type; no inversion could be effected by the use of potassium chloride and potassium hydroxide.

8. The work reported herein shows that in previous work insufficient attention has been given to the influence of the "oil" phase upon the stability

and type of emulsion. The attention of investigators has usually been centered upon the influence of the emulsifying agent and electrolyte present. The data reported above indicates that methyl groups attached to the benzene ring have a beneficial effect on the emulsifiability of the "oil." The amino group, however, seemed to exert an inhibitory influence. Two methyl groups, as in the case of the dimethyl aniline, seemed to overcome this inhibitory influence of the amino group and emulsification took place readily. When two different substituent groups were attached to benzene ring, as in ortho toluidine, influence of the amino group seemed to dominate and the "oil" did not readily emulsify. The nitro group favored emulsification.

Seattle, Washingotn,
August 13, 1928.

DECOMPOSITION OF NITRIC OXIDE BY PLATINUM AT ELEVATED TEMPERATURES AND ITS RETARDATION BY OXYGEN*

BY PAUL W. BACHMAN AND GUY B. TAYLOR

Green and Hinshelwood[1] studied the decomposition of nitric oxide on a heated platinum wire and came to the conclusion that the reaction is unimolecular with respect to nitric oxide and is retarded by oxygen. The conclusion that the reaction is unimolecular was based on the criterion that the fraction decomposed up to 13.5% was independent of the initial concentration of nitric oxide. It was assumed that the retarding effect of oxygen was of minor importance for small percentage decomposition so that the usual criterion of a unimolecular reaction, i.e., equal fractional reaction independent of initial concentration, applied.

The object of the present work was to establish the law by which oxygen retards the decomposition. On the assumption that the rate is proportional to the square of the nitric oxide concentration, *a*, and inversely to that of oxygen, we may write the equation

$$-\frac{dx}{dt} = K_2 \frac{(a-x)^2}{x} \qquad (1)$$

which integrated between limits for the constant, K_2, becomes

$$K_2 = \frac{1}{t}\left(\frac{a}{a-x} - 1 - \ln\frac{a}{a-x}\right) \qquad (2)$$

In this equation the concentration terms appear as ratios just as they do in the usual equation for a straight unimolecular reaction,

$$K_1 = \frac{1}{t}\ln\frac{a}{a-x} \qquad (3)$$

so that the criterion of equal fractional reaction in equal time applies to either case.

Green and Hinshelwood show that the decomposition of nitric oxide is retarded by oxygen by calculating values for the unimolecular constant from equation (3). Values of k_1 fall rapidly with time. On the other hand we have found that values of k_2 computed from equation (2) are nearly constant. Table I gives our values of k_1 and k_2 computed from Green and Hinshelwood's data. From the constancy of k_2 it seemed likely that the reaction was not unimolecular with respect to NO but followed the law given by equation (1).

TABLE I

Time, sec.	60	120	180	300	720	1440
% decomp.	13	18.5	23	29	40	48
$k_1 \times 10^3$	2.3	1.7	1.5	1.1	0.7	0.45
$k_2 \times 10^4$	1.7	1.9	2.0	2.2	2.1	1.9

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* Contribution No. 7 from Experimental Station, E. I. duPont de Nemours & Co.

[1] J. Chem. Soc., 128, 1709-13 (1926).

Experimental

A number of experiments were carried out according to Green and Hinshelwood's method. A wire was sealed axially into a glass tube about 15 cm. long by 3.5 cm. diameter. A three-way cock led to manometer, gas supply, and vacuum pump. The nitric oxide was generated by dropping sulfuric acid into sodium nitrite[1] and dried with sulfuric acid. The temperature of the electrically heated wire was controlled by voltmeter and ammeter. The electrical energy required for a given temperature was determined by calibration with a Leeds and Northrup optical pyrometer[2] by glowing the wire in air before the experiment. The energy required varied somewhat with the pressure, possibly due to the heat losses near the lead-in wires. The temperatures were corrected for emissivity.

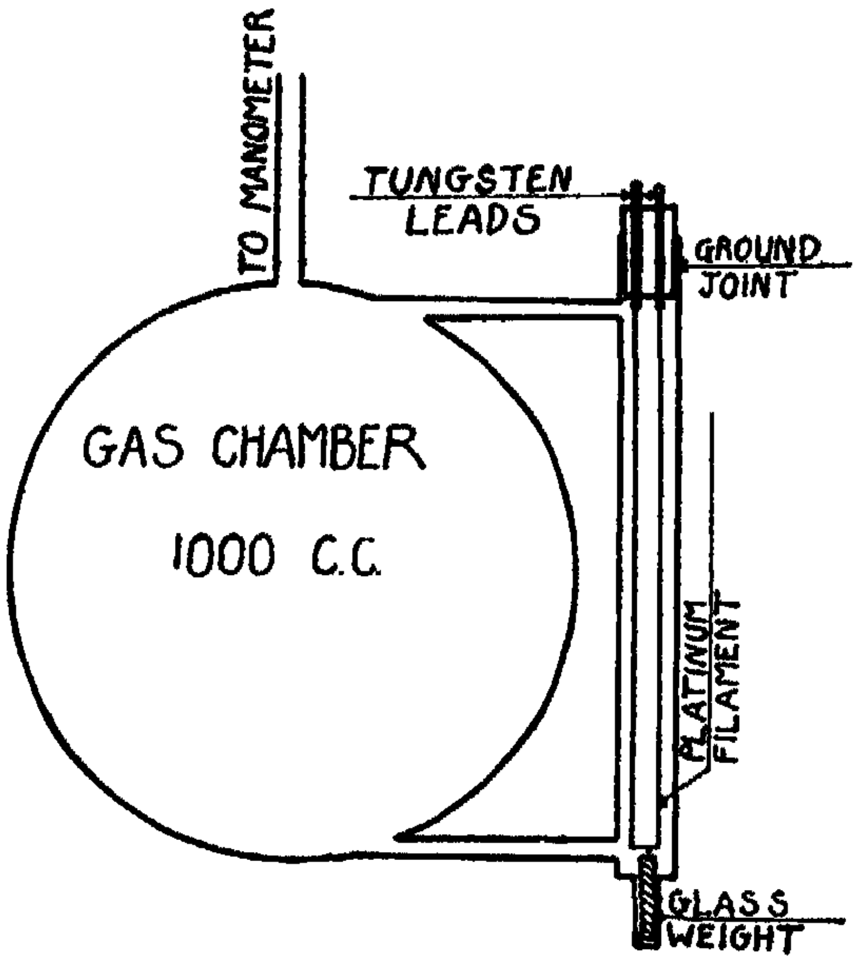

FIG. 1

The experimental procedure consisted in filling the tube to a definite pressure with nitric oxide, glowing the wire for definite time intervals, and reading the pressure decrease after the wire had cooled. The tube was immersed throughout an experiment in a water-bath at 25°C. The decomposition reaction itself, $2NO = N_2 + O_2$, involves no volume change, but, upon cooling, oxygen reacts with nitric oxide, $2NO + O_2 = 2NO_2 \rightleftarrows N_2O_4$. The fraction (x) of nitric oxide decomposed may be calculated from a plot constructed from the formula

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[1] Noyes: J. Am. Chem. Soc., 47, 2170 (1925).

[2] See Kunsman: J. Am. Chem. Soc., 50, 2100 (1928).

$$\text{contraction} = ax + \frac{K}{8} - \frac{\sqrt{8Kax - K^2}}{8}$$

in which *a* is original pressure of NO. The formula holds for values of *x* up to 0.5. K is the equilibrium constant defined by NO_2/N_2O_4. Values of K in the literature[1] are fairly consistent. For concentration expressed in millimeters of mercury, K is 13.5 at 0°C., 106 at 25°, and 237 at 35°. Theoretically the maximum contraction occurs at the point of 50% decomposition; thereafter the pressure increases with decomposition to the original nitric oxide value. In actual experiment, using the literature values for K, the maximum contraction is always less than the theoretical. Green and Hinshelwood got around this difficulty by using an arbitrary constant deduced from the observed maximum contraction. They took K = 35 at 0°C.

In two of our experiments the maximum contractions were 115 and 303 mm. From these values the original pressures of NO calculated were 296 and 719 mm., while the actual measured initial pressures were 338 and 792 mm. The indicated purity of the gas used in the experiments was 88 and 91% respectively while an actual analysis by reaction in 50% CrO_3 in water[2] showed the nitric oxide used to be 99.5% pure. The probable explanation is the very slow rate at which oxygen and nitric oxide combine when present in nearly stoichiometric proportion. In our experiments we have calculated the decomposition by using the literature values of K as given above, ignoring whatever cause is responsible for the low contraction at 50% decomposition. Below 40% it makes little difference what convention is adopted. The nitric oxide as generated and stored for the experiments was considered as 95% pure, the rest being nitrogen.

Table II summarizes the experimental results with 0.25 mm. diameter platinum wire at 1210°C. Calculated values of k_2 are reasonably constant in any given experiment and fairly so between the experiments with different initial pressures of nitric oxide.

Table III summarizes results with a piece of thermocouple wire, platinum-10% rhodium, of the same size, at three different temperatures. Here again, the values of k_2 are reasonably constant at a given temperature and different partial pressures. The temperature coefficient of the reaction appears to be small.

These experiments can hardly be called conclusive in establishing the validity of equation (1), because the actual partial pressures existing at the wire when it is heated can not in the nature of the case be known.

A form of apparatus in which the actual partial pressures at the hot wire can be calculated from the experimental data was suggested to us by Dr. G. B. Kistiakowsky. This is shown diagrammatically in Fig. 1.

To a liter bulb a small vertical side tube was connected at top and bottom. In the side tube was hung a long loop of platinum wire arranged for electrical heating as shown. In an experiment, circulation by convection up the tube

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[1] Bodenstein: Z. physik. Chem., 100, 68 (1922); Schreber: 24, 665 (1897); Wourtzel: Compt. rend., 169, 1397 (1919).

[2] This reagent absorbs NO rapidly when used in ordinary gas analysis apparatus.

TABLE II

Decomposition of NO on pure Platinum at 1210°C

Time Seconds	No. 31 479 mm. Per cent decomp.	k_2 $\times 10^4$	No. 32 342 mm. Per cent decomp.	k_2 $\times 10^4$	No. 33 201 mm. Per cent decomp.	k_2 $\times 10^4$
15	7.5	2.0	7.5	2.0	9.5	3.3
30	10.5	2.2	10.5	2.2	11.5	2.5
60	15	2.2	15.5	2.3	17.5	3.1
120	21	2.5	21	2.5	23	3.0
240	26.5	2.2	28	2.5	31	3.2
420	34	2.4	34	2.5	38	3.2
600	38	2.2	38.5	2.3	—	—

TABLE III

Decomposition of NO on Platinum-10% Rhodium

1035°C

Time Seconds	No. 21 477 mm. Percent decomp.	k_2 $\times 10^4$	No. 22 333 mm. Percent decomp.	k_2 $\times 10^4$	No. 23 183 mm. Percent decomp.	k_2 $\times 10^4$
30	8.5	1.3	6	0.7	6	0.7
60	11	1.2	9	0.7	8.5	0.7
120	15	1.1	13	0.8	11.5	0.6
240	20	1.1	16.5	0.7	15	0.6
420	23.5	0.9	20.5	0.7	19	0.6
660	27	0.8	24	0.6	22.5	0.5
960	30.5	0.8	27	0.6	24.5	0.5
1740	36	0.7	31.5	0.5	30	0.4

1210°C

	No. 26 481 mm.		No. 25 337 mm.		No. 24 182 mm.	
30	13	3.3	11	2.3	12.5	3.0
60	18	3.3	16	2.6	16	2.6
120	24	3.4	21	2.5	23	3.1
240	31.5	3.3	27	2.3	29	2.7
420	37.5	3.1	33	2.2	35	2.5

1385°C

	No. 27 477 mm.		No. 28 332 mm.		No. 29 193 mm.	
30	19	8.0	17	6.0	19	8.0
60	25.5	7.9	23	6.2	24.5	7.3
120	33.5	7.9	30.5	6.2	31	6.5
240	42	7.6	38.5	5.8	39	6.1

EXPERIMENT No. 37

Time Min.	Press. decrease mm.	Percent decomp.	Partial NO	Press. mm. O_2	Δ NO mm.	Ave. NO mm.	Ave. O_2 mm.	$K_1 = \frac{\Delta NO}{\Delta t} \cdot \frac{O_2}{NO}$ $\times 10$	$K_2 = \frac{\Delta NO}{\Delta t} \cdot \frac{O_2}{(NO)}$ $\times 10^4$	$K_1' = \frac{\Delta NO}{\Delta t} \frac{1}{NO}$ $\times 10^2$
0	—	—	721	0	—	—	—	—	—	—
3	14	3.3	683	12	38	702	6	1.1	1.5	1.8
6	23	5.3	661	18	32	672	15	1.6	2.4	1.6
9	32	7.1	639	24	22	650	21	2.4	3.6	1.1
12	39	8.5	622	29	17	631	26.5	2.4	3.8	0.9
15	45	9.6	609	32	13	616	30.5	2.2	3.5	0.7
20	54	11.2	590	37	19	600	34.5	2.2	3.6	0.6
25	60	12.3	577	40	13	584	38.5	1.7	2.9	0.4
30	67	13.7	561	44	16	569	42.0	2.4	4.2	0.6
40	79	16.0	533	51	28	547	47.5	2.4	4.4	0.5
50	90	17.9	510	56	23	522	53.5	2.4	4.5	0.4
60	99	19.6	491	60	19	501	58.0	2.2	4.4	0.4
80	113	22.1	462	66	29	477	63.0	1.9	4.0	0.3
							mean	2.1	3.6	

EXPERIMENT No. 39

Time Min.	Press. Decrease mm.	Percent decomp.	Partial pressure mm. NO	Partial pressure mm. O_2	Δ NO mm.	Aver. NO mm.	Aver. O_2 mm.	$K_1=\frac{\Delta NO}{\Delta t}\cdot\frac{O_2}{NO}$ × 10	$K_2=\frac{\Delta NO}{\Delta t}\cdot\frac{O_2}{(NO)^2}$ × 10^4	$K_1'=\frac{\Delta NO}{\Delta t}\cdot\frac{1}{NO}$ × 10^2
0	—	—	493	0	—	—	—	—	—	—
3	8	2.9	471	7	22	482	3.5	0.5	1.1	1.5
6	15	5.0	454	12.	17	463	9.5	1.2	2.5	1.2
9	21	7.1	437	17	17	446	14.5	1.8	4.1	1.3
12	25	8.3	429	19	8	433	18.0	1.1	2.6	0.6
15	29	9.5	419	22	10	425	20.5	1.6	3.8	0.8
20	35	11.1	406	25	13	413	23.5	1.5	3.6	0.6
25	40	12.5	394	28	12	400	26.5	1.6	4.0	0.6
30	44	13.7	384	31	10	389	29.5	1.5	3.9	0.5
40	52	15.8	368	34	16	376	32.5	1.4	3.7	0.4
50	58	17.6	354	38	14	361	36.0	1.4	3.9	0.4
60	63	18.8	344	40	10	349	39.0	1.1	3.2	0.3
80	70	20.8	325	45	19	335	42.5	1.2	3.6	0.3
						mean =		1.3	3.3	

EXPERIMENT No. 44

Time Mins.	Press. decrease mm.	Percent decomp.	Partial NO	press. mm. O_2	Δ NO mm.	Aver. NO mm.	Aver. O_2 mm.	$K_1 = \frac{\Delta NO}{\Delta t} \cdot \frac{O_2}{NO}$ × 10	$K_2 = \frac{\Delta NO}{\Delta t} \cdot \frac{O_2}{(NO)^2}$ × 10^4	$K_1' = \frac{\Delta NO}{\Delta t} \cdot \frac{1}{NO}$ × 10^2
0	—	—	254	0	—	—	—	—	—	—
3	4	3.2	242	4	12	248	2	0.3	1.3	1.4
6	7	4.7	235	7	7	239	5	0.5	2.0	1.0
9	10	6.7	227	9	8	231	7	0.8	3.2	1.2
12	12	8.3	221	11	6	224	9	0.8	3.2	0.9
15	13	9.1	218	13	3	220	10.5	0.5	2.2	0.5
20	16	10.6	212	15	6	215	12	0.7	3.1	0.6
25	18	11.8	207	16	5	210	13.5	0.6	3.1	0.5
30	20	13.0	202	17	5	205	14.5	0.7	3.5	0.5
40	23	15.0	195	19	7	199	16	0.6	2.8	0.4
50	27	17.3	185	21	9.5	190	18.25	0.9	4.8	0.5
60	29	18.5	181	23	4.5	183	20.25	0.5	2.7	0.2
80	33	20.8	173	25	9	177	22	0.6	3.2	0.3
							mean =	0.6	2.9	

and through the bulb was rapid. The wire was glowed continuously during an experiment while the pressure was followed on a manometer. The bulb was put in a thermostat bath held at 35°C.

The per cent decomposition was calculated from the pressure decrease as in the earlier type of experiment. Partial pressures at the hot wire surface were computed as follows:

Let a = original NO pressure
p = observed pressure at time t
x = fraction decomposed in time t

then $\frac{ax}{2}$ = partial pressure N_2

$p - \frac{ax}{2}$ = sum of partial pressures of NO and O_2

$\frac{1 - x}{1 - x/2}\left(p - \frac{ax}{2}\right)$ = partial pressure NO

Typical experiments, Nos. 37, 39 and 44 are tabulated. They were all duplicated and the separate experiments agreed remarkably well. Expt. No. 44 was run at a total pressure of one atmosphere, using nitrogen as a diluent. An experiment at the same initial pressure of nitric oxide and without nitrogen gave substantially the same result.

Values for rate constants were computed by the method of small differences from point to point as shown in the tables. K_1 is based on an assumption of rate proportional to nitric oxide and inversely proportional to oxygen concentration while K_2 is based on the mechanism expressed by equation (1). K_2 furnishes a reasonable constant at the three different initial pressures while K_1 does not. The per cent decomposition at three different initial pressures is the same after the same elapsed time. The constant K'_1, computed for straight unretarded unimolecular reaction falls rapidly with time in every case.

The apparent heat of activation according to the Arrhenius equation $d \ln k/dt = E/RT^2$ was determined from the data of Table III for the platinum-rhodium wire by the slopes of plots of log t against 1/T for 10, 20, and 30% decomposition. The lines for each percentage were substantially parallel. Values for E for different initial pressures of NO were,—480 mm. 24,600 cal., 335 mm. 25,700 cal., and 185 mm. 26,900 cal.

Discussion

The values for the apparent heat of activation "E" on platinum is reported by Green and Hinshelwood to be approximately 14,000 calories, and on 90% platinum-10% rhodium is found to be approximately 24,000 calories by the present authors. This leads to some deductions regarding the heat of adsorption of nitric oxide. The above values of "E" are connected to "Q," the true heat of activation, by the equation

$$E = Q + \lambda' - \lambda$$

where λ = heat of desorption of reactants,
and λ' = heat of desorption of products.

It has been shown by Langmuir[1] that it is extremely difficult to remove oxygen from a platinum surface even at 1500°C., indicating a high heat of adsorption of oxygen on platinum. Assuming the apparent heat of activation of nitric oxide on platinum to be 14,000 calories it follows that the heat of adsorption of nitric oxide on platinum must be a large positive value for Q to be of real magnitude. Experiments are in progress in this laboratory in an effort to confirm experimentally the above statement.

The present authors visualize the decomposition of nitric oxide on the surface of platinum and platinum-rhodium catalysts as follows. Two nitric oxide molecules are adjacently adsorbed with oxygen towards the catalytic surface. The nitrogen atoms combine and evaporate from the surface, leaving the oxygen in an adsorbed condition to act as a retarding agent.

Summary and Conclusions

The heterogeneous decomposition of nitric oxide on platinum and platinum-rhodium wires at temperatures above 1000°C, is shown to be bimolecular with respect to nitric oxide and to be retarded proportional to the oxygen concentration.

It has been indicated that bimolecular reactions retarded by a product of the reaction are similar to unretarded unimolecular reactions in that the fraction reacting in any time is independent of the initial pressure.

The heat of adsorption of nitric oxide on platinum has been predicted as having a large positive value.

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[1] Langmuir: Trans. Faraday Soc., 17, 621 (1922).

AN EXTENSION OF THE INTERMEDIATE-COMPOUND THEORY OF CATALYSIS IN GAS REACTIONS

BY H. H. STORCH

One of the most important results of recent studies of homogeneous unimolecular reactions is the fact that such reactions frequently involve large molecules, such as nitrogen pentoxide, azomethane, propionaldehyde, etc. That this is not a fortuitous relationship, is the opinion of several experimenters.[1,2] One[2] of these writes: "We believe it is not an accident that all the homogeneous unimolecular reactions so far known are concerned with rather complicated molecules."

In several of the collision theories proposed to explain the mechanism of unimolecular reactions, activation by use of some of the internal energy of the molecule, in addition to the energy obtained by collision was postulated.[1,2,3,4] Such assumptions lead to rates of reaction which are consistent with the experimental data, and with the falling off of the reaction rate at pressures where collisions are either entirely absent or markedly reduced. These theories necessitate a large number of degrees of freedom for the reactant, and hence lend significance to the observation concerning the necessity of a complex molecule for a unimolecular reaction. In the absence of collisions, radiation has been found[5] to be ineffective in the racemization of pinene. The author states, however, that despite this negative result, radiation may contribute to the energy of activation at higher pressures where collisions take place.

These results of the studies of homogeneous unimolecular reactions may be used to correlate some facts concerning catalytic phenomena. A number of reactions which involve the decomposition of a single substance, and which are bimolecular when conducted as homogeneous reactions, have been found to be unimolecular on the surface of a contact catalyst. Examples of this are the decomposition of hydrogen iodide on the surface of platinum, and the decomposition of nitrous oxide on the surface of gold. The decomposition of hydrogen iodide on platinum has been analyzed by Taylor,[6] who shows that the process may be divided into a number of successive reactions, so chosen that the heat of activation is considerably lower in the presence of the contact agent than it is when the reaction is homogeneous. In this way Taylor accounts for the observed difference in heats of activation of the heterogeneous and homogeneous reactions. The steps outlined by Taylor

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[1] Hinshelwood: Proc. Roy. Soc., 113A, 230 (1926).

[2] Fowler and Rideal: Proc. Roy. Soc., 113A, 570 (1927).

[3] Lewis and Smith: J. Am. Chem. Soc., 47, 1508 (1925).

[4] Rice and Rampsberger: J. Am. Chem. Soc., 49, 1617 (1927); 50, 617 (1928).

[5] Mayer: J. Am. Chem. Soc., 49, 3033 (1927).

[6] Proc. Roy. Soc., 113A, 77 (1926).

involve the dissociation of the hydrogen iodide molecule by the platinum surface, followed by the reaction between the adsorbed monatomic hydrogen with another hydrogen iodide molecule to form molecular hydrogen, and another iodine atom, (the latter subsequently reacting with one of its kind to form an iodine molecule.) The high heats of primary adsorption, and the experiments of Gauger[7] and of Wolffenden[8] are cited as support for the dissociation of the molecule.

The following modification of Taylor's mechanism is suggested: The adsorption of hydrogen iodide by platinum results in the formation of addition compounds between the unsaturated platinum atoms and at least two molecules of hydrogen iodide. This assumption of at least two molecules of hydrogen iodide is based upon evidence from reactions involving two reactants where it has been found essential that both substances be adsorbed before reaction take place. The further assumption that both reactants are adsorbed on the same catalyst atom is in harmony with the fact that only isolated patches of contact surfaces are catalytically active, for it is only the highly unsaturated atom which could accommodate two molecules of the reactant. The complex $Pt(HI)_x$, where $X \geqq 2$, is large enough to possess a greater number of degrees of freedom than gaseous HI molecules, and hence may be activated by energy received from its own reservoir of internal energy in addition to that received by collisions. The subsequent rearrangement of this complex may involve the transitory existence of hydrogen and iodine atoms, but this is not essential to the postulated mechanism of the function of the contact catalyst. The latter may be briefly restated as one which provides a sufficiently complex molecule containing catalyst and reactants, so that a large number of degrees of freedom are available to supply part of the energy of activation.

If the rate of formation of $Pt(HI)_x$ is directly proportional to the pressure of the hydrogen iodide, the observed rate of decomposition will correspond to a unimolecular reaction. If, however, the rate of formation of the reactive complex is independent of the pressure, the observed rate of decomposition would correspond to a zero order reaction. This is the case in the decomposition of ammonia by various metal surfaces.

In the field of homogeneous gas reactions, water vapor is one of the most common and most effective catalysts. Thus it is very difficult to explode mixtures of carefully dried carbon monoxide and oxygen or of hydrogen and oxygen. The combustion of carbon bisulfide or of ethylene, however, is not affected by the presence or absence of water vapor.[9] These facts suggest that the efficiency of water vapor in promoting the combustion of hydrogen or carbon monoxide is due to the formation of complex molecules thus permitting the use of the internal energy of these complexes to contribute to the heat of activation. In the case of carbon bisulfide and ethylene, the molecules ap-

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[7] J. Am. Chem. Soc., 46, 674 (1924).

[8] Proc. Roy. Soc., 110A, 464 (1926).

[9] Bone and Townend: "Flame and Combustion in Gases," (1927).

pear to be sufficiently complex to provide the necessary increment from their store of internal energy.

There are, however, serious objections to this theory of the catalytic action of water vapor. If the difficulty of exploding mixtures of hydrogen and oxygen were entirely due to deficiency of energy available for activation, explosion by a spark discharge should not be seriously hindered by the absence of water vapor. The fact that explosion by a spark discharge is greatly facilitated by the presence of water vapor, indicates that some other factor is involved. This factor may be the "screening" action of water vapor on the deactivation of the active molecules by the walls, electrodes, etc. Gibson and Hinshelwood[10] have postulated such screening action in the reaction between hydrogen and oxygen in order to account for the increased speed of the homogeneous reaction when inert gases were present.

Another example of homogeneous catalysis is the gaseous ion catalysis discovered by S. C. Lind.[11] Here the "clustering" of the reactants about the ions produced by alpha radiation is found to be an assumption which explains the observed ratios of the number of molecules reacting to the number of ions present. This assumption is similar to the hypothesis advanced in this paper relative to contact catalysis, but there is this important difference; that Lind's hypothesis included a subsequent bimolecular reaction of two clusters of opposite charges.

An observation is cited by Lind concerning the relative efficiency of "clustering" collisions as compared with dissociating collisions:—"Kullman[12] has shown that in systems where ionized hydrogen is undergoing chemical reaction it is probable that the collisions of the H^{+}_{2} ions with molecules of the other reactant (i.e. clustering collisions) are much more effective than the dissociating ones (to give H^{+} and H^{+}_{3} ions)." This is analogous to the above discussion of the decomposition of HI by a platinum surface, i.e. those collisions of HI with Pt which result in the complex $Pt(HI)_x$ are assumed to be more effective in the decomposition than those resulting in adsorbed monatomic hydrogen.

Summary

The intermediate compound theory of catalysis is extended so as to present a theory of the function of these compounds in gas-phase catalysis. This function is to provide a complex (containing the reactants and the catalyst), of a sufficiently large number of degrees of freedom, so that the energy of these may be available for contribution to the energy of activation.

New Brunswick, N. J.,
September, 1928.

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[10] Proc. Roy. Soc., 119A, 591 (1928).

[11] "Chemical Effects of Alpha Particles and Electrons," 2nd Edition (1928).

[12] Naturwiss, 14, 427 (1926).

COAGULATION OF BLOOD AND MILK BY ELECTROLYTES AND THE SIMILARITY BETWEEN THE CLOTTING OF BLOOD AND THE FORMATION OF JELLIES

BY N. R. DHAR AND SATYA PRAKASH

In publications[1] from these laboratories, we have proved that sols can be divided into two groups:—

(i) The first group of sols consists of ferric hydroxide, aluminium hydroxide, chromium hydroxide, hydrated manganese dioxide, etc. This group of sols does not appreciably adsorb ions carrying the same charge as the sols when coagulated by KCl, K_2SO_4, $BaCl_2$, etc, and this class of sols does not become stable on dilution, does not show the phenomenon of positive acclimatisation, and shows additive relationships when coagulated by mixtures of electrolytes of different valencies. These sols do not show appreciable decrease of viscosity on the addition of small quantities of electrolytes.

(ii) The second class of sols consists of arsenious sulphide, antimony sulphide, mastic, Prussian blue, etc. These sols adsorb appreciably ions carrying the same charge as the sols. They become more stable on dilution, show the phenomenon of positive acclimatisation, and show marked ionic antagonism when coagulated by mixture of electrolytes of different valences; their viscosities decrease appreciably when small quantities of electrolytes are added to them.

In this communication, we are recording our experimental results obtained with blood and milk, showing that blood and milk belong to the second class of colloids which adsorb ions carrying the same charge as the sols. Ordinary sheep's blood was collected in a bottle of capacity 200 cc. containing 1 cc. of toluene. During the course of experimentation a part of the blood clotted. The part which remained unclotted was utilised for the experiments. 50 cc. of unclotted blood were diluted to 250 cc. The volume was kept 10 cc. in every case and 2 cc. of this diluted blood were used for coagulation. In the case of experiments with concentrated blood, 2 cc. of original undiluted blood were taken. Time of observation was kept one hour. In the case of blood,

TABLE I

	Concentration necessary for coagulation in mols	
Electrolytes	Dilute blood	Concentrated blood
Sodium citrate	0.704 M	——
Potassium oxalate	1.05 M	0.855 M
Potassium fluoride	1.653 M	1.368 M
Sodium tartrate	1.139 M	1.015 M
Ammonium nitrate	4.655 M	4.482 M
Hydrochloric acid	0.456 M	0.387 M

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[1] J. Phys. Chem., 29, 435, 659 (1925); 31, 649 (1927).

appearance of turbidity was taken as the coagulation point. For experiments with milk boiled cow's milk was utilised. 20 cc. of it were diluted to 100 cc. and 2 cc. of this diluted milk were used in each case. 2 cc. of original undiluted milk were taken in experiments with concentrated milk.

The experiments were carried on at 30°C. and the results are given in Table I.

TABLE II

Electrolytes	Concentration necessary for coagulation in mols Dilute milk	Concentrated milk
Sodium tartrate	1.210 M	1.121 M
Potassium fluoride	2.470 M	1.960 M
Potassium oxalate	1.155 M	1.050 M
Sodium acetate	3.311 M	2.838 M
Hydrochloric acid	0.228 M	0.159 M

The experimental results show that diluted blood and milk are more stable towards sodium tartrate, citrate, potassium oxalate, fluoride, hydrochloric acid and ammonium nitrate.

In some previous communications[1] we have investigated the sensitising influence of gelatine in different sols and we have advanced a general explanation of the phenomenon of sensitisation. In this paper we have investigated the influence of traces of gelatine and saponin in the coagulation of blood and milk and the experimental results given in Table III have been obtained.

TABLE III

1% solution of Kahlbaum "Golddruck" gelatine was used.
2 cc. of dilute blood used, volume kept 10 cc.
Time of observation—1 hour.

Electrolytes	Concentration necessary for coagulation in mols Dilute Blood	with gelatine 0.2 c.c.	0.5 c.c.	1.0 c.c.
Sodium citrate	0.704 M	0.660 M	0.627 M	
Sodium tartrate	1.139 M	1.121 M	1.068 M	1.032 M
Potassium oxalate	1.05 M	0.975 M	0.945 M	0.990 M
Potassium fluoride	1.653 M	——	1.586 M	1.528 M
Hydrochloric acid	0.452 M	0.452 M	——	0.445 M

TABLE IV

One percert solution of saponin was used.

Electrolytes	Concentration necessary for coagulation in mols Dilute Blood	with saponin 0.2 c.c	0.5 c.c.	1 0 c.c.
Sodium citrate	0.704 M	0.693 M	——	——
Potassium oxalate	1.05 M	0.990 M	1.005 M	1.035 M
Potassium fluoride	1.710 M	1.653 M	1.606 M	——
Hydrochloric acid	0.452 M	0.452 M	0.445 M	——

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[1] Kolloid-Z., 38, 14 (1926); 39, 346 (1926); 41, 229 (1927).

TABLE V

1% solution of gelatine and 1% of saponin were used.
2 c.c. of dilute milk made up to 10 c.c.
Time of observation—1 hour.

Electrolytes	Concentration necessary for coagulation in mols						
	Dilute milk	with gelatine			with saponin		
		0.2 c.c.	0.5 c.c.	1.0 c.c.	0.2 c.c.	0.5 c.c.	1.0 c.c.
Sodium tartrate	1.210M	1.157M	1.121M	1.085M	—	—	—
Hydrochloric acid	0.228M	0.228M	0.228M	0.228M	0.216M	0.205M	0.182M

The above experimental results show that saponin and gelatine render blood and milk unstable towards salts. With acids gelatine does not sensitise blood and milk. It seems likely, therefore, that the sensitising influence of gelatine is really due to the hydrogen ions present in it.

The sensitising influence of saponin is difficult to explain. It will be interesting to note that saponin sensitises the coagulation of blood and milk by salts as well as by acids. It appears, therefore, that the hemolytic action of saponin on blood is due to its rendering blood unstable towards electrolytes. In presence of saponin the blood particles are rendered unstable and hence coagulation and hemolysis become easier.

In previous papers, we have shown that the sensitising influence of gelatine towards different sols is due to its containing acids. From our experimental results, it will be seen that hydrochloric acid coagulates blood and milk more readily than salts of the same concentration. In other words, both blood and milk are very sensitive to the coagulating influence of $H^{\cdot}$ ions. In this respect, blood and milk resemble mastic, gamboge and other readily hydrolysable sols. The view that the sensitising influence of gelatine is due to the presence of $H^{\cdot}$ ions present in gelatine is supported by the fact that there is no sensitisation by the presence of gelatine when blood, and milk are coagulated by hydrochloric acid. Consequently, the sensitising influence of gelatine on blood and milk is due to the presence of acid in gelatine.

We have carried on experiments on the coagulation of a sol of hemoglobin by different electrolytes and we have found that the sol of hemoglobin is rendered unstable towards electrolytes by the presence of saponin.

The stabilisation of blood and milk by the addition of small quantities of oxalate, citrate fluoride, tartrate and sulphate ions is certainly due to the adsorption of the negative ions from various electrolytes, and the consequent increase of the negative charge on blood and milk. We are of the opinion that blood and milk will show marked ionic antagonism when coagulated by ions of varying valencies.

The following experimental results were obtained in the coagulation of blood by ammonium nitrate and by cupric sulphate in presence of small quantities of sodium citrate, sodium acetate, potassium fluoride, sodium tartrate and potassium hydroxide.

TABLE VI

2 c.c. of blood made up to 10 cc.

Time = 1 hour.

Amount of electrolyte added in mols		Concentration of ammonium nitrate necessary for coagulation
No salt added	M	4.482 M
Sodium citrate	0.022 M	5.258 M
Potassium fluoride	0.114 M	4.741 M
Sodium acetate	0.095 M	4.913 M
Potassium hydroxide	0.002 M	4.999 M

TABLE VII

2 c.c. of dilute blood made up to 10 c.c.

Time = 1 hour

Amount of electrolyte added in mols		Concentration of copper sulphate necessary for coagulation
No salt added		0.000025 M
Sodium acetate	.0966 M	0.000175 M
Sodium tartrate	.0178 M	0.000950 M
Sodium citrate	.0022 M	0.000200 M
Potassium hydroxide	.0020 M	0.000700 M

The following results were obtained in the coagulation of dilute milk by cupric sulphate in presence of sodium acetate, sodium tartrate, sodium citrate and potassium hydroxide.

TABLE VIII

2 c.c. of dilute milk made up to 10 c.c.

Time = 1 hour

Electrolytes added in mols		Concentration of copper sulphate necessary for coagulation
No salt added		0.0011 M
Sodium acetate	0.00946 M	0.0015 M
Sodium tartrate	0.00356 M	0.0015 M
Sodium citrate	0.0022 M	0.0027 M
Potassium hydroxide	0.002 M	0.0017 M

The experimental results given in Tables VI–VIII, prove conclusively that blood and milk show ionic antagonism markedly when coagulated by ammonium nitrate or copper sulphate in presence of small quantities of sodium citrate, potassium fluoride, sodium acetate and potassium hydroxide. In presence of the above substances the particles of blood and milk are stabilised by the adsorption of OH′ and other negative ions from the above electrolytes. This stabilisation of blood and milk is due to the increase in the amount of negative charge on the particles and is exactly identical with the behaviour of sols of arsenious sulphide, antimony sulphide, prussian blue, etc., already investigated.

Our experimental results show that the explanation of the stability of blood and milk due to the presence of small amounts of citrate, tartrate, oxalate, fluoride, etc., based on the view of the removal of the precipitating calcium ions by the above negative ions is incorrect. The real explanation of the stabilisation of both blood and milk by the presence of sodium or potassium salts of the the above acids, is the increase in the charge on the particles of blood and milk due to the adsorption of the negative ions and of OH′ ions derived from the hydrolysis of the sodium or the potassium salts of the weak acids already mentioned.

Recently medical men are using solutions of sodium citrate with great success for stopping the outflow of blood with sputum in cases of tuberculosis. Concentrated solutions of sodium citrate are intraveneously injected and the outflow of blood is stopped in a short time. From the experimental results recorded in this paper, it will be evident that the stopping of outflow of blood is due to its coagulation by concentrated solutions of sodium citrate. These results are interesting in view of the well-known fact that dilute solutions of sodium citrate hinder the coagulation of blood. Our results explain satisfactorily the peculiar behaviour of blood, that it is stabilised and clotting is hindered in presence of dilute solutions of sodium citrate, oxalate, fluoride, etc., and that the outflow of blood is stopped by concentrated solutions of sodium citrate.

In previous communications[1] from these laboratories, we have investigated the conditions of the formation of jellies of different substances. We have proved that jellies can be divided into three groups. The first group consists of gelatine, starch, agar, silicic acid, soaps, manganese arsenate, zinc arsenate, vanadium pentoxide, ceric hydroxide, etc. In this group, the particles forming the jellies, consist of some kind of network. These substances produce most stable jellies and are formed very readily. The second group of jellies is obtained by the slow coagulation of the sol throughout its whole mass. Possibly, hydroxides of iron, aluminum, and chromium, form typical members of this group and the particles of this group need not consist of a network. The stability of this group is less than that of the first group. Both these groups have marked affinity for water. The third group forms the von Weimarn jellies which are the least stable ones. These jellies consist of finely divided substances which are precipitated very suddenly.

We are of the opinion that clotted blood is nothing but a jelly which is similar to that obtained in the first group of substances consisting of particles forming a net-work. In previous papers, we have proved that the stable jellies of ceric hydroxide, vanadium pentoxide, and silicic acid undergo syneresis in course of time due to the decrease of the hydration tendency of the particles forming the jelly.

It seems likely that the blood as a whole is an unstable hydrophile colloid, which sets to a jelly very readily. In many respects, blood is something like ceric hydroxide sol. On keeping blood, it forms a gel very readily; in

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[1] Z. anorg. allgem. Chem., 152, 399 (1926); 164, 63 (1927).

this respect, it is certainly less stable than ceric hydroxide sol prepared in the cold. When blood sets, it undergoes syneresis very readily. The syneresis in case of blood is a much quicker process than in the case of other inorganic and organic jellies. It seems likely that the coagulation of blood or of milk by concentrated solutions of sodium tartrate, citrate, potassium fluoride, oxalate, etc., is real coagulation and not clotting or gelation. When syneresis sets in in the case of blood, the hydration tendency of the blood decreases and dehydration begins with the separation of fibrin. We must try to find out with a sol of ceric hydroxide prepared in the cold whether there are two different points. (i) the gelation or the clotting point and (ii) the actual coagulation point. The clotting point would be similar to that of the clotting of blood, and the coagulation point would be similar to the point obtained with blood, with the concentrated salt solutions of sodium, potassium or ammonium salts already mentioned and with salts of heavy metals like silver nitrate, copper chloride and ferric chloride etc., and possibly HCl. There is an interesting point that the coagulation of blood and milk can be effected very readily with acids, and in this respect it resembles mastic, gamboge, and other readily hydrolysable sols.

We have shown that when from a sol, a jelly is formed readily, the particles must have a tendency to form a network or mesh and we are convinced that the blood also consists of particles which form network or mesh very readily. Consequently, blood belongs to the group of sols like those of vanadium pentoxide, ceric hydroxide, gelatine, albumin, starch, etc. When viewed with a powerful microscope, the fibrin crystal appears as wooly, finely divided crystals. We have observed that when a jelly, like that of zinc arsenate or manganese arsenate is broken up, it cannot re-form the jelly because the network which is formed from the particles is destroyed. Now with blood, exactly similar behaviour is observed. If a big blood clot is taken out and churned, the clot is broken up into a mobile fluid which does not re-set readily. Similarly, starch jelly and gelatine jelly, when broken, do not re-set readily. Consequently, in many respects blood and possibly milk resemble a sol of vanadium pentoxide or ceric hydroxide or manganese arsenate, though blood is far less stable than the other sols. The important question which now arises and remains unanswered is—why do blood and milk not coagulate in the animal system? In the case of blood, it seems likely that the clotting is prevented in the system by the motion of the fluid. When the motion is disturbed by some means or other, clots or thrombi are formed.

Moreover, from some recent experiments, it has been proved that the clotting tendency is most marked near the neutral point of blood. On the acid side and alkaline side, the charge on the blood is increased and hence the hydration tendency is less and hence clotting happens with greater difficulty in alkaline or acid solutions of blood.

If blood received in a vessel is not stirred, the clot forms uniformly throughout the whole quantity of blood, converting it to a solid, rather dry, firm mass. Such a clot is of uniform dark red colour. If it be squeezed, a dark red fluid is forced out which is identical with defibrinated blood. If the fresh blood be kept very cold or if it be received in an oiled dish, it will not clot so quickly; and since the red corpuscles are heavier than the plasma, there may be time for them to sink to the bottom in a very thick layer. The leucocytes are lighter and rest in a layer on top of the red corpuscles, whilst above, there is some plasma almost free from cells. By this time, clotting occurs throughout, the clot differing from the uniform red one formed by rapid coagulation in the presence of a greyish yellow upper layer which contains most of the leucocytes and platelets. This slow clotting showing the effect of gravity is seen very commonly in the heart at autopsy, for the intact endothelial lining of the heart keeps its contents a long time without clotting. Then the deep red portion of the clot is in the dependent part, while the tough, elastic, translucent yellowish substance occupies the uppermost part of the heart.

The foregoing results can be explained from the view that blood consists of a mixture of colloids having different densities. If the clotting is very rapid as it usually happens when the blood is shed, network or meshes are formed and the whole of the liquid is adsorbed in the network, and a uniform jelly is obtained, there being no time for the separation of the colloids according to their difference in densities. When the clotting is retarded, there is time for different colloids to be separated in different layers, and we get clotting in different layers. We are of the opinion, therefore, that blood consists of a mixture of colloids and forms a very unstable system, and has a great tendency to clot. This clotting tendency is very likely caused by the same forces which cause the gelation of sols of silicic acid, vanadium pentoxide, ceric hydroxide, starch, gelatine, etc., and is probably due to the increase in the hydration tendency of the particles which form a network.

It is well-known that the action of copper on nitric acid is an autocatalytic process, because the product nitrous acid markedly accelerates the reaction. It seems likely that the clotting of blood is also autocatalytic in its nature, because the liquid given out immediately after clotting accelerates the clotting process. Hence we are of the opinion that the clotting of blood is a process which takes place by itself due to the extremely unstable nature of blood and is not initiated by thrombin or any other substance. It seems likely, however, that thrombin and other products derived after clotting markedly accelerate the clotting process. The syneresis that is observed is really an ageing phenomenon which is observed with most other gels and is due to the decrease in the free surface and the activity and hydration tendency of the particles forming the jelly. We have repeatedly observed that sols of silicic acid, vanadium pentoxide, ceric hydroxide, etc., form transparent jellies by merely keeping in a stoppered bottle at the ordinary temperature. In course of time these stable jellies undergo syneresis. Exactly similar behaviour is observable with blood, the only difference being that the blood is far less stable than the inorganic sols; and the clotting and syneresis are quicker processes in blood than the gelatin and syneresis observed with the inorganic sols.

Summary

1. Dilute blood and milk are more stable than concentrated blood and milk towards their coagulation by sodium citrate, sodium tartrate, sodium acetate, potassium oxalate, potassium fluoride, ammonium nitrate, and hydrochloric acid.

2. In presence of small quantities of sodium citrate, potassium fluoride, sodium acetate, sodium tartrate, or caustic potash, blood and milk are stabilised towards their coagulation by ammonium nitrate, or copper sulphate. This stabilisation is due to the increase in the amount of negative charge on the particles of blood and milk by the adsorption of OH' and other negative ions from the salt solutions.

3. Blood and milk behave like sols of arsenious sulphide, antimony sulphide, Prussian blue, etc., which are known to adsorb ions carrying the same charge as the sols.

4. Saponin and gelatine render blood and milk unstable towards salts, with acids, gelatine does not sensitise blood and milk. It seems that the sensitising influence of gelatine is due to the $H^{\bullet}$ ions present in it.

5. It appears that the hemolytic action of saponin on blood is due to its sensitising influence and its rendering blood unstable towards electrolytes.

6. The explanation of the stability of blood and milk in presence of small amounts of nitrate, oxalate, fluoride, etc., is based on the fact that the electric charge of the particles is increased by the adsorption of negative ions and not on the removal of precipitating calcium ions by the above negative ions as has been hitherto believed.

7. The clotting of blood seems to be guided by the same laws as the formation of jellies of vanadium pentoxide, ceric hydroxide, silicic acid, etc. The only difference seems to be that blood is far less stable than the inorganic sols; and the clotting and syneresis are quicker processes in blood than the gelation and syneresis observed in organic and inorganic sols.

Chemical Laboratory,
Allahabad University,
Allahabad, India.
October 24, 1927.

NEW BOOKS

Physiology and Biochemistry of Bacteria. *By R. E. Buchanan and E. I. Fulmer. Vol. I. 23 × 15 cm; pp. xii + 516. Baltimore: The Williams and Wilkins Company, 1928. Price: $7.50.* "The present volumes are the result of a belief on the part of the authors that there exists a need for a compilation and systematization of material relating to the physiology of microörganisms, particularly of the bacteria, yeasts, and molds, material which has been published in widely scattered contributions. They constitute essentially a combination and revision of the lectures on physiology of bacteria and on biophysical chemistry given at the Iowa State College to students of bacteriology," p. xi.

The chapters are entitled: introduction and scope of physiological bacteria; chemical composition of the cells of microörganisms; physico-chemical and physical characteristics of microörganisms and their environment; energy relationships, growth and movement of microörganisms.

An explanation of the lag phase more in accord with observed facts may be found in the assumption by the bacterial cells of the 'rest period' comparable to the resting stages so often assumed by higher forms. "It is a well known fact that at certain stages in the life history of many plants certain cells or tissues are developed which pass into a resting stage. When these are morphologically well differentiated they are termed spores, sclerotia, etc., in the lower forms, and seeds, bulbs, tubers, etc., among the higher types. In many cases cells or tissues pass into a similar resting stage as a result of certain environmental influences, without showing marked morphological differentiation. These resting cells are usually aroused to renewed growth and activity only as a result of certain stimuli. The cold of winter followed by the warmth of spring may be the stimulus which causes buds to develop. Some seeds will germinate only after the seed coat has decayed or has been scratched or corroded by acid. Bacterial spores form at certain stages in the life history of the bacteria, but do not usually germinate in the parent culture in spite of abundant moisture, food and optimum temperature. Germination takes place under the stimulus of change to some new medium. It is altogether probable that most bacteria, whether endospore producers or not, enter into such a resting stage, (anthrosporous condition). When the cell is not morphologically differentiated as a spore this resting period is probably more transitory than in a spore, but it is nevertheless just as real.

"What happens, then, when a considerable number of bacteria in the resting stage are transferred to a medium suitable for development? If we were to examine the culture microscopically we would find that the bacteria would not all begin development at once, probably for the same reason that seeds placed under uniform favorable conditions for growth do not all germinate at the same instant. Cell divisions will occur in a few cells first, followed by larger numbers at succeeding intervals of time until a maximum has been reached and passed, and at last all cells have 'germinated.' As soon as a cell has actually germinated, there would seem to be no *a priori* reason why it should not thereafter multiply rapidly, showing practically at once a minimum generation time. There is no more reason to suppose that the length of time it takes a bacterial cell to germinate will affect its subsequent rate of growth than to assume that plants derived from seeds slow in sprouting grow more slowly than those from seeds soonest sprouted. After any cell has once 'germinated,' then, it would proceed to increase in numbers in geometrical progression. It is evident that as more and more of the dormant cells 'germinate' and start to divide the *average* generation time will continue to decrease until all have 'germinated.' Theoretically the lag period would continue until the last viable cell had started to multiply; practically, however, it ceases before this as the rapid increase in the bacteria which have germinated soon makes the ungerminated cells such a small fraction of the whole number that their inclusion is within the limits of error of measurement of the numbers present. It should be noted that this does not imply that there cannot be acceleration of growth due to the presence of other growing cells. Robertson (1924) has shown that when two protozoan cells are planted in a drop of nutrient medium more than twice as many cells may be produced in a given time than would be produced from a single cell isolated in this fashion. This mutual effect he has termed *allelocatalysis*," p. 26.

"Many investigators have concluded that when bacteria are subjected to the action of unfavorable environment, such as would exist in an old culture or would be due to the presence of disinfectants, they die off in approximate conformity with the law which governs monomolecular reactions. If the logarithms of the numbers of bacteria surviving after various lengths of time are plotted against time, they will be found to lie on a straight line," p. 42.

"Unna has proposed a system of *chromolysis* for identification and differentiation of cell constituents. It has been used by him and his associates largely in the study of tissues of animals and the cells of protozoa, but it is not improbable that the method may be adapted to the study of other microörganisms. The method consists in the utilization of a careful selection of dyes, frequently used in combination and mixtures, and of reagents which will dissolve certain cell constituents. By use of the various stains and reagents it is possible to determine with a considerable degree of accuracy the distribution of the components of the cell. Unna and Tielemann (1917, p. 66) studied by this method the chemistry of an ameba. A review of this work and results will give the form the technique must assume when applied to microörganisms. Amebae from hay infusion were fixed upon a glass slide by means of the vapor of osmic acid. By treatment with various stains and preliminary treatment with various solvents, it is possible to determine something as to the chemical nature of the various parts of the ameba cell. These cell constituents are divided primarily into the basic proteins, the acid proteins, and the lipoids. The basic proteins most difficultly soluble are stained with hematoxylin and are dissolved by a 1 per cent trypsin solution; they are present in the inner nucleus, outer nucleus, endoplasm, and ectoplasm. The more easily soluble basic proteins are stained also with hematoxylin. Those soluble in distilled water are present only in the endoplasm in the reticular structure. Those soluble in 2 per cent NaCl are present only near this reticulum. The protamins are stained red by Giemsa stain and are not soluble in potassium hydrate solution or in pepsin. They are prominent in the outer portion of the nucleus. Among the acid proteins the globulin is stained by polychrome methylene blue. It is soluble in 2 per cent NaCl, and is present in the inner nucleus, and in some parts of the endoplasm, and the ectoplasm. The albumoses, soluble in distilled water, are present in the recticulum of both the endoplasm and the ectoplasm. Lipoids such as fatty acids, glycerinated fats, cholesterol esters, and lecithin, stain with polychrome methylene blue, are soluble in acetone alcohol, and benzine, and are present both in endoplasm and ectoplasm.

"Gutstein (1925) by the use of tinctorial methods believes it possible definitely to designate the chemical constituents of various parts of the bacterial (or yeast) cell. The nucleus (macrogranule or macronucleus) which he finds uniformly present he believes contains a protein phosphatid compound in which the acid constituent is probably a lecithin proteid. The microgranule (or micronucleus) which he also believes to be present in all cases consists of lipoid-protein compounds. In cells which produce spores he finds consistently bodies (Sporenanlagen) consisting of neutral lipoid (a cholesterol ester) and surrounded by an outer membrane consisting of a lipoid-protein compound," p. 63.

Nucleic acid contains combined phosphoric acid, p. 87. "Nucleoproteins are present in yeasts. The nucleins and more particularly the nucleic acids have been frequently studied. The nucleic acid is easily soluble in dilute alkalies, and precipitated by acids. Concentrated solutions of sodium nucleinate are readily gelatinized. The work of Levene and his co-workers has shown the nucleic acid probably to be composed of four mononucleotides united," p. 89.

"Many species of bacteria, yeasts, and molds are known to contain granules of a nitrogenous 'reserve food stuff.' These take the basic aniline dyes when stained, and are termed metachromatic granules because of their staining resemblance to chromatin. These are so characteristic of some microörganisms (as the diphtheria bacillus) that they are used in microscopic differentiation.

"Grimme (1902) and Meyer (1912) term these volutin granules. They appear in the protoplasm of the cell as small, colorless, amorphous masses which are somewhat more refractive than the cytoplasm, but less refractive than the fat droplets. The crushing of a large cell containing the granules shows them to be somewhat viscous and plastic, never brittle. They may occur singly or in groups, irregularly distributed, in a row, or at the poles. Their chief microchemical characters are the following: The volutin granules disappear from dead bacteria kept in water for two or two to three days. They dissolve in water at 80°C, in five minutes, in boiling water still more quickly. When fixed in the flame, by alcohol, or formaldehyde they dissolve less readily. They are insoluble in picric acid, alcohol, chloroform and ether, and are slowly dissolved by chloral hydrate. They are readily soluble in dilute and concentrated alkalies, soluble in strong but not in weak acids. Eau de Javelle dissolves the granules within five minutes. They are not dissolved by trypsin or pepsin. Volutin is stained blue by methylene blue, and retains the stain even when treated with 1 per cent sulphuric acid. It is Gram negative. It takes up fuchsin and ruthenium red. "Meyer (1912) believes the volutin granules to be nucleic acid compounds, but not nucleoproteins. These granules have been described for many species of bacteria, yeasts, fungi and even higher plants," p. 90.

"Chitin is so closely related to the polysaccharids, and in plants so frequently occupies a corresponding position to cellulose in the cell structure, that it is considered at this point even though it is a nitrogenous compound. Chitin apparently (Zeuplen, 1922) is a polymer of glucosamine in which each amino group is acetylated," p. 98.

"Glycogen is another compound with the condensed formula $(C_6H_{10}O_5)n$. The work of Karrer and his associates shows it apparently to be very closely related to starch, the products of hydrolysis being identical. Possibly the principal difference is in degree of polymerization. It may be recognized in microörganisms as cell granules which color a beautiful reddish brown with iodine potassium iodide. The absence of color, however, is not proof of the absence of glycogen, as when present in small quantities it does not show the characteristic color with iodine.

"In bacteria these granules are not visible in uncolored preparations, they appear brown red when treated with strong iodine potassium iodide. In fresh (i.e., unfixed) preparations dyes do not stain the granules readily. In fixed preparations strong dyes reveal the glucogen as light colored masses. Fuchsin, methylene blue and Gram's stain all color the granules.

"Glycogen is the common reserve carbohydrate of animal tissues. Apparently the glycogens of fungi and animals are identical, at least they resemble each other in their chemical reactions and in their relationships to the enzyme glycogenase. The question has been raised (Kruse) however, as to whether all granules which give this coloration with iodine are glycogen. Attention is called to the fact that erythrodextrin also gives it.

"Meyer (1912) includes all the carbohydrate granules of bacteria under the names glycogen and iogen. He states that both are developed in cytoplasmic vacuoles. The glycogen may be diffuse, but is usually in the form of more or less viscous colorless masses. The granules of iogen appear somewhat more refractive. The glycogen and iogen are differentiated by their reaction to iodine, the former becoming brown, the latter blue. . . . From 25 percent even to 40 percent (Henneberg) of the dry substance of yeast is glycogen. It is quite variable in amount, depending upon the age of the culture. If yeast is made glycogen-free by starvation, the glycogen appears again in two to three hours after the cells are placed in a glucose solution," p. 102.

"The lipins may be defined (MacLean, 1918) as substances of a fat-like nature, yielding on hydrolysis fatty acids or derivatives of fatty acids, and containing in their molecule either nitrogen or nitrogen and phosphorus. The lipins may be classified into those containing fatty acids, nitrogen, and phosphorus (the phosphatides), and those containing fatty acids, nitrogen, and a carbohydrate group, but no phosphorus (the cerebrisides)," p. 113.

"Several inorganic elements and compounds have been noted as granules, crystals, etc., in or on microörganisms. The most important of these are free sulphur, ferric iron compounds, and salts (carbonate and oxalate) of calcium.

"*Free sulphur.* Globules of free sulphur are found in many of the *Thiobacteriales*, though not in all. They are particularly prominent in the filaments of *Beggiatoa*, and certain spirilla. The abundance of the granules is apparently dependent upon the supply of hydrogen sulphide to the organisms. *They exist in the protoplasm as spherical*, oleaginous, strongly refractive droplets. In dried preparations the sulphur will dissolve in absolute alcohol, in caustic alkalies, and warm sodium sulphite, and very readily in carbon disulphide. It does not dissolve in boiling water or glycerol or in hydrochloric acid. Osmic acid stains the granules brown. If filaments rich in sulphur globules are heated to 70° the droplets flow together. In dead filaments the sulphur crystallizes in long transparent monoclinic prisms or small black rhombic octahedrons. Gasperini questioned the nature of the globules because he found they dissolved in acetic acid. Corsini (1905), however, found that sulphur globules are thus dissolved, and appear on the outside of the cell in crystalline form," p. 137.

"A curious anomaly was reported by Berczeller (1917). He found that salts which raised the surface tension of water have the opposite effect when added to colloidal solutions, especially of gelatin and other proteins. This change he associates with the driving of the protein into the surface, i.e., a salting out effect. Furthermore, the addition of salts to a dilute phenol solution produces a lowering of surface tension even greater than that of proteins solutions. This is of particular importance in the media used in the bacteriological laboratory. It may be emphasized that the effects of capillary active and inactive substances are not additive. A medium containing proteins or other colloidal substances may have its surface tension decreased by the addition of a salt which would increase the surface tension of pure water," p. 161.

"In recent years investigators have attempted to secure quantitative relationships between hydrogen ion concentration and sourness. Harvey (1920) showed that the sour taste depends on both the hydrogen ion concentration and the total free acid present. Paul (1922) pointed out the fact that acids of the same dissociation constant vary considerably in sourness at equivalent concentrations. He arranged the following acids in the order of increasing equivalent sourness: carbonic acid, cream of tartar, acetic acid, lactic acid, hydrochloric acid and tartaric acid. Ostwald and Kuhn (1921) point out the general relation between the sourness of an acid and its effect upon the swelling of tissues, i.e., the sourer acids cause the greater swelling. They state that solutions which contain buffers are considerably more sour than solutions of the pure acid at the same hydrogen ion concentration. This effect of buffers has been emphasized by Liljestrand (1922)," p. 248.

"It is apparent that the suspension of nonconducting particles in an aqueous solution of electrolytes will tend to reduce its conductivity due to the mechanical blocking of the passage of ions. That this actually occurs has been shown by Oker-Blom who found that a suspension of finely divided quartz reduced the conductivity of a solution in direct proportion to the quantity in suspension. When 61 parts of quartz were added to a solution of NaCl the conductivity was reduced by 75 per cent," p. 370.

"Bacteriologists recognize a large order or group of bacteria, the socalled sulphur bacteria, or *Thiobacteriales* which exhibit a special sulphur metabolism. Many of these grow only where hydrogen sulphide is present in small amounts. Such presence of hydrogen sulphide is evident in water of certain springs (socalled sulphur springs) is developed under anaerobic conditions by various microörganisms from sulphates and from organic compounds. They have been found to be most abundant in certain regions in salt water. A considerable area in the Black Sea shows this characteristic. . . .

"In order to secure cultures of bacteria of this group various methods have been proposed. If mud from a bog containing decaying roots is placed in a tall jar of water, and some gypsum added, there will be a gradual reduction of the sulphate with formation of hydrogen sulphid under the anaerobic conditions existing at the bottom. Oxygen will be absorbed through the surface of the water. Many of the sulphur bacteria are microaerophilic, in consequence they begin to grow in a layer or ring some distance from the surface. Frequently a membrane is formed at this point which has short tassel-like outgrowths which project downward.

"Microscopic examination of certain of these sulphur bacteria will show highly refractive granules which may be readily determined to be sulphur by microchemical tests, such as solubility in carbon disulphide, and by the crystals formed upon evaporation of the carbon disulphide upon a glass slide. A further study of the microörganism will show that the sulphur in the cells may be oxidized in a basic solution of calcium salts. To the organisms which are able to produce these changes hydrogen sulphide is so essential that growth will not occur in a medium from which it is absent. Apparently the observation of sulphur granules was first made by Cramer (1870) in the cell of *Beggiatoa*. They have since been recorded for a number of species of bacteria and *Oscillatoria* (Corsini, 1925).

"The amount of hydrogen sulphid which may be oxidized by organisms such as Beggiatoa may amount daily to from twice to four times their weight. Whether any organic substances are necessary for growth is not entirely clear but if necessary, they need be present only in very small amounts. The addition of sugar, peptone, etc., apparently is unfavorable, although this may be due to the encouragement of the growth of other kinds of bacteria.

"The evidence that CO_2 is assimilated is strong, but the difficulties in the way of pure culturing of these bacteria have interfered with positive proof," p. 417.

"A considerable group of the sheathed bacteria (*Chlamydobacteriales*) are commonly termed iron bacteria because they grow only in waters containing iron or manganese, and deposit the oxides of these elements in the sheaths or membranes surrounding them. The action is so pronounced as to be of economic importance. Cities using a water supply high in iron find it necessary to remove this iron before distribution in the mains to prevent the deposition of 'iron rust' in such amounts as to clog them. It is probable that many of the great bodies of iron ore have been deposited largely as a result of this type of action.

"Microscopic examination shows that the sheaths of organisms such as the Crenothrix polyspora and Leptothrix ochracea are encrusted with a layer which gives the reactions of iron oxyhydrate. Winogradsky (1888) believed that the oxidation of ferrous to ferric iron was an essential part of the life activities of the organism. Ferrous carbonate is taken up from the water and in the cell transformed into soluble ferric salts, and finally deposited as insoluble ferric salts in the sheath. He concluded that this oxidation process constituted a valuable source of growth energy to the plant," p. 247.

As these quotations show, there is a good deal of interesting matter in this book. On the other hand, a surprisingly large proportion of the text is devoted to introductory physical chemistry. The authors seem to have tried to do two independent things. One is to give the physiology and biochemistry of bacteria. The other is to teach physical chemistry to the biologists. The second is a praiseworthy aim and this may be the only way to do it; but it does seem to the layman as though two books would have been better than one. It is quite possible that this book was written to meet existing conditions at Iowa State College; but the reading public is not particularly interested in purely local needs. Probably the later volumes will be better in this respect than this one.

Wilder D. Bancroft

Colloid Chemistry. *By The Svedberg. Second edition. 24 × 16 cm; pp. 302. New York: Chemical Catalog Company, 1928. Price: $5.50.* The first edition was reviewed about five years ago (**28**, 772). In the preface to the second edition, the author says: "This new edition has been thoroughly revised and considerably enlarged. In the four years that have elapsed since the completion of the manuscript for the first edition considerable advances have been achieved in colloid chemistry. The application of X-ray analysis to the study of sols and gels has proved of fundamental importance in the elucidation of the structure of the colloidal particle. More space has therefore been given to the discussion and demonstration of the X-ray method and the results attained by it. Improvements in the technique of ultramicroscopy are reported and some interesting new results concerning oriented coagulation are mentioned. Improved methods for the measurement of diffusion and cataphoresis and some results gained by these methods are described. The recognition of the high importance of the so-called Donnan potentials in a great many colloid phenomena has necessitated a revision of the chapter dealing with this phenomenon.

"In the present edition as well as in the first one relatively more space has been devoted to the description of investigations made in the author's laboratory than to the reporting of other work. Thus a comparatively complete review of the new methods of colloid analysis by means of the ultracentrifuge is given in this edition. It was thought that the advance already achieved by the application of these methods to the study of the size and to the distribution of sizes of particles as well as to the determination of molecular weights would justify the relatively extensive description."

"As to the mechanism of the formation of spray, we do not know very much, but it does seem that it would not be a simple disintegration of the liquid by the gas jet but must rather be due to the formation of bubbles or thin lamellae of the liquid. These lamellae then explode when we have the air bubble rising through the liquid to the surface. A very thin liquid film is formed. That means an immense increase of the surface and this film breaks up in pieces of liquid lamellae and these pieces of the liquid will, according to the surface tension, contract to minute drops," p. 25.

"A very interesting method for preparing sols by condensation *in vacuo* has quite recently been developed by Roginsky and Scholnikoff. Their apparatus consists of a glass vessel with two containers for the dispersion medium (for example benzene), one for the substance to be dispersed (for example sodium) and one to collect the resulting sol. The ground-glass stopper carries a tube for liquid air. Before starting the experiment the benzene containers are kept in liquid air for some time, and the whole vessel is evacuated by the aid of an aggregate of Langmuir pumps to about 10^{-6} mm. mercury. Then the upper tube is filled with liquid air and the temperature of the benzene is allowed to rise a bit. Benzene then condenses on the walls of the liquid air tube. If now the tube with sodium is heated (with an electric oven arrangement) sodium vapors condense together with the benzene, and we get a frozen highly dispersed sol of sodium in benzene on the walls of the liquid air tubes. When sufficient condensate has been formed, the liquid air is removed, and the tube is allowed to warm up. The sol, therefore, melts, and drips down into the sol container. The method seems especially valuable in cases in which the dispersion medium is easily decomposed when the ordinary electric methods are used. In fact Roginsky and Scholnikoff succeeded by this method in the preparation of sols of alkali metals in benzene, hexane, xylene and toluene, which earlier had not been possible," p. 32.

"In any case electrodialysis reduces the time necessary for purification to a considerable extent. But this is not the only advantage. It also enables the removal of the last traces of electrolytes from certain biocolloids. As it is often just the last traces of salts, which cannot be removed by ordinary dialysis, that are important in determining the state of the sol, this method has been widely used in the preparation of proteins, starch enzymes, and antibodies in a hitherto unknown degree of purification. Some proteins, for example, are soluble only in water of a certain electrolyte content, and can be partly precipitated by ordinary dialysis, but to precipitate them completely electrodialysis is necessary. In this way it has been possible to separate globulins from solutions of egg albumin, serum albumin, hemoglobin and so on. Even solutions of egg albumin that had been recrystallized three times and then dialyzed seemed to contain some substance of high molecular weight that could be removed by electrodialysis," p. 90.

"Adair measured the osmotic pressure of salt-free, isoelectric hemoglobin solutions and obtained a value, corresponding to a molecular weight of about 67000. This corresponds to about four times the minimum molecular weight 16700 that we obtain from the iron content of hemo-globin if we assume that each molecule only contains one Fe atom. Earlier osmotic measurements of Hüfner gave values of about 16700 and were given much attention, but are probably in error. Both Sörensen's and Adair's results agree very well with those obtained by extensive molecular weight determinations by centrifugal methods, performed in the author's laboratory," p. 139.

"For high centrifugal forces—from 8000 up to 110,000 times gravity—another type of ultracentrifuge has been built. The cells are similar to those used in the low speed centrifuge. The steel collar with its cell is put into a steel shell together with the discs and diaphragms mentioned above. The rotor of the centrifuge, 15 cm. in diameter and 6 cm. thick, is made of a solid chrome nickel steel forging. It is kept in motion by means of two small turbines, one at each end of the shaft of the rotor, and driven by high pressure oil, giving it a maximum speed of 44,000 r.p.m. The axis of rotation is horizontal. The bearings carrying the rotor shaft are lubricated and cooled by means of a rapid current of oil pressed through the bearing clearances and oil grooves," p. 152.

"These two methods [of sedimentation velocity and sedimentation equilibrium] have been used extensively in the author's laboratory for the important and *interesting problem* of the determination of the molecular weights of proteins. They give results that agree well among themselves. The osmotic pressure method was the only one by which it had *previously been possible to get* any information about the molecular weights of the proteins. A great many attempts were made to apply it to this problem, but only a few of them have given reliable results. The centrifugal methods have several advantages over this procedure. All the difficulties that are connected with the use of membranes are avoided. The determinations can be performed in very dilute solutions (a few hundredths of 1 per cent) which facilitates the determination in cases in which complications are due to aggregation, gel formation and so on appear in more concentrated solutions. Furthermore, the solubility of some proteins is so low, that *only low concentrations can be used.* There is no possibility of measuring the osmotic pressure in concentrations like those mentioned above. Some proteins have such a high molecular weight that the centrifugal method is the only possibility. An example of this is hemocyanin (from the snail helix), with $M = 5 \times 10^6$.

"It is interesting that in cases where a protein has several light absorption bands it is possible to determine whether these bands all belong to a compound of one definite molecular weight. Nichols was able to show in the case of very pure hemoglobin that the light absorption in the yellow, green, blue, long-waved ultraviolet ($\lambda = 366\mu\mu$) and short-waved ultraviolet ($\lambda = 270\mu\mu$) all belong to a substance of the molecular weight $M = 68,000$," p. 163.

When a colloid is studied by the Debye-Scherrer-Hull X-ray analysis, an experimental difficulty is that the colloid to be studied must contain the disperse phase in a rather high concentration. "For most colloids studied the sol itself has not been used but only the disperse phase as obtained by ultrafiltration, evaporation, or centrifuging. Sols often coagulate very rapidly under the intense X-ray illumination. To avoid this, Björnstahl has used an X-ray camera with the sol streaming in a fine cylindrical jet through the center of the camera. It is important to note that if the substance can exist in several allotropic modifications, the method renders it possible to decide which of them constitutes the particles, by comparing the colloid X-ray diagram with diagrams of macroscopic crystals of *those modifications*," p. 185.

"Szegvari and Zocher investigated old and concentrated V_2O_5-sols in the ultramicroscope, using the cardioid condenser and azimuth diaphragm. Figure 155 shows a photograph taken with this arrangement. It appears as if the particles had arranged themselves in cloud-like swarms. If the position of the azimuth diaphragm is changed, these swarms seem to disappear but others appear instead. This shows that the particles in each swarm must be oriented to a certain degree, the direction of orientation being different for different swarms. This is also evident from observations made in polarized light between *crossed* Nicol prisms. Figure 156 shows a picture from experiments by Zocher by this method. Evidently the swarms possess a double refraction. With the first arrangement one could *even observe* a weak scintillation within the clouds, due to the Brownian movement of the particles. The orienting forces are not very strong. In fact, if the sol is shaken up a little, the clouds disappear, but after some time they were formed again.

"Scintillations could be seen only in the light spots, but not at all in the dark parts. Therefore Szegvari drew the conclusion that the particles perform an oscillating, rotatory

Brownian movement about a certain equilibrium position. These oscillations should be insufficient to change the orientation to such an extent that the particles in the dark regions now and then could be observed. The translatory Brownian movement of certain particles could be observed directly and was found oscillatory.

"Similar phenomena can be observed in some other sols with non-symmetrical particles, e.g. benzopurpurine solutions. Iron oxide sols, the particles of which probably are disk-shaped, when settling may form equidistant layers showing beautiful interference colors, p. 273.

"A special interest attaches to the so-called fiber diagrams first observed by Scherrer and by Herzog, Jancke and Polányi. If, for example, in investigating silk or cotton, fibers are used without having been ground to a fine powder, and are placed with their axes parallel to the axis of the cylindric camera, diagrams similar to those in Figure 167 A (silk) and B (cotton) are obtained. Polányi showed that this kind of diagram must be obtained from preparations in which there is a certain orientation as for example the length axis of the crystals.

"From X-ray investigations we can also get some information as to the mechanism of swelling. After swelling in salt solutions the diagram of cellulose is not changed. Therefore, in this case, the swelling water does not penetrate into the crystals themsleves, but probably only between them. For inulin, swelling in water, however, the diagram shows that the crystal lattice dimensions really are changed," p. 292.

It is an interesting commentary on what interests Svedberg that Weiser's name is not to be found in the author index.

Wilder D. Bancroft.

Radio-Elements as Indicators. *By Fritz Paneth. 23 × 16 cm; pp. 166. New York: McGraw-Hill Book Company, 1928. Price: $2.50.* These lectures were delivered at Cornell University during the first semester of 1926-1927 under the George Fisher Baker Lectureship in Chemistry.

The book contains a general lecture on ancient and modern alchemy. The first part of the course dealt with the use of radioactive elements as indicators, the nine lectures in this group being entitled: the significance of radio-chemistry; chemical character of the radio-elements; use of the radio-elements as indicators; radio-elements as indicators in analytical chemistry; radio-elements as indicators in electrochemistry further conclusions to be drawn from the radioactive method of determining surfaces; radio-elements as indicators in the chemistry of inorganic preparations; radio-elements as indicators in technology, in physics, and in physiology.

The second part of the course had to do with the group of volatile hydrides, with four lectures on: classification of the hydrides; preparation of volatile hydrides of the heavy metals; a comparison of the constants of the volatile hydrides; comparison of the volatile hydrides with other volatile compounds. The third topic is the natural system of the chemical elements with the following lectures: periodic and non-periodic properties in the natural system of the elements; isotopes—definition of the concepts "Chemical Element," "Simple Element," "Complex Element."

"Had the radio-elements been available for use as indicators during the last quarter of the nineteenth century one extremely important service might, with their aid, have been rendered to the then newly-advanced theory of electrolytic dissociation. Proof of the actual fact of dissociation, and of the interchange of ions, is readily obtainable with the help of the radio-elements when they are mixed with their inactive isotopes. It is possible to demonstrate in this way the fact that the particular atoms or radicals assumed to be liberated by electrolytic dissociation do not retain their places in given molecules, but are free to move back and forth from one place to another. It may also be shown that the atoms or radicals of molecules that undergo no dissociation do not tend to shift their positions from one molecule to another.

"If, for example, equimolecular amounts of an inactive lead chloride and a radio-chemically sensitized lead nitrate in aqueous solution are mixed together, and the lead chloride is allowed again to crystallise, it will be found that the active lead atoms are distributed proportionally between chloride and nitrate, and must therefore have migrated in solution from lead nitrate to lead chloride until the kinetic equilibrium has been established.

"Similar results are obtained when lead chloride and lead nitrate are dissolved in pyridine, when lead formate and plumbous acetate are dissolved in water, or plumbous acetate and plumbic acetate in glacial acetic acid. The last case is of especial interest from the electrochemical view-point, in that the reversible replaceability of divalent and quadrivalent lead ions within the short period of time of the experiment could not have been predicted from the dissociation theory *with the same degree of certainty* as in the other two cases mentioned above.

"Very different results are obtained, however, in all cases in which the lead atom is joined to carbon. Between lead chloride and lead tetraphenyl in pyridine, between lead nitrate and lead tetraphenyl in amyl alcohol, and between lead nitrate and diphenyl lead nitrate in aqueous ethyl alcohol, no change in the places of the lead atoms could be established, although in every combination investigated one of the molecular types was capable of electrolytic dissociation. The interchange of atoms between molecules is therefore seen to be dependent upon the existence of an electrolytic dissociation.

"Correspondingly, no interchange of lead atoms takes place in strongly alkaline plumbite and plumbate solutions *owing to the lack of lead ions* in appreciable concentration. In solid lead sesquioxide, $Pb_2O_3.3H_2O$, the lead atoms also retain their degree of oxidation." p. 47.

"When lead sulphate is shaken with its saturated solution, there is a constant kinetic exchange between the molecules of lead sulphate in the solution and those on the surface of the solid. If it were possible to mark certain of the lead sulphate molecules without changing their properties, and to observe the distribution of these marked molecules between the surface of the solid and the solution, it would be found, after equilibrium had been attained, that the numerical ratio of marked molecules on the surface, to those in solution, is identical with that of total molecules on the surface to total molecules in solution. For it must be assumed that the marked molecules distribute themselves uniformly among the molecules that are undergoing change in position.

"This marking of the molecules may in effect be accomplished by the use of the "radio-elements as indicators." If for example, thorium B, a radioactive isotope of lead, is added to the solution of lead sulphate, the isotope will distribute itself proportionally among the lead atoms on the surface of the adsorbent and in the solution. This phenomenon, when followed by the electroscope, is found to be manifestly an adsorption of radioactive thorium B, and the measurement of the adsorption equilibrium *furnishes the necessary data for* computation of the surface," p. 57.

With dyes adsorbed by crystals, the author finds, p. 72, that "all of the dyes reach the *maximum of adsorption* before one hundred percent of the surface is covered with a mono-molecular layer." As the author did not know that the amount of adsorption of a dye is a function of the acidity of the solution, all his work with dyes is subject to an unknown and uncontrolled error. Paneth also ignores the specific factor in dyeing, such as differences between cotton and wool. "It may be mentioned in this connection that the ultra-microscopic textile test indicates that acetate silk is of unusually simple structure. Its well-known inferiority as an adsorbent of dyestuffs seems therefore a necessary result of its low specific surface, which amounts to but one *sixty-fifth of that of nitro-silk* [as determined by dyeing]," p. 78.

"Since bismuth compounds of very diverse composition have recently been investigated from the viewpoint of therapeutics, as a substitute for arsenic, it was of interest to physiologists to learn in what proportions the bismuth ingested is stored up in the different organs of the body, and is eliminated in the urine and faeces.

"Since small amounts only are involved, the qualitative and quantitative determination can best be accomplished by the radioactive method. Radium E was employed as indicator for bismuth, in place of thorium C, in view of the fact that the experiments extended over a period of several days. It was mixed with the bismuth preparation and injected intra-muscularly into the guinea pigs employed in the experiments. The products of excretion were ashed and measured electroscopically, and at the end of the experiment, the organs of the animals were similarly treated. One conclusion to be drawn from the chart showing the exact distribution of the bismuth, is that the accumulation of this element takes place chiefly in the kidneys," p. 87.

"The hydrides are compounds which in a physical sense, resemble the rare gases, their physical properties will therefore correspond more closely to a molecular structure containing hydrogen nuclei, and showing a 'rare gas surface.' Hence the tetra-hydrides are the most perfect 'rare gases.' This finds striking expression in the almost exact agreement of the melting points of the tetra-hydrides with those of the rare gases. The di-hydrides differ most, and the tri-hydrides somewhat less, from the rare gas type. No attempt will be made here to explain these relations theoretically, by assuming for the molecule a dipolar or quadri-polar character," p. 120.

"The tabular presentation of the system of elements may be effected in two different ways: by the 'long-period' and by the 'short-period' method. If the curve of atomic volumes is transposed into tabular form, by starting a new line for every maximum of the curve, the long period system is obtained, as represented in Table XXV. The long periods of the atomic curve, each of which contains eighteen elements, are chosen to determine the length each of the short periods, as well as the two elements of the first period, are placed in the corresponding upper spaces in accordance with the chemical view-point, while in the sixth period, which comprises thirty-two elements, is assigned a single place for the fifteen rare earths. It is obvious that the vacant spaces, found of necessity in the short period system, carry no implication that the discovery of new elements is to be expected. The serial numbers, indeed, show no gaps. The vacant spaces do, on the other hand, permit recognition of the lack of ten elements of the 'transition type' in the short periods. Many authors prefer, however, to enlarge the spaces for the elements of the short periods, or to put them closely together in order that no vacancies shall occur; but in this way the definite collocation of the elements of the short periods with those most closely related to them in the long period is lost, and it becomes necessary to indicate relationships by drawing lines, or by a diagonal subdivision of the field. By dividing the lines which come from the elements of the first two periods, the more remote chemical relationships, otherwise represented only in the short period system, may be expressed also in the long period system. The medium of polychromatic coloring has also been employed for this purpose," p. 128.

"A chemical element is a substance which by no chemical process can be decomposed into simpler substances. For precisely this chemical stability of the elements, valid for all practical purposes, is the reason why these substances, may be considered to persist in all chemical changes, and may therefore be correctly called chemical elements. In investigations of other than a chemical nature, these same substances are not of necessity undecomposable. With the aid of certain physical devices the separation of a mixture of isotopic atoms may be effected, and with others an atomic disintegration may be accomplished. Since neither method, however, plays a part in chemistry, this complexity of elements, in its twofold sense, may be neglected in the entire enormous domain of practical chemistry," p. 139.

"It is primarily of interest to learn, as a result of the analysis of meteorites, that no element unknown on eath has ever been obtained from this source. Moreover, the elements of the meteorites show a distribution frequency strikingly similar to the frequency of their occurrence on earth. The same rules hold, that the elements with low atomic numbers greatly predominate in quantity, and that the elements with even atomic numbers are more abundant than those with uneven,—a regularity which was first pointed out by Harkins.

"This speaks strongly for the idea that the material of the meteorites, and of the celestial bodies of which they are fragments, has its origin under the same conditions as the material of which the earth is composed. The efficacy of the test is appreciably enhanced, however, by the knowledge, resulting from the discovery of the phenomena of isotopy, that the formation of new elements would manifest itself by an abnormal value of the combining weights. This has been observed to be the case with the radio-elements," p. 144.

Wilder D. Bancroft.

Muscular Activity. *By Archibald Vivian Hill. 22 × 15 cm; pp. 115. Baltimore: The Williams and Wilkins Company, 1926. Price: $2.75.* "In the preface to his book "The Respiratory Function of the Blood," Mr. Joseph Barcroft quite rightly tells us that long ago, by spending his leisure is sailing boats, he learnt what he knows (which is no little) of the way to venture beyond the visible horizon. Now, the practice of running is just as ancient and respectable as that of sailing, and the reader may perhaps see signs of the source of my inspiration, at any rate in the fourth lecture of this series: indeed to tell the truth, it may well have been my struggles and failures, on track and field, and the stiffness and exhaustion that sometimes befell, which led me to ask many questions which I have attempted to answer here."

These are the Herter Lectures for 1924. The single lectures were entitled: dynamics of muscular activity; the heat production of muscle; chemical change accompanying muscular activity; the recovery process after exercise in man.

"Some of the most consistent physiological data available are contained, not in books on physiology, not even in books on medicine, but in the world's records for running different horizontal distances. If one plots the average speed at which the record was made, against the length of the race (compressed in some manner—as by taking its logarithm—to bring all the points on to the same diagram), then a curve of almost perfect smoothness is obtained, in which a few points only lie just below the curve. These latter are for the races in which athletes have not been so concerned to break the record as in the rest. The relation shown in the curve may be accepted practically as a natural constant for the human race; it would require almost a superhuman effort to change one of the points by two per cent; and it is interesting to consider what determines in general the shape of this relation. At very short distances the speed is constant; it is the maximum which a man can attain, though it falls off a little as the accumulation of lactic acid in the muscles affects—first—their speed of relaxation. At very long distances the speed again tends to become constant, practically a steady state being attained. It is determined here by the maximum rate at which the athlete can take in oxygen to provide his muscles with their necessary energy, and by the economy with which he uses it. Speed at intermediate distances is determined, partly by the maximum oxygen debt which the body can incur, partly by its maximum oxygen intake. We assume, of course, that we are dealing with a man in perfect condition, highly trained to carry out his movements in the most economical manner possible, ready and willing in a race to exhaust himself completely. In the magnitude of the oxygen debt, that is in the concentration of lactic acid which his muscles can tolerate, we have what we may regard as a man's "capital." In his oxygen intake, determined by the capacity of his heart and lungs, we have what we may regard as his "income." In a race an athlete will finish—if he can, if the race be not too short—with the whole of his reserves gone, having spent both "capital" and "income" completely. In a short race, therefore, he can spread his "capital" over a shorter time, he can expend energy more rapidly than he can in a long one; the form of the curve is determined mainly by these factors," p. 98.

Muscles behave as though we are dealing both with an elastic and with a viscous medium. These two factors are very important in determining the amount of work that an athlete can do in unit time. The chemical side of muscular activity seems to consist in the conversion of a carbohydrate—usually glucose or glycogen—into lactic acid, the oxidation of a portion of that lactic acid and the simultaneous conversion of lactic acid in some unknown way into glycogen. The ratio of the lactic acid converted into glycogen to the lactic acid oxidized may be three (or even more) for healthy people, p. 65, or almost zero for people suffering from cancer.

According to the biological chemists, the conversion of glucose or glycogen into lactic acid is quantitative, there being no other products formed, p. 61. In the laboratory the organic chemist has, as yet, never succeeded in getting more than about a fifty percent yield of lactic acid from glucose, showing that his technique is apparently much inferior to that of the contracting muscle. Although glucose is optically active, the organic chemist gets an inactive lactic acid from it, while the muscle forms optically active lactic acid. We seem to have here a pretty clear-cut problem for the physical chemist. This may be some justification for reviewing this book even though it was published three years ago.

Wilder D. Bancroft

Chemistry. *By W. H. Barrett. 19 × 13 cm; pp. viii + 152. New York and Oxford: Oxford University Press, 1927. Price: $1.75.* In the preface the author says: "The main ideas behind the "General Science" movement in schools are the broadening of the basis of school science and the bringing of it into closer relation with the facts of everyday life. Bearing this in mind I have tried, in this volume, to present some important facts—especially those which have a bearing on everyday life—arranged to illustrate the principles of chemistry and to lead in a logical manner up to the deduction of the relative weights of the atoms. A final chapter, which reviews briefly some of the modern developments of the science, is added to give the reader some idea of the fascinating vista that unfolds before him as he pursues the subject further."

It is very desirable to give facts which have a bearing on everyday life in such a manner as to illustrate the general principles of chemistry. It is more doubtful whether the object of an elementary book is to lead in a logical manner up to the deduction of the relative weights of the atoms. That seems to the reviewer to be laying the emphasis on the wrong things. Of course if one defines chemistry as the science of the atom and the molecule, there is nothing more to be said.

The general order of treatment is: historical development; mixtures and compounds, oxygen and oxides, acids and bases, water, solubility; lime, cement, and hard water; definite and multiple proportions, atomic weights, radicals and ions; electrolysis and ionisation, the ionic theory; carbon and its compounds; fuels and foods; nitrogen and the nitrogen cycle; nitric acid and explosives; sulphur and its compounds; alkali and chlorine, bromine and iodine; properties of gases, Brownian movements, Avogadro's hypothesis, structure of matter; periodic law, atomic structure, isotopes.

The author has done rather a good job. His book is readable and clear. There are some minor errors, which should be corrected in a later edition. In the preparation of oxygen, p. 15, one does not see why the tube containing the chlorate should point down rather than up, and there is no mention of the air in the tube. On p. 17 is the statement that acids are formed by the combination of acidic oxides with water, which leaves hydrochloric acid rather up in the air. The author uses the German spelling, kathode, p. 54. In copper refining it is not true that all the impurities in the copper anodes go into the slimes, p. 55. Zinc and iron do not. They do not use a copper ingot as anode. Faraday coined the word 'ion' but he adhered to the Grotthuss theory and he should not be classed, p. 56, as in any way originating the conception of the ionic theory. On p. 112 it is of course true that sodium sulphite is used in photographic developers; but this either is or should be a misprint for sodium hyposulphite.

Two quotations, pp. 23, 34, will give some idea of the book. "Biologists are almost certain that life started in the sea, and the earliest organic remains known to the geologist are those of marine animals. An interesting piece of evidence in favour of the marine origin of animals is found in the fact that the salts found in the blood serum of vertibrates living on dry land are essentially the same as those in sea water. The relative proportions of sodium, potassium, and calcium salts are similar in both, and in both sodium chloride is the predominant salt. The total salt concentration, however, is higher in the sea than in the blood serum, a fact which suggests that the concentration of salts in the sea, since dry-land vertebrates left it, has been gradually growing by accumulation."

"In a large cylindrical tank is first placed a deep layer of sodium permutite between two layers of sand which hold the sodium permutite in place. This sodium permutite is a complex substance containing, besides sodium, the elements silicon, aluminium, and oxygen. When hard water is allowed to flow through the tank, the calcium bicarbonate reacts with the sodium permutite to form calcium permutite and sodium bicarbonate. Both the sodium and calcium permutite are insoluble in water, so that the water which enters the tank hard flows out softened, the small quantity of sodium bicarbonate in it being unobjectionable. After a considerable quantity of hard water has flowed through the tank one would expect its efficiency to be impaired by the conversion of the sodium permutite into calcium permutite. However, it is at this point that the real simplicity of the process is manifest. Although calcium bicarbonate will react with sodium permutite to form calcium permutite in dilute solutions such as are found in natural hard waters, yet the reverse reaction takes place when the concentration of the sodium compounds is greatly increased. Thus, if, when the charge in the tank is sufficiently converted to calcium permutite, the hard-water supply be turned off and a *saturated* solution of sodium chloride be allowed to flow slowly over the calcium permutite, the reverse reaction takes place and the sodium chloride and calcium permutite form sodium permutite and calcium chloride. The calcium chloride is soluble in water and so can be allowed to run away. A little clean water is run through the tank to wash out any sodium or calcium chloride, and the water-supply again connected. Thus, with two of these tanks, the softening of water can be made continuous."

The chief criticism that the reviewer has to make about the book is as to the treatment of metals. In the index there are two references to metals. On p. 16 the author says that "the elements can be divided into two classes, metals and non-metals. The metals on combustion form basic oxides, and the non-metals acidic oxides." On p. 59 is given the order of the metals in the electrochemical series. Neither of these ties in very closely with everyday life. The word 'alloy' does not appear in the index, and the reviewer did not notice anything about alloys in the text. This does not seem right when one considers the importance of metals and the number of them with which every child is familiar.

Wilder D. Bancroft.

Eminent Chemists of Our Time. *By Benjamin Harrow. Second edition—enlarged. 22 × 15 cm; pp. xx + 471. New York: D. Van Nostrand Company, 1927. Price: $3.00.* The first edition contained only the lives of the eleven chemists. This new edition contains also a detailed account of their work with many references to the original literature. "Formidable as this task seems when one considers the extensive literature which had to be consulted, it hardly seemed so during the time (some five years) when the book was gradually being put into shape; because, for my own part, I know of nothing quite so exhilarating as to read and re-read the original papers of the masters of our science."

The new material nearly doubles the size of the book; but it is well worth it. It is now a book which all graduate students should read. That is not saying that the first part of the book is not good; but merely that it is a better-rounded and more satisfactory piece of work in its new form.

On p. 6 there is a passage which appealed especially to the reviewer on this reading. "Some have described Perkin's discovery as accidental. Perhaps it was. But consider the way it was perfected and made available; consider with what extraordinary ability every related topic was handled; consider how every move was a new move, with no previous experience to guide him; and who but one endowed with the quality of genius could have overcome all this? Hertz discovered the key to wireless telegraphy, but Marconi brought it within the reach of all of us; Baeyer first synthesized indigo, but the combined labors of chemists in the largest chemical factory in the world were necessary before artificial indigo began to compete with the natural product; Perkin both isolated the first artificial dyestuff and made it useful to man.

"In less than six months aniline purple—"Tyrian purple" it was at first called—was being used for silk dyeing in a Mr. Keith's dye-house. The demand for it became so great that many other concerns in England, and particularly in France, began its manufacture. In France it was renamed "mauve," and "mauve" it has remained to this day.

"Perkin's improvements continued uninterruptedly, and his financial success grew beyond all expectations. He found that the uneven color often obtained in dyeing on silk could be entirely remedied by dyeing in a soap bath. The use of tannin as one of the mordants made it applicable to cotton, and shades of various kinds and depths to any degree could be attained without any difficulty. A process for its use in calico printing was also worked out successfully.

"When, three years later, Verguin discovered the important magenta—or, as it is sometimes called, fuchsine—and later still Hofmann, his rosaniline, various details in the manufacture of mauve and its application to silk, cotton and calico printing, were appropriated bodily."

The reviewer is sorry that the author did not delete the fallacious statement, p. 72, that changing the atomic weight of copper from 63.2 to 63.6 increased the apparent amount of copper in a copper ore.

Wilder D. Bancroft.

The Spectroscopy of the Extreme Ultra-Violet. *By Theodore Lyman. Second edition. 23 × 15 cm; pp. vi + 160. London: Longmans, Green and Co., Ltd., 1928. Price: 10 shillings, 6 pence.* Since the appearance of the first edition of this monograph some fourteen years ago, very considerable progress has been made in the investigation of the far ultra-violet. At that time the short wave limit stood about 900. A.U., in 1915 it was carried to 600 A.U. by Lyman, in 1917 he pushed the limit to 500 A.U., while in 1924 Millikan, using a hot spark between aluminum poles reached the present limit of 140 A.U. Approaching from the soft X-ray region a wave-length as long as 121 A.U. was obtained in 1927 by Dauvillier using a crystal lattice, so that the gap which formerly existed between soft X-rays and the far ultra-violet region can now be considered as completely bridged. This record of progress, involving as it does the researches of many workers, both in the perfecting of experimental technique and the forging of new methods of attack, is a story worth the telling, and a second edition of this monograph by Lyman is very opportune and will be most acceptable to the increasing number of workers in this field. The importance of the Schumann region (as also of that other difficult, but easily neglected region,—the infra-red) to theoretical spectroscopists cannot be over-estimated. If the increasing record of progress in this book stimulates further research in so wide a field, it will in itself have rendered a most valuable contribution.

The method of this monograph is largely historical, and contains a wealth of experimental detail and useful information. The absorption of solids and gases is dealt with at considerable length, especially in relation to the limits they impose on spectroscopic investigation in the short wave region. There is also a full treatment of the reflecting power of pure metals, alloys, and other solids, with its important bearing on the material most suitable for reflexion gratings. There is a useful section dealing with the vacuum grating spectograph, both with its construction and use by various workers. Absorption and emission spectra of the large number of elements and compounds examined are dealt with in separate chapters, and there are numerous tables of wave-lengths. We could wish that the interpretation, which is now available, of many of the measured lines and bands, had been recorded also. The theoretical importance of the data is scarcely presented to the reader. There are, however very complete references to the original papers,—a feature of great value in such a book. In particular there is a good up-to-date bibliography: its value might have been enhanced however by an attempted "subject" classification of the papers rather than an alphabetical one under the authors' names.

R. C. Johnson.

THE MANGANESE EQUILIBRIUM IN GLASSES*

BY WILDER D. BANCROFT AND R. L. NUGENT

Introduction

The knowledge of the colors of glasses and minerals has suffered from the failure to attack fundamental problems first. Much attention for example has been given to the possibility that manganese is responsible for the color of the amethyst.[1] Berthelot originally proposed the idea based largely on the similarity of the color of the mineral and that of glasses containing manganese. The latest evidence points to iron rather than manganese[2] and Sir Herbert Jackson[3] says that none of it is conclusive, but the fact remains that the people who attempted to prove that manganese was responsible didn't know the cause of the color produced by manganese in simple glasses. In this latter connection, Bancroft[4] says: "Once one gets started on the color of glasses, there at once comes up the question of manganese. Manganese is very troublesome because it colors glass amethyst to violet and no two people agree as to why. . . . The real truth of the matter is that we are hopelessly ignorant all along the line, in spite of the fact that the coloring and decolorizing action of manganese in glass is mentioned in every course in introductory chemistry every year."

Any amount of important work is being done on the effect of various radiations on the colors of glasses and minerals. Glasses are simpler than minerals, because the coloring agent is ordinarily known to start with. The most familiar case of this sort of thing is the production of a violet color in glasses containing manganese[5] on prolonged exposure to sunlight. Here the first step should be to clear up the question of the pinks in glasses originally colored with manganese, the second the elucidation of the colors obtained by the irradiation of manganese-bearing glasses, and the third the study of radiation pinks and violets in minerals thought to be due to manganese. The last has been too often the first.

Mellor[6] states that manganese colors alkaline glasses pink to violet under oxidizing conditions. The color has been called amethyst in lead, bluish violet in potash and reddish violet in soda glasses.[7] The cause for this varia-

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* This paper is part of a programme now being carried out at Cornell University under a grant to Professor Bancroft from the Heckscher Foundation for the Advancement of Research, established at Cornell University by August Heckscher.

[1] Berthelot: Compt. rend., 143, 477 (1906); Simon: Neues Jahrb. Mineral. Geol. Beilage-Band, 26, 249 (1908); Watson and Beard: Proc. U. S. Nat. Museum, 53, 553 (1917).

[2] Wild and Liesegang: Centralbl. Mineral. Geol., 1923, 737; Holden: Am. Mineral., 10, 203 (1925); Koenigsberger: Centralbl. Mineral. Geol., 1927A, 15.

[3] Nature, 120, 303 (1927).

[4] Trans. Am. Electrochem. Soc., 50, 24 (1926).

[5] Gortner: Am. Chem. J., 39, 157 (1908); Harper: Science, 27, 894 (1908); Chem. Abs., 3, 1674 (1907).

[6] "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 6, 523 (1925).

[7] Chem. Abs., 15, 421 (1921).

tion of tint with composition is not well understood.[1] We have noted particularly such a difference in sodium borate and sodium phosphate beads. The former is much more red and the latter much more blue.

According to Thorpe[2] the full color is only developed when manganese is in a fully oxidized condition (Mn^{IV}). Actually there has developed a fairly general opinion that the color is due to the trivalent form. Scholes[3] quotes Dralle and Hovestadt as agreeing to manganic oxide, and describes the first experiments to demonstrate the presence of trivalent manganese in glasses. Samples colored with manganese were pulverized and treated with hydrofluoric or thirty percent sulphuric acid. Pink solutions were obtained whose color could be discharged by reducing agents, and which gave brown flocculent precipitates on dilution with water. Permanganate was ruled out, because no color was obtained on disintegrating a glass in water, and the color of the pink solutions when obtained resembled that of solutions of manganic salts rather than of permanganates.

As Scholes says, these experiments seem to indicate the presence of trivalent manganese in the glasses. The assumption that the pink of the solution is the same as the pink of the glass is most probable, but still an assumption. It seems even more probable in view of an experiment performed by us in which a borax bead, containing enough manganese to render it black in appearance, was allowed to stand in 1:3 sulphuric acid for several days. Its center was still black, but its outer layer was white and the solution was pink. The acid had leached the color without destroying the structure which contained it. This indeed looks like a direct connection between the color of the glass and that of the solution.

It was found that manganese dioxide, manganous carbonate, and manganous borate supplied by standard dealers, as well as trimanganese tetroxide and manganic oxide, gave pink solutions on treatment with 1:3 sulphuric acid which behaved just as Scholes' did. Those in the first three cases may be ascribed to traces of trivalent manganese present in the respective compounds. They indicate that Scholes' identification of trivalent manganese may have told very little definitely as to the state of the larger part of the manganese in his glasses.[4]

Fuwa,[5] as the result of 591 melts in the investigation of manganese as a glass colorant concluded that manganic oxide is responsible for the pink color and that colorless manganese in glasses is divalent. He suggests that when manganese dioxide is added to a melt, there results a mixture of manganese dioxide, and manganic and manganous oxides. The color is determined by the proportions of these three which are in turn affected by the constitution of the glass. The idea of a mixture of oxides should be particularly borne in mind in the light of what follows.

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[1] Scholes: J. Soc. Chem. Ind., 35, 518 (1916).

[2] "Dictionary of Applied Chemistry," 2, 721 (1912); 3, 386 (1922).

[3] J. Ind. Eng. Chem., 7, 1037 (1915).

[4] It is called purple manganese proxide by so good a man as Sir Herbert Jackson: Nature, 120, 303 (1927).

[5] Chem. Abs., 17, 3583 (1923).

Manganese in the Borax Bead

Introduction. According to Bancroft[1] the only sensible thing to do is to find out what known coloring agents do when dissolved or dispersed in easily fusible glasses. "One should start with the oxides of copper, manganese, chromium and iron in borax beads and find out what they do." The present paper is the first in the direct attack of this problem. Manganese was chosen to start with because it seemed the most interesting and important of the four.

Everyone knows that a borax bead containing manganese is pink-violet in the oxidizing flame of the Bunsen burner and colorless in the reducing flame. The great question all along has been as to the valence of the manganese in the colored form. Bivalent manganese has been generally assumed in the colorless bead, but even here no actual proof has come to the writer's attention. This paper presents experimental evidence which seems to decide these points once and for all. In addition the work leading to the valence conclusions has thrown considerable light upon the part played by manganese in glass-making and as a mineral colorant.

Preliminary Experiments. Borax melts were made in air in No. 0 porcelain crucibles over the full flame of a Fisher burner. Constancy of atmosphere was assured by supporting the crucibles in an inclined asbestos board. Under these conditions one-tenth percent of manganese was found to give a convenient depth of color. The color conditions in the melts could be determined at any time by removing a small bead on the tip of a glass rod.

Oxidizing and reducing agents added to melts containing manganese cause the same changes as observed in the oxidizing and reducing atmospheres of the burner flame. This was observed using potassium nitrate as the oxidizing agent and Rochelle salts as the reducing agent. The melt could be made colored or colorless at will. The depth and character of the color under these conditions seemed to depend only on the total manganese in the compound and not upon the specific compound. A melt decolorized with tartrate regained its full color on prolonged heating in air. A definite effect of temperature on the color was observed, in that beads removed from a hot melt were always less deeply colored than those removed from the same melt on heating for some time at a lower temperature.

Sodium hydroxide was added to a melt with the idea that if an acid form of manganese were responsible for the color it would be favored by the addition of the alkali. Actually the color of the melt was deepened. Conversely the addition of boric oxide to a melt would favor the colorless form. This was also observed. By adding excess boric oxide the strong color of the original borax melt could be made so faint as to be scarcely visible. At this point the evidence seemed to favor an acid oxide of manganese as the colored form. Manganite seemed probable in accord with the statement that the full color is attained when the manganese is in the tetravalent condition.

There thus evolved the picture of an equilibrium between a colored and a colorless form of manganese varying with the atmosphere or more exactly

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[1] Trans. Am. Electrochem. Soc., 50, 26 (1926).

with the oxygen pressure, as well known, with the temperature, and with the acid-base composition of the melt; an oxidizing atmosphere, low temperature and alkali favoring the colored form. The best way to get at such an equilibrium is to investigate the quantitative shift with variation of one condition. The variation of the state of oxidation of the manganese in these melts could be measured with variation of oxygen pressure, temperature, or acid-base composition of the melt, keeping the other two factors constant. The last seemed the simplest experimentally and was undertaken.

The Sodium Oxide-Boric Oxide System. 0.05 gram samples of manganese dioxide[1] were charged in No. 0 porcelain crucibles with varying proportions of borax glass, boric oxide and sodium hydroxide calculated to give three grams of a mixture of sodium oxide and boric oxide on fusion. The crucibles were held in an inclined asbestos board and heated with a Fisher burner. The board prevented burner gases from reaching the melt and thus assured a constant atmospheric atmosphere. The heating was carried out in the same manner for each melt thus assuring approximate temperature equality. After fusion, fining, and cooling, the crucible and its contents were pulverized in a mortar, and the mixture placed in a 250 cc. Erlenmeyer flask. A few cc. of water were next added and brought to a boil to expel air. Twenty-five cc. of a sulphuric acid-ferrous sulphate solution (15 gms. $(NH_4)_2 Fe(SO_4)_2 \cdot 6H_2O$ in 200 cc. 1:3 H_2SO_4) were added at this point by means of a pipette and the glass dissolved by boiling. After solution, the contents of the flask were diluted with 150 cc. of water and titrated with standard permanganate.[2] The decrease of the ferrous content of the solution under these conditions is equivalent to the available oxygen associated with the manganese of the melt, that is to the oxygen combined with the manganese over and above that necessary for the manganous condition.

If all the manganese in any melt were divalent, no iron would be oxidized, and the result would be zero grams of available oxygen per gram of manganese. If it were all in the form of trimanganese tetroxide, the result would be 0.0971 grams of available oxygen per gram of manganese, etc. The compounds of manganese with oxygen are shown in Table I together with

TABLE I

The Oxides of Manganese

Name	Formula	Manganese Valence	Grams of Available Oxygen per Gram of Manganese
Manganous oxide	MnO	2	0.0000
Trimanganese tetroxide	Mn_3O_4	2 and 3	0.0971
Manganic oxide	Mn_2O_3	3	0.1456
Manganese dioxide	MnO_2	4	0.2913
Manganese trioxide	MnO_3	6	0.5826
Dimanganese heptoxide	Mn_2O_7	7	0.7282

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[1] The manganese content of the manganese dioxide used was checked by analysis.

[2] See also Treadwell-Hall: "Analytical Chemistry," 2, 531 (1928).

the corresponding amounts of available oxygen per gram of manganese and the probable valence of the manganese in each case.

It is seen that the result of one melt and analysis with pure borax glass is most significant. If all the manganese were in any one form the fact would immediately appear. As a matter of fact such a run gave 0.059 grams of available oxygen per gram of manganese showing the latter to be more than half in the divalent condition and an equilibrium between divalent manganese and some higher form to be on the divalent side. A series of such runs was carried out with results as shown in Table II.

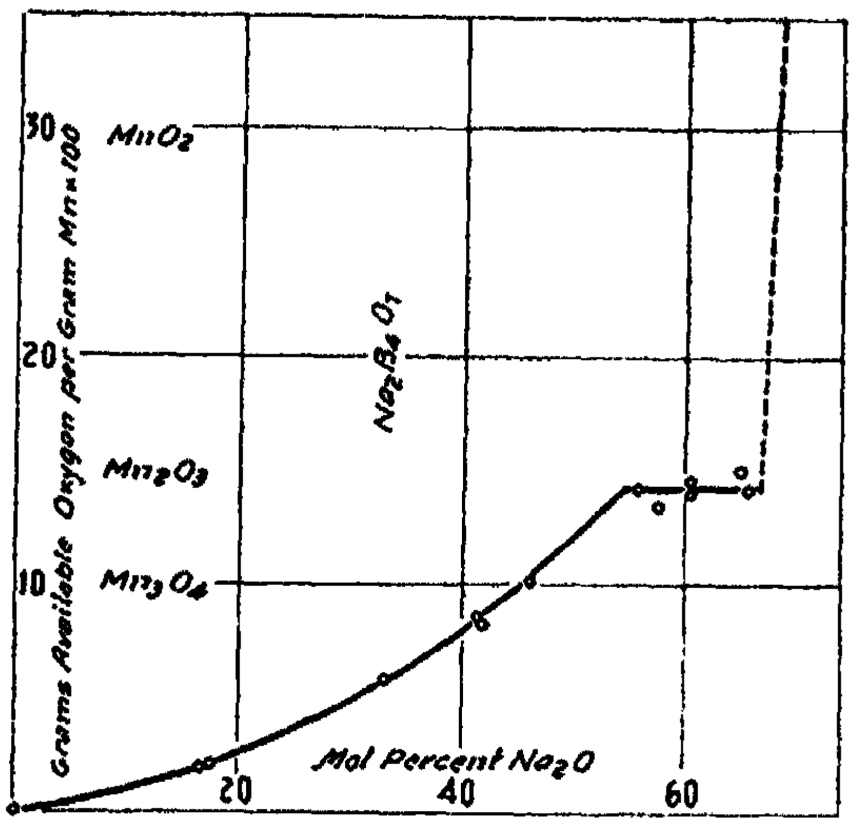

FIG. 1
Grams of Available Oxygen per Gram of Manganese in Melts of Different Proportions of Na_2O and B_2O_3

TABLE II
Grams of Available Oxygen per Gram of Manganese in Melts of Different Proportions of Na_2O and B_2O_3

Number	Mol Percent Na_2O	Grams Available Oxygen per Gram of Manganese	Number	Mol Percent Na_2O	Grams Available Oxygen per Gram of Manganese
1	0.0	0.000	8	55.3	0.143
2	16.9	0.020	9	57.7	0.135
3	17.0	0.020	10	60.4	0.145
4	33.3*	0.059	11	60.4	0.141
5	41.6	0.085	12	65.5	0.150
6	41.9	0.083	13	65.7	0.144
7	46.0	0.102			

*Anhydrous borax, $Na_2B_4O_7$.

The results are shown graphically in Fig. 1. The ordinates are grams of available oxygen per gram of manganese multiplied by one hundred and the abcissas are mol percents of sodium oxide.

The general result is most clear-cut. There can hardly be any doubt but that in sodium oxide-boric oxide melts, including that in pure borax glass, there exists an equilibrium between colorless divalent manganese and colored trivalent manganese. The melt in pure boric oxide was quite colorless. It follows that the colorless form is divalent because it gave no available oxygen. This agrees with the observation quoted in Abegg[1] that manganese dioxide dissolves in boric oxide with stormy evolution of oxygen to form manganous borate. As the proportion of sodium oxide is gradually increased, the pink color appears and gradually increases in depth to about fifty percent where it is a rich, reddish, wine color. Above sixty-seven percent sodium oxide the resulting glasses were brownish green to deep blue-green in color. No attempt was made to get exact points in this region, but the general direction of the curve was indicated and has been shown in dotted line.

The full wine color appears when the manganese is all in the trivalent form as shown by the value at which the flat occurs, 0.144 grams, as compared with the theoretical value for manganic oxide, 0.1456 grams. The appearance of the green color signifies that the proportion of alkali has become sufficient to cause the well-known conversion to manganate which manganese oxides undergo on fusion with sodium hydroxide under oxidizing conditions.[2] The pink-violet of the manganese borax bead is then due to trivalent manganese, and the manganese in the colorless bead is divalent. Under ordinary conditions in the oxidizing flame the two forms are in equilibrium at about forty percent manganic manganese. The essential oxides are respectively manganic and manganous oxides.

One cannot feel the greatest confidence in the demonstration of an equilibrium until it is approached from both sides. This dual approach has been demonstrated in the present case. Melts containing originally 0.05 grams of manganese dioxide were fused and heated in a reducing atmosphere to a

TABLE III

The Manganous-Manganic Equilibrium approached from Both Sides in Borax Melts

Procedure	Grams of Available Oxygen per Gram of Manganese
Fused and fined in air	0.059
Fused in a reducing atmosphere to a colorless condition and then fined in air for twenty minutes	0.042
Fused in a reducing atmosphere to a colorless condition and then fined in air for several hours	0.047

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[1] "Handbuch der anorganischen Chemie," 4 (2), 772 (1913).

[2] Lowry: "Inorganic Chemistry," 758 (1922).

colorless condition. On continuing the heating in air, color reappeared as would be expected. It should continue to increase until the equilibrium point is reached when the grams of available oxygen per gram of manganese should theoretically be the same as in a melt heated in air from the beginning. The fining temperature was the same in each case. Table III contains the results.

The ordinary run, the first in Table III, shows the approach to equilibrium from the more highly oxidized condition. The second and third results show the approach from the reduced side. These were borax glass melts. A similar experiment was attempted in a melt in which the manganese should all be trivalent at equilibrium. 0.0530 grams of trimanganese tetroxide was charged in a 65.5 percent sodium oxide melt. It has been demonstrated that when manganese dioxide is used in a melt of this composition the valence goes from four to three and the available oxygen value from 0.2913 to 0.1456 grams per gram of manganese. Theoretically, using trimanganese tetroxide, the available oxygen value should increase from 0.0971 to 0.1456. The melt was heated for some time in air at the usual temperature and on analysis showed 0.1280 grams of available oxygen per gram of manganese clearly indicating the approach to equilibrium in this case also.

It is apparent from these experiments that the return to equilibrium from the reduced state is a slow process as compared with the approach from the more highly oxidized side. The latter simply involves the evolution of oxygen, whereas the rate of the former is determined by the rate at which unoxidized portions can be brought in contact with the air. In an unstirred melt, convection currents and diffusion are necessarily slow in bringing this about.

Some question arose as to possible considerable loss of alkali oxide due to volatilization during fusion and fining, since the surface of the melts was large as compared with their size. This factor was ruled out both by experiments in which the crucible and contents were weighed before and after heating and by titration of total alkali in identical charges, one with and one without fusion and fining.

Effect of Temperature on the Equilibrium. Since the preliminary experiments indicated a shift to the colorless form with rising temperature and the foregoing experiments show a parallelism between color and oxidizing power of the manganese, it was desirable to check up the temperature effect by observation of the oxidizing power of identical charges fined at different temperatures.

TABLE IV

Temperatures of the Interior of a Porcelain Crucible heated in Four Different Ways as observed with a Leeds and Northrup Optical Pyrometer

Method of Heating	Observed Temperature
Fisher burner turned low	790°
Fisher burner full flame	900°
Fisher burner full flame in covered furnace	1040°
Blast Méker burner in covered furnace	1170°

The temperatures recorded are those observed with a Leeds and Northrup optical pyrometer without correction. They are therefore not to be considered as absolute measurements. However a series of runs with similar melts may be controlled at approximately the same temperature by this method and one melt may be distinguished as considerably hotter or colder than another. For example, a heated porcelain crucible was observed under four conditions with results as shown in Table IV.

Some idea of the absolute value of such temperature observations is given by comparison of the facts that borax melts at about 740° and the temperature of a borax melt brought just to a well-fused condition was read as 765° with the pyrometer.

0.05 gram of manganese dioxide was charged in each of three No. 0 porcelain crucibles with three grams of borax glass. They were fused and fined respectively at 985°, 870°, and 765° as indicated by the optical pyrometer. Two runs were also made in 60.4 percent sodium oxide melts with fusion and fining at 870° and 765° respectively. The results are shown in Table V.

TABLE V

The Effect of Temperature on the Manganous-Manganic Equilibrium

Composition of Melt	Observed Temperature	Grams of Available Oxygen per Gram of Manganese
Borax glass	985°	0.035
"	870°	0.059
"	765°	0.069
60.4 percent Na_2O-39.6 percent B_2O_3	870°	0.103
"	756°	0.141

It can only be said as a result of this experiment that the equilibrium shifts definitely to the manganous side with rise of temperature. The experiment is not quantitative since the temperatures are not known with any accuracy. The qualitative demonstration is the important thing here, however, and this is clearly demonstrated.

Extension to Lead Borate and Sodium Phosphate Glasses

Introduction. The question immediately arises as to whether the results of the preceding section are applicable to glass systems generally. As a first step the matter has been investigated quantitatively in the case of the litharge-boric oxide system and qualitatively in the case of the sodium oxide-phosphorus pentoxide system. We thus have the acid and base of the sodium oxide-boric oxide system each combined with a different oxide of the opposite type.

The Lead Oxide-Boric Oxide System. 0.05 gram samples of manganese dioxide were weighed out as before and charged in No. 0 porcelain crucibles, this time with three grams of mixtures of different proportions of litharge and boric oxide, and data on the available oxygen in each case determined. The analytical procedure was necessarily modified as lead borate glasses are not sufficiently soluble in sulphuric acid.

The crucible and fined melt were pulverized in a mortar and charged in a small retort which connected with the rest of the apparatus by means of a ground-glass joint. The apparatus is shown in Fig. 2. The Erlenmeyer flask contains 50 cc. of 5 percent potassium iodide solution which rises in the bulbed tube when the retort is heated. Glass beads moistened with the potassium iodide solution are contained in the top section of the bulbed tube. 15 cc. of 3:1 hydrochloric acid are added to the material in the retort, which is then heated with bubbling through the liquid in the bulbed tube until the equivalent of chlorine set free by the available oxygen of the melt has all gone over and liberated an equivalent quantity of iodine, which is titrated with standard thiosulphate solution.[1] The method is a standard one slightly modified.

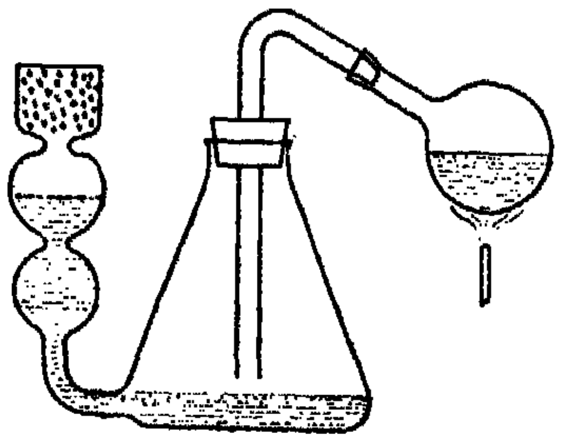

FIG. 2

Apparatus used in determining the Available Oxygen per gram of Manganese in Lead Borate Glasses.

Curves analogous to the sodium oxide-boric oxide one were run for two temperatures, controlled with the optical pyrometer. Here again all that can really be said is that one was done at a considerably higher temperature than the other. The data are given in Table VI.

The data of Table VI are shown graphically in Fig. 3, which includes, for comparison, the sodium oxide-boric oxide curve in broken line. The ordinates are grams of available oxygen per gram of manganese multiplied by one hundred and the abcissas are mol percents of the respective basic oxides. The lead curves clearly show the equilibrium between di- and trivalent manganese and its shift to the trivalent colored form with increase in the mol fraction of

TABLE VI

Grams of Available Oxygen per Gram of Manganese in Melts of Different Proportions of PbO and B_2O_3 at Two Temperatures

A. Low Temperature Runs

Number	Mol percent PbO	Grams Available Oxygen per Gram of Manganese	Number	Mol percent PbO	Grams Available Oxygen per Gram of Manganese
1	0.0	0.000	6	92.4	0.137
2	23.8	0.006	7	95.3	0.140
3	48.9	0.034	8	96.8	0.147
4	50.1	0.031	9	98.4	0.142
5	78.1	0.094	10	100.0	0.141

B. High Temperature Runs

1	0.0	0.000	4	78.2	0.057
2	59.2	0.027	5	95.3	0.089
3	78.2	0.052	6	95.3	0.089

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[1] See also Treadwell-Hall: "Analytical Chemistry," 2. 564 (1928).

basic oxide and lowered temperature. Interesting points are the comparatively weak effect of lead as compared with sodium, manganate not forming even in pure molten lead oxide, and the fact that the complete oxidation to the trivalent form is shown at the lower temperature, but not at the higher.

The Sodium Oxide-Phosphorus Pentoxide System. Two No. 0 porcelain crucibles were charged with 0.05 gram of manganese dioxide and sodium dihydrogen phosphate to give three grams of metaphosphate glass ($NaPO_3$). They were supported on asbestos boards and heated in air, one with the low flame of the Fisher burner and the other with a blast Méker burner. On cooling, a direct comparison of the two showed a distinctly lighter color in the case of the latter. This gives a qualitative demonstration of the shift to the colorless divalent form with higher temperature. The color was removed from a phosphate melt by the addition of phosphorus pentoxide and brought back in the same melt by the addition of sodium hydroxide, demonstrating the effect of shift in the acid-base ratio to be qualitatively similar in the case of this system.

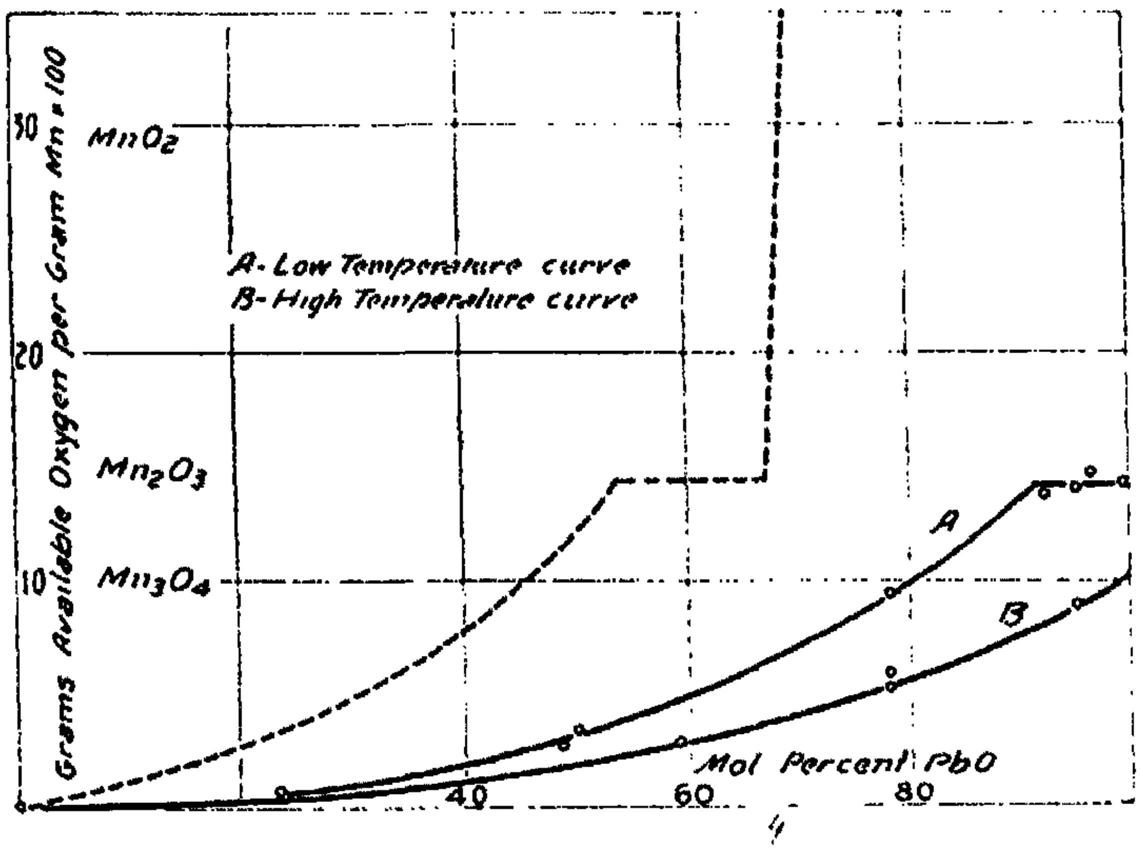

FIG. 3

Grams of Available Oxygen per Gram of Manganese in Melts of Different Proportions of PbO and B_2O_3 at two Temperatures. The $Na_2O-B_2O_3$ curve is shown for comparison in dotted line.

The same sort of thing undoubtedly occurs in silicate systems. Quite a long line of evidence for this can be developed from a consideration of well-known phenomena in the case of manganese-bearing silicate glasses, several of which are discussed later in this paper. It should of course be demonstrated experimentally. Simple qualitative experiments as reported here for the phosphate system should be easy if one had the proper furnace. The quantitative demonstration might well involve considerable experimental difficulty.

Applications in Glass-Making

Assuming that the foregoing results may be directly extended to silicate glasses, important possibilities may be adduced with regard to glass-making and various phenomena explained. The decolorizing action of manganese is an important aspect of this subject and since this directly involves iron, some study of iron in the borax bead makes a valuable preliminary.

Briefly, it has been shown that, as opposed to the case of manganese where two states of oxidation are in equilibrium in comparable amounts, iron is all or very nearly all ferric in borax glass heated in air with a Fisher burner 0.05 gram samples of ferric oxide were charged with three grams of borax glass in No. 0 porcelain crucibles and the latter supported in an asbestos board and heated with the full flame of a Fisher burner. After fusion, fining and solution in dilute sulphuric acid the iron was shown to be practically all trivalent either by titration with permanganate when the titre was zero or with stannous chloride[1] when the titre was equivalent to the total iron. This result was checked using ferroso-ferric oxide in place of ferric oxide, eliminating the possibility that the ferric oxide was losing oxygen slowly in the first experiments. Actually such proof was hardly necessary since the melts with ferric oxide melts could be heated for hours without decrease in their oxidizing capacity.

A simple but rather interesting decolorization experiment was performed· A melt colored yellow with iron was decolorized by adding manganese dioxide. In glass-making manganese dioxide is supposed to act in two ways, by oxidation of ferrous iron to ferric and neutralization of the resulting ferric color with its own pink. In this case it is known that the iron was all ferric to start with. It is therefore a case of decolorization in which the action is simply optical.

The coloring or decolorizing action of manganese in a glass depends upon the depth of color which it produces, visible in the first case and neutralized by the iron color in the latter. It has been shown that the pink produced by a given amount of manganese depends not only upon the oxidizing and reducing conditions, but also upon the acid-base composition of the glass and upon the temperature, since the depth of color depends upon the position of a manganous-manganic equilibrium which shifts with these factors. Any sort of satisfaction using manganese in glass-making must depend first upon an empirical determination of the proper amount of manganese for the particular conditions and secondly upon uniformity of composition and temperature throughout the batch. The theory can be of use in directing the initial experiments to determine the proper amount of manganese in any case.

Scholes' observation[2] that only a small part of the manganese used is effective in producing color, not more than about ten percent in some cases, meets with an obvious explanation. Under the particular conditions observed,

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[1] Treadwell-Hall: "Analytical Chemistry," 2, 594 (1928); Nugent: Dissertation, University of Arizona (1925).

[2] J. Soc. Chem. Ind., 35, 518 (1916).

the equilibrium must have been well over on the manganous side, apparently at about ninety percent manganic and ten percent manganous manganese.

We have made a borax melt yellow with iron; then added manganese through the colorless stage to a definite pink, stable at the comparatively low temperature employed. The same melt was next heated at a temperature several hundred degrees higher than the first and a colorless glass resulted on cooling. The equilibrium had shifted sufficiently to the colorless side to leave only sufficient depth of color to neutralize the iron. Presumably at a still higher temperature the manganese equilibrium could have been shifted almost completely to the manganous side and the yellow color of iron caused to reappear. Such a melt with extreme temperature differences would be pink, yellow, and colorless in different portions. The fact that the hotter pots in elliptical regenerative furnaces require more manganese is readily explicable on this basis.[1] A borax melt containing manganese and no iron has also been observed from which, when heated at a low temperature, colored beads could be obtained by removing them on a glass rod and plunging them quickly into water. When the same melt was heated at a temperature several hundred degrees higher, this same procedure produced perfectly colorless beads.

Bunting[2] has observed that glass decolorized with manganese, when heated at 1400° under three-hundredths atmosphere pressure of air, resumed the green color due to iron. With reduced oxygen pressure the manganese equilibrium shifted completely to the colorless side. In one particular case a frozen melt was obtained in which the process could be observed partially complete. There were three layers, the bottom one green and containing no bubbles, the middle one colorless with many fine bubbles and the top layer pink and full of large bubbles. The manganese contents of the three layers were the same.

Some difference of opinion has arisen as to the cause for these differences in color. Tillotson[3] suggested that the succession of colors from the bottom up was due to the progressive decomposition of manganate. This assumes that the original glass contained manganate and should therefore have been green, which as far as one can gather it was not. Bunting attributes the pink of the top layer to increase in trivalent manganese due to excess oxygen from decomposing oxides in the melt. This was most probably a factor. However if uniform temperature had prevailed throughout, the manganic oxide in the top layer should have decomposed first because of the lower pressure in the upper part of the melt. On this basis it should have been greener than the rest rather than pinker.

The writers prefer an explanation including the shift of the manganese equilibrium with temperature, which follows if it is assumed that the bottom of Bunting's crucible was hotter than the top. Under those conditions a color

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[1] J. Soc. Chem. Ind., 35, 518 (1916).

[2] J. Am. Ceramic Soc., 5, 594 (1922).

[3] J. Am. Ceramic Soc., 5, 595 (1922).

gradient would be expected which might well go from green to pink with an intermediate colorless region. In the green high-temperature layer the manganese equilibrium might well have been shifted so far to the colorless side as to prevent its masking the green of the iron and in the top pink layer so far to the other side as to give excess pink aided by oxygen from decomposing oxides.

The violet color which appears in ordinary glass on prolonged exposure to sunlight is most probably due to manganese although Jackson[1] states that the nature of the material causing the color is unknown. Assuming it to be manganese, it is significant that the pink which produced in glasses purposely colored with manganese is somewhat similar. This has been shown to be due to the trivalent form. Building on this, it is possible that the effect of the light is to shift the manganous-manganic equilibrium to the manganic side.[2] In the dark the original equilibrium state cannot be regained at a perceptible rate because of the rigidity of the structure, but on heating this can and does happen, the colorless state being regained because of the greater freedom of movement in the system at the higher temperature. This is at present the best way to regard the situation. The shift may be accompanied either by absorption of the necessary oxygen from the atmosphere on oxidation within the glass[3].

Jackson goes on to say that so far as he knows, all colors produced in glasses and minerals by radiation may be destroyed by heating. The general process is probably as described in the preceding paragraph, a return from the photochemical equilibrium state to the normal one made possible by greater freedom of movement in the structure at the higher temperature. Jackson further states that he has never been able to decolorize by heat a glass purposely colored with manganese, even by heating it to its melting point. The ready explanation for this fact is that he was always necessarily heating his glasses at a lower temperature than that at which they were originally formed. Under these conditions the equilibrium would tend to shift to the colored manganic side. The only possible result would thus be a deepening of the pink color rather than its disappearance as looked for by Jackson.

According to Scholes,[4] when a glass decolorized with manganese is annealed for a long time below its melting point, the decolorizing effect is apparently lost in that the glass becomes green. The striking thing is, however, that the green which appears is deeper than that which would have resulted if no manganese had been used originally. The old theory was that ferrous iron reduced manganic manganese under these conditions. Scholes prefers the view that the green which appears is manganate because he thinks that all the iron in the glass is ferric to start with, and secondly because the green is

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[1] Compare Berthe of Compt. rend., 143, 477 (1906).

[2] Nature, 120, 303 (1927).

[3] In this connection see Berthelot. Compt. rend., 143, 477 (1906); Simon: Neues Jahrb. Mineral. Geol. Berlage-Band, 26, 249 (1908); Hermann: Z. anorg. Chem., 60, 369 (1908); Find and Bardwell: Am. Mineral., 8, 171 (1923).

[4] J. Soc. Chem. Ind., 35, 519 (1916).

too green for ferrous iron as stated. He feels that a colloidal change is ruled out because the pink color cannot be restored by further heat treatment as it can in the case of certain ruby glasses.

We have not produced this annealing effect proper in borax, but have performed an experiment which demonstrates the formation of manganate without gross melting. A manganese bead was taken from a 69.6 percent sodium oxide mixture. It was deep green in color and remained so in the oxidizing flame of the Bunsen burner. In the reducing flame it went from green to pink to colorless as would be expected. It was next brought back to the pink condition in the oxidizing flame and then heated in a shallow porcelain dish in air at such a temperature that melting did not occur. Nevertheless development of green color was observed in the external portions of the bead. The conclusion is that a glass made under one set of conditions and showing no manganate green may develop it without melting. It is probable in this experiment that softening did occur in the outer layers which rendered access of air for the oxidation to manganate more easy. It would be interesting to know whether the green color observed in glasses on annealing is always *uniform throughout the glass or sometimes more concentrated* near the surface. Cases are known in which the color of purple manganese glasses was all in the surface layer.[1]

The examples which have been discussed serve to indicate the application of the manganese equilibrium to problems in glass making. Numerous others might be mentioned, but a complete list would be too long since the principles of the equilibrium must be applicable in every case in which manganese enters the batch.

An Application in Mineralogy

After iron, chromium and manganese have been called the most important metallic mineral colorants.[2] As examples of minerals colored amethyst, rose, and pink by manganese Holden[3] gives rose quartz, pink beryl, kunzite, rubellite, thulite, pink andalusite and piedmontite. Holden states that the color is due to manganese in the trivalent form but quotes Scholes as having proved this to be the case in pink glasses.

Holden himself has studied the cause of color in rose quartz and concluded trivalent manganese to be responsible. Certain of his observations and those of others reported in his paper point to a shift of the manganous-manganic equilibrium in this mineral with temperature. A discussion of these serves to exemplify the application of the present view of the situation in mineralogy.

True rose quartz, it appears, occurs only in massive form and never in clear-cut crystalline forms like the amethyst. Geological evidence indicates that rose quartz is formed below 575° whereas colorless quartz from the same

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[1] J. Soc. Chem. Ind., 35, 520 (1916).

[2] Hermann: Z. anorg. Chem., 60, 369 (1908).

[3] Am. Mineral., 9, April-May (1924).

type of environment is generally formed above this temperature.[1] This is a point of great interest, because it was found that the color actually does disappear from rose quartz when it is heated to about 575° in air. The phenomenon is quite general, because it was shown by specimens from all parts of the world. No relation was found between the disappearance of color and the change from α to β quartz which occurs near the same temperature. In no case was there a tendency toward a change in color but rather a gradual fading of the original rose. Silica gel, purposely colored pink with manganese, lost its color at an even lower temperature than rose quartz, a crowning piece of evidence. This decolorization is entirely different from that produced by heating in the amethyst and in general in minerals and glasses which owe their color to irradiation, because it is impossible to reproduce the color in the heat-decolorized specimens or to strengthen the color by means of strong radium preparations.

Holden says: "Manganese compounds readily change their state of oxidation under conditions of rising temperature and the loss of the rose color at or near 575° is certainly not opposed to a coloring by Mn^{+++}, especially since the manganese compound in rose quartz must be in a very finely divided state, and would be therefore likely to be more than usually susceptible to temperature changes. Either a reduction to MnO or oxidation to MnO_2 would discharge the color. Whatever the mechanism of the loss of color, it is certainly one that can be undergone by Mn_2O_3, for the dried silica gel colored by Mn^{+++}, described in part IX of this paper, loses its color on heating even more readily than does the rose quartz. This is probably because the gel is more porous."

The whole phenomenon can be described in terms of the shift of the manganous-manganic equilibrium to the manganous side with rise of temperature as described in the present paper. The matter can be carried further for the oxidation to MnO_2 as a possible cause for the color disappearance may be ruled out. The question comes up as to whether oxygen is actually given off by the mineral or whether some constituent is oxidized. Holden's reference to the silica gel being more porous indicates that he favors the first explanation. The gel structure did not break down when decolorized by heating. This same general question has been mentioned in the case of glass colored by sunlight.

Theoretical Points

Several points seem of particular theoretical interest.

1. In sodium oxide-boric oxide mixtures the manganous-manganic equilibrium shifts from 100 percent manganous in pure boric oxide to 100 percent manganic in a 55 percent sodium oxide mixture at the temperature employed. The question arises as to why additional base should favor the formation of a basic form of manganese which presumably requires more molecules of boric oxide per molecule than manganous manganese, in the ratio of three to two.

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[1] Wright and Larsen: Am. J. Sci., 27, 421 (1909).

2. As shown in Fig. 1, manganate is first formed when the molecular ratio of sodium oxide to boric oxide is two to one.

3. Under the same conditions in a melt of 50 mol percent basic oxide and 50 mol percent acidic oxide, manganese is 89 percent manganic in a sodium oxide-boric oxide mixture, 23 percent manganic in a litharge-boric oxide mixture. The question is to offer a qualitative explanation for these differences.

4. In a borax melt under the same conditions manganese is 40 percent manganic whereas iron is certainly close to 100 percent ferric.

Manganese in pure boric oxide is all in the form of manganous borate. The strong base sodium oxide tends to displace the weaker base manganous oxide from combination with boric oxide. It cannot conceivably do this with the formation of manganic borate requiring more boric oxide than the original manganous borate. Actually very few manganic salts have been made and none with such weak acids as boric. The probable thing then is that sodium oxide displaces manganous oxide from combination, which promptly oxidizes to manganic oxide which is the stable combination of manganese and oxygen in free condition in a melt at this temperature and oxygen pressure. The manganic oxide causing the pink color is thus probably in the free form in the melt.

The first appearance of manganate when the molecular ratio of sodium oxide to boric oxide is two to one probably corresponds to the first appearance of free sodium oxide in the melt. Presumably up to this point it is all in combination with boric oxide.

Lead oxide is a weaker base than sodium oxide and therefore a greater molecular concentration should be required to displace the manganous-manganic equilibrium to the same extent; as was found to be the case.

The first thing that comes to mind on comparing the cases of manganese and iron in borax glass is the relative ease of oxidation from the ferrous to the ferric condition as compared with that from the manganous to the manganic condition.[1] The prime cause in producing the manganous-manganic equilibrium is the much greater affinity of boric oxide for strongly basic manganous oxide than for weakly basic manganic oxide. This difference is sufficient to overcome the normal tendency for manganese to go to the trivalent state at this temperature and oxygen pressure. Ferrous oxide is likewise much more strongly basic than ferric oxide, but here the greater tendency to oxidize to the trivalent condition must be the dominant factor.

For the present these explanations must be considered only as rather interesting speculation. They suggest the way however to researches of possibly great general importance. Particular attention is directed to the evidence leading to the conclusion that manganic oxide is in the free condition in glass melts.

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[1] Lowry: "Inorganic Chemistry," 777 (1922).

Summary

The pink-violet color of the manganese borax bead under oxidizing conditions is due to trivalent manganese, probably in the form of free manganic oxide. The manganese in the colorless bead in the reducing flame is divalent and is probably in combination as manganous borate.

Under ordinary conditions in the oxidizing flame, the two forms are in equilibrium at about forty percent manganic manganese. Higher oxygen pressure, lower temperature, and increased alkali in the melt favor the colored form by shifting the equilibrium to the manganic side. Lower oxygen pressure, higher temperature, and increased acidic oxide in the melt do the opposite.

The behavior as shown by the sodium oxide-boric oxide system has also been demonstrated, quantitatively in the case of the litharge-boric oxide system and qualitatively in the case of the sodium oxide-phosphorus pentoxide system.

Assuming it to obtain also in silicate systems various applications of the knowledge of the equilibrium to problems in glass-making have been discussed. The principles involved must be applicable in every case in which manganese enters the batch.

An application in mineralogy has also been discussed. The loss of color of rose quartz on heating is attributed to a shift of a manganous-manganic equilibrium.

Under the same conditions in which manganese is about forty percent manganic and sixty percent manganous in borax melts, iron is certainly nearly 100 percent ferric. A possible theoretical reason for this difference has been discussed together with certain other points of theoretical interest.

Cornell University.

THE DISSOCIATION PRESSURE OF VANADIUM PENTOXIDE*

BY E. F. MILAN

In view of the importance of vanadium pentoxide as an oxidation catalyst, it was thought advisable to study its dissociation pressure. Such a study was evidently quite necessary when one considers that in the chemical literature[1] vanadium pentoxide is stated to be a stable compound up to 1750°C. In view of the fact that it is an active catalyst and also oxidizes hydrochloric acid, we were led to suspect a rather high dissociation pressure of oxygen. Preliminary experiments in which nitrogen or carbon dioxide was passed over V_2O_5 at 925°C. showed that about 50% of the pentoxide had decomposed into lower oxides.

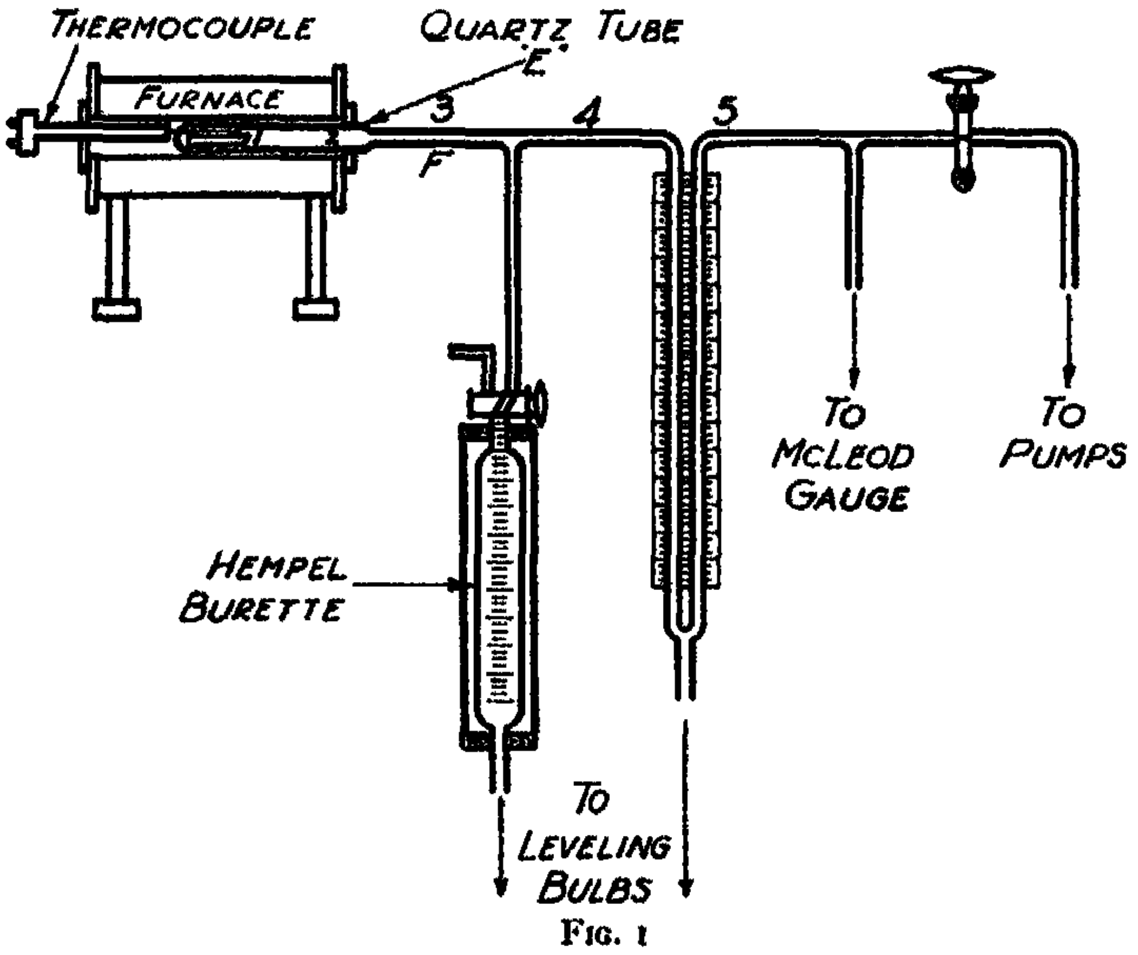

FIG. 1

Preparation of Material

The V_2O_5 was prepared by a method similar to that used by C. Matignon.[2] Ammonium metavanadate was heated in an electric furnace at a temperature of 280°-300°. The ammonia evolved was pumped off by means of a high-

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[*] Contribution from the Chemistry Laboratory of The Johns Hopkins University. This article has been taken from the dissertation submitted by E. F. Milan to the Board of University Studies of the The Johns Hopkins University in partial requirement for the degree of Doctor of Philosophy.

[1] Read: J. Chem. Soc., **65**, 313 (1894); Tiede and Birnbauer: Z. anorg. Chem., **87**, 161 (1914).

[2] C. Matignon: Chem. Ztg., **29**, 986 (1905).

vacuum pump. The resultant powder was treated with nitric acid and evaporated to dryness three times. This powder was heated in air to a temperature of 400° in order to remove traces of nitric acid. The resulting V_2O_5 was then heated in a platinum boat in an atmosphere of oxygen at a temperature of 750°–800° for two and one-half hours. The fused V_2O_5 was allowed to cool and crystallize under the same pressure of pure oxygen. The oxygen introduced into the furnace was purified by passage over hot copper oxide, calcium chloride, soda lime, and phosphorus pentoxide. The V_2O_5 obtained consisted of beautiful needle-like crystals of a glossy, reddish cast, which when analyzed proved to be pure vanadium pentoxide.

Our method of measuring the dissociation pressure of V_2O_5 at various temperatures may best be understood by referring to Fig. 1. The method of operation was as follows:

Experimental Procedure

A weighed sample of pure vanadium pentoxide in a pletinum boat was placed in the quartz tube E. This tube was then sealed off at one end and connected to the system through the quartz to Pyrex seal F. The electric furnace was set in such a way that the platinum boat containing the vanadium pentoxide was exactly in the center. The thermocouple was placed in the furnace and connected to a Leeds and Northrup indicating pyrometer. The electric furnace was connected in series with a rheostat, lamp bank and ammeter to a 110-volt supply. The furnace was kept in a horizontal position and the quartz tube was supported outside the furnace by means of clamps. This allowed the removal of the thermocouple and furnace without disturbing any part of the system. The Hempel burette and U-tube together with the leveling bulbs were mounted on suitable stands and supported by iron clamps.

The leveling bulbs attached to the Hempel burette and the U-tube were placed in their lowest position and the mercury-seal stopcock opened. This placed every portion of the system in communication with the pumps, which were then started. Evacuation was kept up for several hours keeping the system at room temperature. In order to remove all traces of water vapor and adsorbed gases from the walls of the system and from the sample, the quartz tube E was heated at 200°C. and the Pyrex tubing constituting the remainder of the system was heated with a free flame while evacuating at the same time with both pumps. The pumping and heating were continued until the pressure remaining in the apparatus was approximately 10^{-5} mm. of mercury as shown by the McLeod gauge. The mercury in the Hempel burette was raised above the upper stopcock by aid of the leveling bulb which was then clamped in this upper position. The stopcock of the Hempel burette was then closed. The leveling bulb attached to the U-tube was raised and the mercury in both arms brought to the zero mark of the scale. No difference in pressure between the two arms could be detected. The mercury-seal stopcock was then closed and the pumps were stopped. The McLeod gauge indicated the pressure in the right hand side of the U-tube and system and was read whenever pressure readings were taken. This pressure was maintained at approximately 10^{-6} mm. throughout all of the runs. The difference in levels between the two arms of the U-tube gave the actual pressure in the left-hand side of the system directly. The mercury-seal stopcock held the vacuum very well and the right-hand side of the system had to be pumped out only at intervals of about 24 hours.

The sample was then heated up to 1100 degrees centigrade very gradually. During this heating the temperature was kept constant at certain values (25 to 50 degrees intervals throughout the range) by means of the rheostat and lamp bank. A constant current could be maintained in the heating circuit in this way. Readings of time, current, furnace temperature, oxygen pressure, room temperature and volume were taken at regular intervals. The difference in height read on the U-tube manometer gave the oxygen pressure reading. Room temperature was read on a thermometer suspended near the U-tube. The volume of the system was obtained from a calibration curve and was determined by the height of the mercury in the left hand side of the U-tube. This calibration curve was obtained by dividing the system into four parts, filling each part with mercury and weighing the mercury required to fill each portion. The sum of these four volumes gave the total volume up to the zero mark on the left arm of the U-tube. The left arm of the U-tube was calibrated in the usual manner by weighing measured lengths of mercury throughout its whole length. The volume of the four portions plus the volume of the left arm up to the mercury level as read on the U-tube gave the total volume of the system. The temperature was kept constant at each value selected until temperature and pressure equilibrium was established. It was found that this equilibrium adjusted itself very rapidly.

After reaching a temperature of about 1100°C. the current in the heating circuit was reduced and the temperature of the furnace (and of the sample) was lowered in steps or intervals of 25° to 50°C. Time was allowed for pressure and temperature to reach constant values and readings were taken as before throughout the temperature range. This heating and cooling was repeated in order to ascertain the degree to which the results were reproduciable. The sample was then heated again to about 1100°C. and the oxygen in the gas phase was allowed to expand into the Hempel burette (the leveling bulb being clamped in a lower position). The leveling bulb was adjusted so that 100 cc. of oxygen was admitted to the burette at the temperature of the surrounding jacket and at the pressure indicated by the difference in height of the mercury in the U-tube. The upper stopcock of the burette was closed and the temperature and pressure at which the oxygen was removed was then recorded. This oxygen was removed from the burette by means of the leveling bulb and the mercury was brought back to the original position above the stopcock. The mercury was kept above the stopcock in order to eliminate the possibility of any leak of gas either from the system or to the system from the outside. Since the only other stopcock in the system was beyond the U-tube, leaks were impossible.

The sample was again heated and cooled and readings were taken as in the preceding runs. A sample of oxygen was removed by the same procedure as before and similar readings of pressure, temperature and volume taken. In this way a large number of volumes of oxygen were removed, the composition of the sample varying accordingly.

After the last run the sample was cooled very gradually to room temperature. The thermocouple and furnace were removed and air was admitted to the system. The platinum boat containing the sample was removed from the quartz tube and the sample analyzed for lower oxides.

The temperature gradient of the system was determined in the following manner: The furnace was replaced over the quartz tube so that it occupied the same position as during all of the previous runs. Care was also taken to replace the Pt-PtRh thermocouple in its former position. An iron-cromel metal thermocouple was placed just inside of the right-hand end of the furnace (shown by point 2, Fig. 1). The asbestos boards were replaced at the ends of the furnace and everything was arranged just as in all of the previous runs in order to have conditions comparable. Thermometers were placed at points 3, 4 and 5. The furnace was heated up from room temperature to 1100°C. Simultaneous readings of temperature were taken at points 1,2,3,4 and 5 at regular temperature intervals throughout the whole range. These observations gave the average temperature of each of the five portions of the system at a corresponding furnace temperature as registered at point 1.

Results

The readings and results of the experiments on the measurement of the oxygen pressure of vanadium pentoxide are given in the following tables.

Table I represents a few of the measurements in which pure vanadium pentoxide was used at the beginning. Zero time was recorded at the start

TABLE I

Measurement of Oxygen Pressure of Vanadium Pentoxide

Weight of sample 2.1017 grams

(Composition of sample—Pure V_2O_5 (at beginning of expt.)

Time elapsed hrs.	Furnace Temperature °C	Oxygen Pressure mm.	Time elapsed hrs.	Furnace Temperature °C	Oxygen Pressure mm.
0.0	24.8	0.0	41.5	875	49.0
2.0	580	6.5	43.33	700	14.2
3.17	700	16.0	48.08	800	29.0
3.67	800	31.5	48.67	850	42.0
4.50	875	49.0	52.17	1075	146.5
4.58	900	60.5	65.75	700	14.0
4.67	925	67.5	69.58	850	42.0
5.67	1025	119.0	70.0	900	58.0
6.91	1050	131.5	71.75	1075	146.0
8.67	1090	156.5			

TABLE Ia

Furnace Temp. °C.	Pressure mm.	Mols O_2 in Gas Phase	% V_2O_4	Furnace Temp. °C.	Pressure mm.	Mols O_2 in Gas Phase	% V_2O_4
550	7.5	1.4×10^{-5}	0.24	900	60.0	9.7×10^{-5}	1.70
600	9.5	1.7×10^{-5}	0.30	950	76.0	1.2×10^{-4}	2.12
650	7.5	1.3×10^{-5}	0.23	1000	100.0	1.6×10^{-4}	2.75
700	14.2	2.5×10^{-5}	0.43	1050	130.0	2.05×10^{-4}	3.55
750	19.0	3.2×10^{-5}	0.56	1100	162.0	2.5×10^{-4}	4.37
800	29.0	4.9×10^{-6}	0.85	1125	176.0	2.7×10^{-4}	4.72
850	41.5	6.9×10^{-5}	1.20				

TABLE II

Measurement of Oxygen Pressure of Vanadium Pentoxide

Sample: 2.1017 g. Pure V_2O_5 less 0.00026 moles oxygen removed at end of preceding run. Equivalent to 95.5% V_2O_5–4.50% V_2O_4 (at beginning of Expt. II).

Time elapsed hrs.	Furnace Temp. °C.	Pressure mm.	Percent V_2O_4	Time elapsed hrs.	Furnace Temp. °C.	Pressure mm.	Percent V_2O_4
3.55	700	0.0	4.50	18.0	600	0.5	4.51
3.75	775	0.5	4.51	19.35	850	1.9	4.55
3.83	800	0.5	4.51	20.17	975	12.0	4.83
3.91	825	1.0	4.53	20.67	1050	36.0	5.46
4.67	975	11.6	4.82	21.25	1075	48.15	5.81
6.25	1125	76.3	6.54				

TABLE III

Measurement of Oxygen Pressure of Vanadium Pentoxide

Sample: 2.1017 g. Pure V_2O_5 less 0.00042 moles oxygen removed at end of runs 1 and 2 incl. Equivalent to 92.71% V_2O_5–7.29% V_2O_4 (at beginning of Expt. III)

Time elapsed hrs.	Furnace Temp. °C.	Pressure mm.	Percent V_2O_4	Time elapsed hrs.	Furnace Temp. °C.	Pressure mm.	Percent V_2O_4
1.00	925	1.7	7.34	2.85	1000	6.8	7.48
1.42	800	0.0	7.29	3.17	1050	15.8	7.72
2.42	900	1.0	7.32	3.67	1100	30.9	8.12
2.67	950	2.8	7.37				

of the heating period and subsequent readings of furnace temperature, and oxygen pressure are shown in columns 2 and 3. It is to be noted that as the temperature increased the oxyegn pressure also increased.

The amount of oxygen in the gas phase at any time, as shown in Table Ia, was obtained by a summation of the amounts in each of the portions into which the system had been divided. The amount in each portion was obtained by means of the perfect gas law ($PV = nRT$). P was the pressure read on the U-tube and is given in column 2, T_x was the absolute temperature of the oxygen under consideration in each volume V_x, R was taken as 82.07 (cc. atm.) and n_x was the calculated number of mols of oxygen in the gas phase of each portion.

TABLE IV

Measurement of Oxygen Pressure of Vanadium Pentoxide

Sample: 2.1017 g. Pure V_2O_5 less 0.00055 mols oxygen removed at end of runs, 1, 2, and 3 incl. Equivalent to 90.47% V_2O_5–9.53% V_2O_4 (at beginning of Expt. IV)

Time elapsed hrs.	Furnace Temp. °C.	Pressure mm.	Percent V_2O_4	Time elapsed hrs.	Furnace Temp. °C.	Pressure mm.	Percent V_2O_4
1.0	975	1.8	9.58	15.67	1000	2.8	9.61
1.50	875	0.0	9.53	17.25	1075	11.6	9.84
15.0	950	0.8	9.56				

TABLE V

Measurement of Oxygen Pressure of Vanadium Pentoxide

Sample: 2.1017 g. Pure V_2O_5 less 0.00063 mols oxygen removed at end of runs 1, 2, 3 and 4 incl. Equivalent to 89.07% V_2O_5–10.93% V_2O_4 (at beginning of Expt. V)

Time elapsed hrs.	Furnace Temp. °C.	Pressure mm.	Percent V_2O_4	Time elapsed hrs.	Furnace Temp. °C.	Pressure mm.	Percent V_2O_4
2.17	965	1.0	—	4.50	1025	3.0	11.01
3.08	825	0.0	10.93	4.58	1050	5.0	11.06
3.67	900	0.4	10.94	4.83	1100	11.8	11.24
4.0	950	0.9	10.95				

TABLE VI

Measurement of Oxygen Pressure of Vanadium Pentoxide

Sample: 2.1017 g. Pure V_2O_5 less 0.00072 mols oxygen removed at end of runs 1 to 5 incl. Equivalent to 87.53% V_2O_5–12.47% V_2O_4 (at beginning of Expt. VI)[2]

Time elapsed hrs.	Furnace Temp. °C.	Pressure mm.	Percent V_2O_4	Time elapsed hrs.	Furnace Temp. °C.	Pressure mm.	Percent V_2O_4
9.42	900	0.6	12.49	13.0	1000	2.1	12.53
12.0	850	0.7	12.49	13.33	1050	4.1	12.58
12.50	900	1.0	12.50	19.5	1100	10.0	12.74
12.75	950	1.4	12.51				

Experiment II was carried out using the same sample of V_2O_5 as in the preceding run except that 100 cc. of the evolved oxygen was removed at 23.0°C. and 48.0 mm. pressure leaving a sample corresponding to a composition of 95.5% V_2O_5 –4.5% V_2O_4. Similar readings and calculations as in Tables I and Ia were made and are given in tabular form in Table II. It is to be noted that the pressures read in this experiment are considerably lower than the pressures at the corresponding temperatures in Table I. As the total volumes in this experiment at corresponding temperatures were approximately the same as in the preceding experiment and as the pressures were much lower, the amounts of oxygen in the gas phase were also considerably less than in the preceding run. The oxygen pressure at 1125°C. was 76.3 mm. while it was approximately 176 mm. at this temperature in the first run. The number of mols of oxygen in the gas phase was proportionately less, being less than one-half that in the first run. The increase in V_2O_4 at this temperature and pressure (1125°C. and 76.3 mm) was about 2 mol percent over the amount present at the beginning of the run.

The composition of the $V_2O_5-V_2O_4$ mixture was further varied by removing additional amounts of oxygen. Readings and calculations were made as in the preceding runs and are shown in Tabular form in Tables III-VI. Behavior similar to that reported above was noted in all of these experiments. As smaller amounts of oxygen were removed in the successive runs the pressure differences at the higher temperatures were not as great as between experiments I and II.

TABLE VII

Oxygen removed at End of Runs

Started with 2.1017 g. V_2O_5

No. Run	Volume Removed cc.	Temp. °C.	Pressure mm.	Mols O_2 Removed	Mol % Removed
1	100	23.0	48.0	0.00026	4.50
2	100	25.3	30.0	0.00016	2.79
3	100	25.0	24.0	0.00013	2.24
4	100	25.0	15.0	0.00008	1.40
5	100	25.0	16.5	0.00009	1.54
6	0	—	—	—	—
			Totals	0.00072	12.47

The oxygen removed at the end of each run is given in tabular form in Table VII. Column 2 gives the volumes removed at the temperatures and pressures given in columns 3 and 4. The mols of oxygen are calculated by means of the perfect gas law and the amounts (in mols) removed are given in column 5 while column 6 gives the mol percents.

An analysis of the sample (melt) after the completion of Run 6 was performed as follows:

The mixture of vanadium oxides was taken from the furnace, weighed and treated with nitric acid. After evaporating to dryness three times, the powder was heated in an electric furnace at a temperature of 400°C. Upon reweighing, it was found to have increased in weight by an amount corresponding to that required if 12.46% of the original melt had been there as V_2O_4. This analysis was repeated with the result that the above figures were again duplicated. This is a conclusive proof that our calculation of the percentage of V_2O_4 in the melt from a measurement of the volume of oxygen taken from the system is remarkably accurate.

Discussion of Results

Curves II to VI inclusive give the results of the temperature and pressure measurements after the composition of the initial V_2O_5 sample had been altered. The curves II to VI were plotted from the data of Tables II to VI respectively. The pressures in experiment II, Table II are considerably lower than the pressures at corresponding temperatures in experiment I, Tables I and Ia. Similarly the pressures obtained at corresponding temperatures in experiments III to VI inclusive (after still more oxygen was removed) are lower than those of experiments I and II. The total oxygen removed in all of these experiments amounted to about 12.5 mol percent. This slight change in the composition had the effect of lowering the oxygen pressure from 176 mm. at 1125°C. in the first run to 11 mm. at 1125°C. in the sixth run.

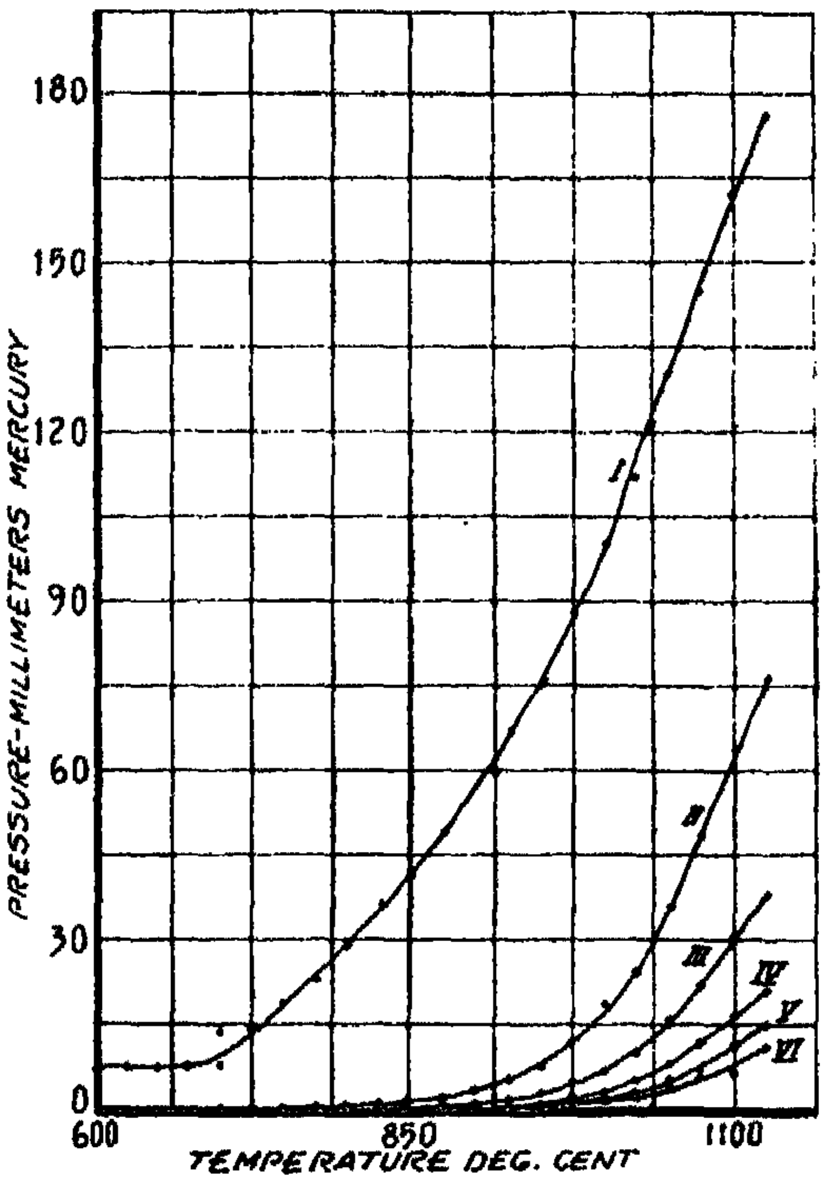

Fig. 2

I. Pure V_2O_5 (at beginning of Expt. I)
II. 95.5% V_2O_5 – 4.5% V_2O_4 (at begin. of Expt. II)
III. 92.71% V_2O_5 – 7.29% V_2O_4 (at begin. of Expt. III.)
IV. 90.47% V_2O_5 – 9.53% V_2O_4 (at begin. of Expt. IV).
V. 89.07% V_2O_5 – 10.93% V_2O_4 (at begin. of Expt. V).
VI. 87.53% V_2O_5 – 12.47% V_2O_4 (at begin. of Expt. VI).

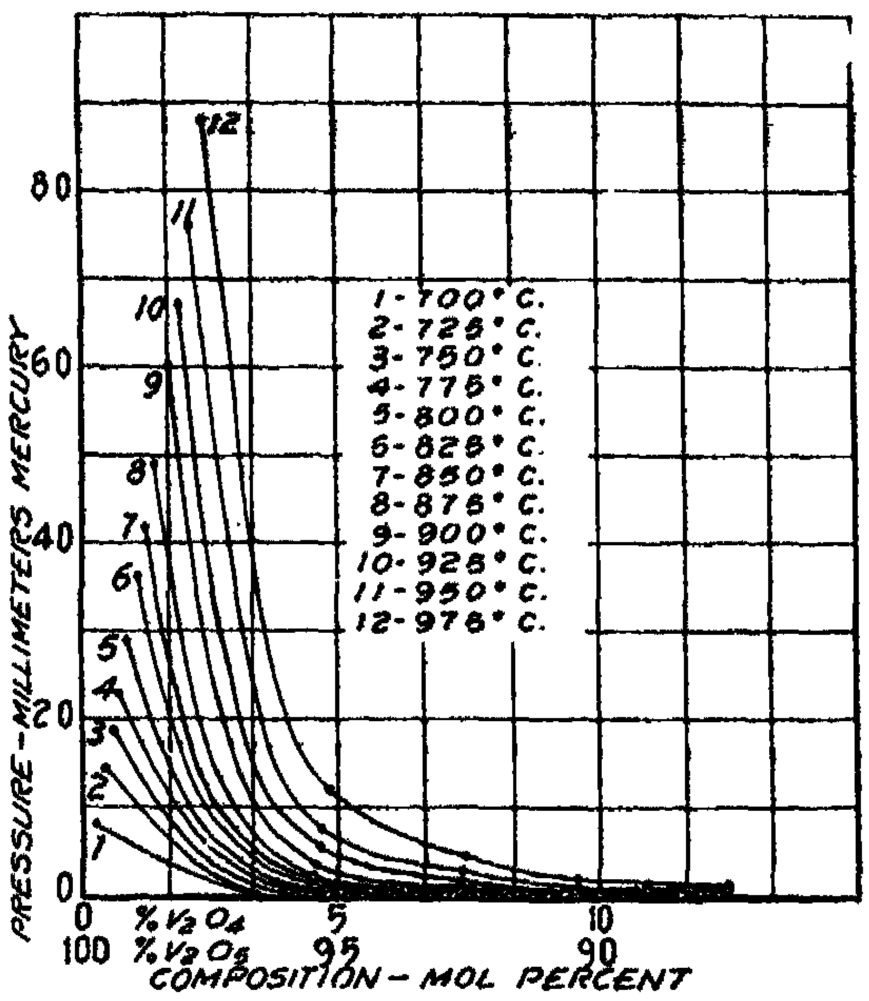
PRESSURE - MILLIMETERS MERCURY
80
60
40
20
0
0 % V_2O_4 5 10
100 % V_2O_5 95 90
COMPOSITION - MOL PERCENT
1-700° C.
2-725° C.
3-750° C.
4-775° C.
5-800° C.
6-825° C.
7-850° C.
8-875° C.
9-900° C.
10-925° C.
11-950° C.
12-975° C.
1
2
3
4
5
6
7
8
9
10
11
12

FIG. 3

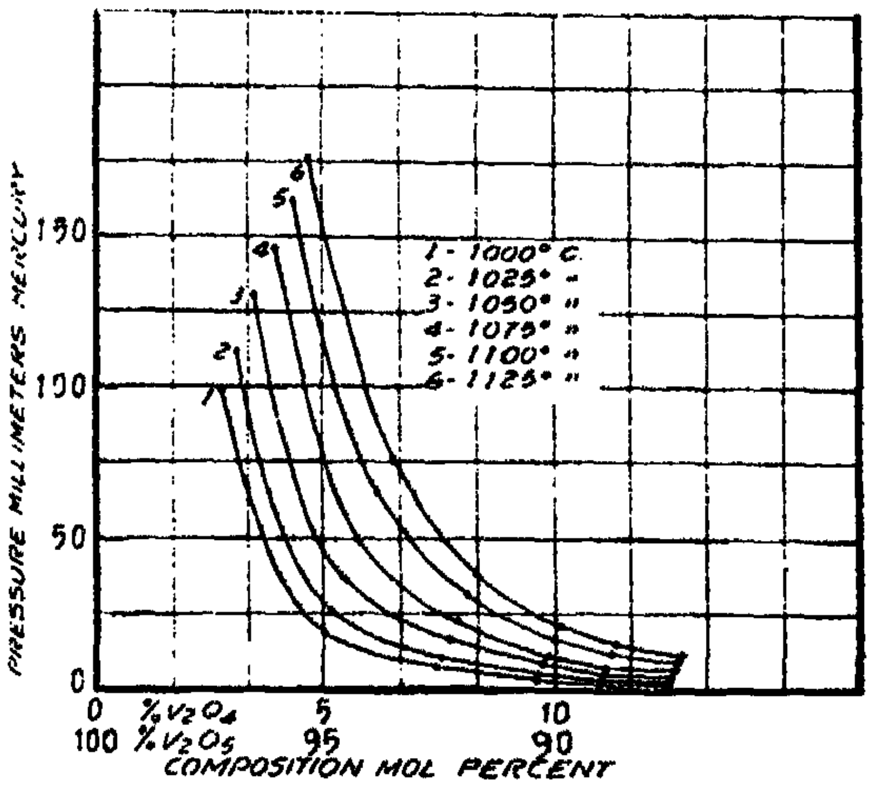
PRESSURE MILLIMETERS MERCURY
150
100
50
0
0 % V_2O_4 5 10
100 % V_2O_5 95 90
COMPOSITION MOL PERCENT
1-1000° C.
2-1025° "
3-1050° "
4-1075° "
5-1100° "
6-1125° "
1
2
3
4
5
6

FIG. 4

The curves in Figs. 3 and 4 show how the pressures changed with changes in composition for 25°C. temperature intervals from 1125°C. to 700°C. The pressure changes most rapidly with composition in the region between pure V_2O_5 and 95% V_2O_5–5% V_2O_4 as is shown by the slope of the isotherms in this region. Beyond this composition (95% V_2O_4–5% V_2O_4) the pressure changes are not as pronounced but the tendency to decrease with decreasing V_2O_5 content still exists.

The isobars at 125 mm. to 25 mm. intervals are plotted in Fig. 5. These curves show the variation of the temperature with the composition for constant oxygen pressures. From the above results we can conclude that vanadium pentoxide on dissociation does not behave as a phase of constant composition.

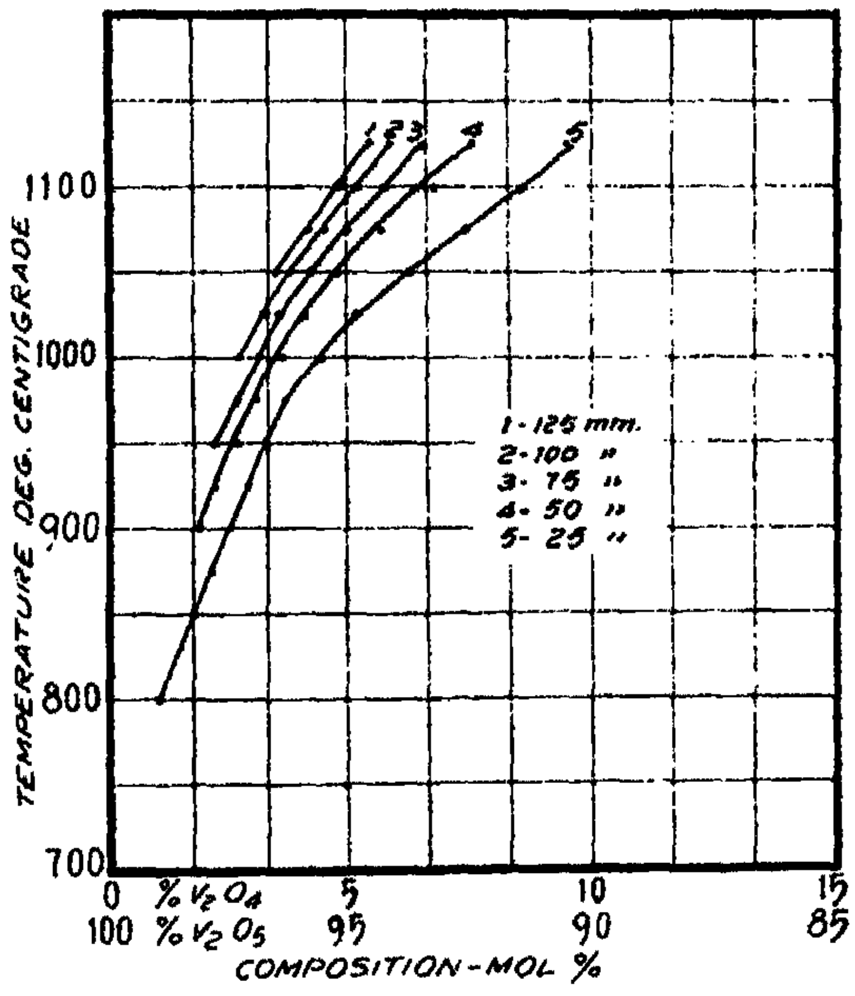

Fig. 5

It is evident from the preceding results that V_2O_5 dissociates appreciably into V_2O_4 and O_2 at temperatures only slightly above its melting point. Furthermore it is apparent that this dissociation is reversible provided the composition of the condensed phase remains unchanged.

It is also of interest to note that the fused oxide presents a divariant system, in other words it is impossible to fix the dissociation pressure of pure V_2O_5 except by an extrapolation of the curves in Fig. 3. This behavior is undoubtedly due to the solution of V_2O_4 in the molten V_2O_5.

According to Raoult's Law for dilute solutions it is possible to calculate the fractional vapor pressure lowering provided the mol fraction of the solute is known. In this case (V_2O_5) the pressure-composition curves were extrapolated in order to get the oxygen pressure of the pure V_2O_5. These values multiplied by various mol fractions should give the corresponding oxygen pressure lowerings at these compositions. However it was found that the oxygen pressure lowerings were widely different from the values that would be expected by Raoult's Law.

The point of interest however is the large effect on the dissociation pressure of small amounts of the lower oxide. It is suggested that this great change in oxygen pressure accompanying small changes in composition is closely associated with the catalytic behaviour of this material.

In conclusion, the author welcomes this opportunity to express his appreciation to Dr. W. A. Patrick and to Dr. J. C. W. Frazer who suggested this work and under whose direction it was performed.

Summary

1. Vanadium pentoxide was shown to be unstable above its melting point.
2. Oxygen pressures over different mixtures of vanadium pentoxide-vanadium tetroxide were measured at temperatures from 700°C.–1125°C.
3. It was shown that decomposition pressures at definite constant temperatures depended upon the composition of the melt. Similarly, the decomposition temperatures at definite constant pressures also depended upon the composition of the melt.
4. Oxygen pressures over melts containing practically 100% V_2O_5 were shown to be very much greater than those in which the V_2O_4 content was 10% or more.
5. Raoult's law of fractional vapor-pressure lowering does not hold for the system studied.
6. Pressure-temperature, pressure-composition and temperature-composition diagrams have been plotted.

ELECTRICAL CONDUCTION IN TEXTILES. III

Anomalous Properties of Conduction in Textiles

BY E. J. MURPHY

In previous papers the direct-current resistivity[1] and the alternating-current capacity and conductivity[2] of textiles have been discussed. This paper deals with several phenomena which may be conveniently collected under the term "anomalous properties," since they deviate from the behavior usually regarded as normal in conduction in ideal solid dielectrics. These phenomena will be discussed in three separate sections, the first of which deals with the dependence of insulation resistance on applied voltage, the second with the residual electromotive force which remains in a textile after the removal of the applied e.m.f., and the third with the changes which are made in the distribution of resistance in a textile by the passage of a current through it.

These anomalous phenomena are the source of a large number of complicating factors in the interpretation of electrical measurements on moisture absorbing materials. For example, since the apparent resistivity is a function of the applied voltage, it is possible that the value corresponding to some particular voltage represents more nearly the normal resistivity of the material than the values corresponding to other voltages. Also the existence of a residual e.m.f. suggests that part of the apparent resistivity may be due to a back-e.m.f. which reduces the effective e.m.f. over the conduction paths, but on the other hand it is also possible that the residual e.m.f. is due to a dielectric polarization which does not affect the direct-current resistivity. Further, since the passage of a current through a textile tends to change the distribution of its resistance, the current used for measuring the resistance of a sample may disturb the uniformity of distribution of its resistance sufficiently to make the observed resistance unsuitable for calculating the resistivity of the material. Therefore, in order to determine the nature of the apparent resistivity of textiles and other moisture-absorbing dielectrics and to define their true resistivity, a study of the anomalous phenomena enumerated in the first paragraph is necessary. Moreover, the explanations of several of the properties of alternating-current conduction in moisture-absorbing dielectrics involve these anomalous phenomena. For example, dielectric losses in alternating electric fields are usually attributed to the charging current by which the residual charge is formed, but have also been attributed to a conduction current which decreases rapidly with time of flow of the current, owing to an increase in the effective resistance of the dielectric. It has also been found in many cases that the power factor of moisture-absorbing dielectrics depends on the applied voltage.

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[1] J. Phys. Chem., 32, 1761 (1928).

[2] J. Phys. Chem., 33, 197 (1929).

The experimental investigation reported here consisted in measuring the insulation resistance of cotton samples of several different types as a function of applied voltage and humidity; in measuring the residual electromotive force in cotton at several humidities in order to determine how its main characteristics vary with humidity; and in determining the distribution of resistance in cotton threads and how it is affected by the passage of current through the thread. The experiments were confined to cotton, but the conclusions are probably applicable in a general way to silk and wool and possibly to other moisture-absorbing dielectrics.

The most general conclusion reached is that the anomalous properties of conduction in textiles at humidities above 20–30% can be explained in terms of the properties of electrolytic cells if assumptions are made as to the probable effect of the distribution of the absorbed water in the solid dielectric. This conclusion is consistent with the conception of conduction in textiles which was proposed in the preceding paper,[2] namely, that a textile material connecting two electrodes acts in many respects as an electrolytic cell in parallel with a condenser, and that the electrolytic cell component is chiefly responsible for the observed characteristics of the textile except at low humidities. Most of the conclusions apply only to humidities greater than 20–30%, for the behavior at humidities lower than this was not very definitely determined in the present investigation.

Variation of Insulation Resistance with Applied Voltage
(The Evershed Effect)

That the insulation resistance of moisture-absorbing dielectrics is a function of the applied voltage has been demonstrated by Evershed,[3] who also proposed a theory to account for it based upon the redistribution of the absorbed moisture by the electric field. The present investigation was undertaken chiefly to determine whether the insulation resistance-humidity relationships[1] for cotton are similar or different for different applied voltages.

The experimental procedure was described in the first paper of this series with the exception of the arrangements for varying the voltage. These consisted in a switch by which the voltage could be changed by a factor of 10 and a potential divider by which it could be varied continuously from a fraction of a volt to 180 volts. The samples of cotton used were also described in the earlier paper. The chief difficulty in making the measurements was the increase of resistance with time of application of the voltage (called "polarization" in the remainder of this paper). This is very rapid at high humidities, but was minimized by making the measurements by rapid methods when necessary.[1] Since the increases in resistance due to polarization are cumulative, errors due to this cause could be detected by making the measurements in a cycle such as: 1, low-voltage measurement; 2, high-voltage measurement; 3, repetition of 1.

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[3] S. Evershed: J. Inst. Elec. Eng., **52**, 51 (1914).

The error in the individual measurements has already been discussed;[1] but, in comparing measurements made at different voltages with all other conditions constant, differences in resistance which are considerably smaller than the error in the individual measurements may be significant; differences of less than 1% are probably significant in some cases. In the range 30–75% humidity the error in the ratios given in Table III probably does not exceed 10%, but outside this range it is probably greater. Because polarization is more rapid for the higher voltage than the lower, the values for the ratios in Table III may be about 20% too small at the highest humidity used, but this error decreases rapidly with decreasing humidity and is probably negligible at 75% humidity.

The characteristic form of the insulation resistance-applied voltage curve for cotton at humidities above 20–30% is illustrated by Fig. 1. For applied voltages of less than 1 or 2 the insulation resistance is abnormally high as compared with its values at higher voltages. This characteristic would be expected if cotton conducts by the electrolysis of the aqueous solutions which it contains, for the resistance of an electrolytic cell is abnormally high for voltages of this order, i.e., less than decomposition potentials and over-voltages (cf. the current-voltage curve for electrolytic cells.[4]) When an e.m.f. of about 1 volt or less is applied to a cotton insulation there is a relatively large initial current which rapidly falls to a small residual current; and when the applied e.m.f. is increased by a fraction of a volt this process is repeated but the residual current is larger. This behavior is qualitatively the same as that of an electrolytic cell in the same range of voltage. The form of curve shown in Fig. 1 could be predicted, for voltages less than about 50, on the assumption that a piece of cotton joining two electrodes acts as an electrolytic cell which develops a back-e.m.f. of polarization of the order

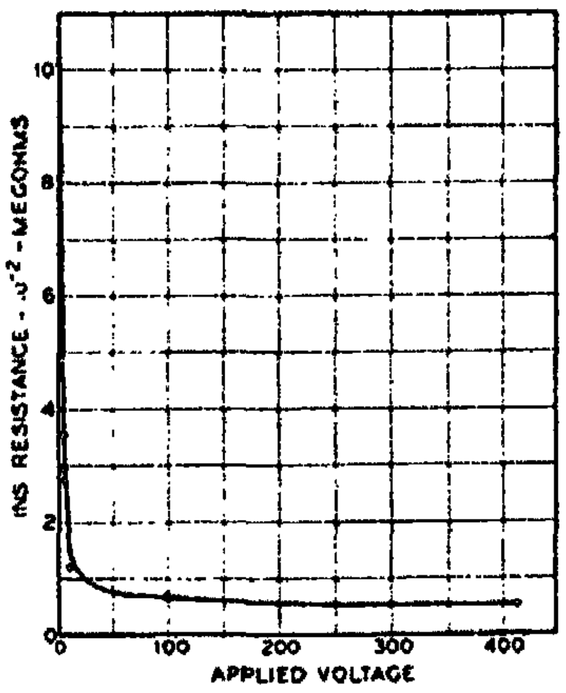

FIG. 1
Variation with Voltage of the Insulation Resistance of Cotton. Plotted from Table I.

TABLE I

Insulation Resistance v. Applied Voltage
Twisted Pairs II. Humidity 59%. Temp. 25°C

Applied Voltage	Insulation Resistance	Applied Voltage	Insulation Resistance
0.2	1018 megohms	1.0	120.5
0.4	352	100.0	73.5
0.6	293	412.	54.2
0.8	279		

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[4] See, for example, Allmand: "Applied Electrochemistry," p. 112.

of 2 volts. The above statements apply only to the humidity range above 20–30%; at lower humidities they require modification to take account of the larger back electromotive forces (see next section). The small amount of data obtained at humidities lower than 25% indicate that in this range the insulation resistance also decreases with increasing applied voltage, though the back-e.m.f. may be due to causes other than electrolytic polarization. Table II shows that Ohm's law is obeyed in the range 4–40 volts when the calculation of the resistance is based on the effective e.m.f. obtained by subtracting the back-e.m.f. of polarization from the applied voltage. However, since the back-e.m.f. of polarization in cotton at humidities above 20–30% apparently does not exceed 2 or 3 volts, it is able to produce a reduction of only 2 or 3% in the effective e.m.f. when the applied voltage is 100 or more, and therefore does not completely explain the decrease of resistance with voltage for voltages higher than 100.

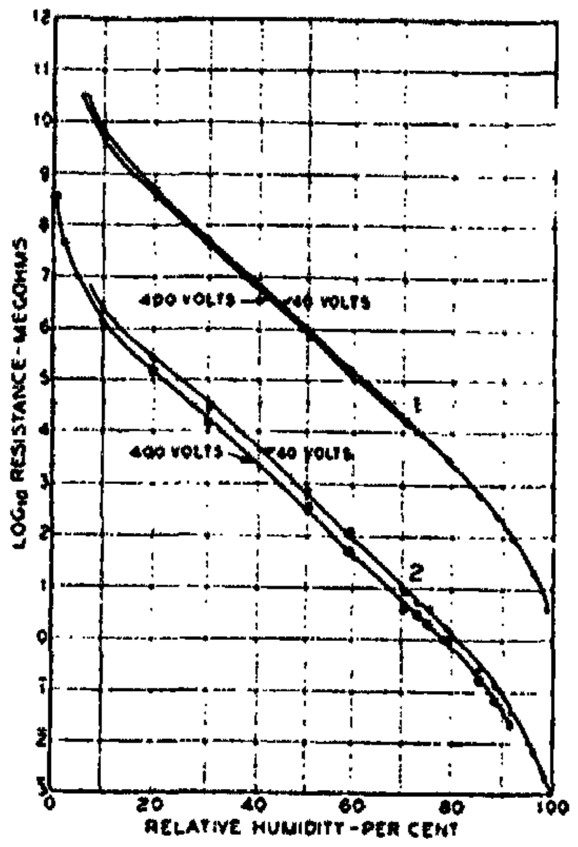

FIG. 2

Comparison of Insulation Resistance-Relative Humidity Curves for Different Applied Voltages

1. Cotton Threads I
2. Twisted Pairs I (Cotton)

Fig. 2 shows that the insulation resistance-relative humidity curves for applied voltages of 40 and 400 are parallel within the possible experimental error. The curves for 100 volts for the same samples were given in a previous paper[1] and would fall between those for 40 and 400 volts and be approximately parallel to them, but have not been plotted to avoid crowding. Table III contains the data from which these curves were plotted and in addition data for other samples which differ only in containing a smaller amount of electrolytic material. These data show that the difference between the resistance at 40 volts and

TABLE II

Effect of Polarization E.M.F. on Apparent (Insulation) Resistance. Humidity 98.6%. Temp. 25°C

	Applied E.M.F. (volts)	Residual E.M.F.	Effective E.M.F.	Apparent Resistance	Corrected Resistance (megohms)
Cotton Thread A	5.4	−1.4	4.0	11.0	7.9
	41.4	−1.4	40.0	8.1	7.9
Cotton Thread B	5.42	−1.3	4.12	6.47	4.7
	42.5	−1.3	41.2	4.87	4.7

After the residual e.m.f. had been measured (see next section) the applied voltage was adjusted so that the effective e.m.f. in the second measurement was ten times that in the first. (The back e.m.f. of polarization should not be less than the residual e.m.f.)

TABLE III

Insulation Resistance of Cotton as a Function of Applied Voltage and Relative Humidity for Samples containing Different Amounts of Electrolytic Material and having Different Electrode Separations. Resistances in megohms. Temp. 25°C.

Electrode Separation:	0.025 cm.						1.3 cm.					
Electrolyte Content:	Normal			Low			Normal			Low		
Sample:	Twisted Pairs I			Twisted Pairs II			Cotton Threads I			Cotton Threads II		
Rel. Humidity Percent	R_{40}	R_{400}	$\frac{R_{40}}{R_{400}}$	R_{40}	R_{400}	$\frac{R_{40}}{R_{400}}$	R_{40}	R_{400}	$\frac{R_{40}}{R_{400}}$	R_{50}*	R_{400}	$\frac{R_{50}}{R_{400}}$
0.	—	3.3×10^{8}	—	—	—	—	—	—	—	—	—	—
2.	—	4.3×10^{7}	—	—	—	—	—	—	—	—	—	—
6.	—	—	—	—	—	—	4.3×10^{10}	2.7×10^{10}	1.6	—	—	—
10.0	2.33×10^{6}	1.46×10^{6}	1.6	—	—	—	6.2×10^{9}	4.2×10^{9}	1.5			
19.5	2.78×10^{5}	1.42×10^{5}	1.96	2.02×10^{6}	1.22×10^{6}	1.65	4.56×10^{8}	4.56×10^{8}	1.0a)			
30.0	2.95×10^{4}	1.57×10^{4}	1.88	2.49×10^{5}	1.48×10^{5}	1.68	5.07×10^{7}	4.44×10^{7}	1.14	—	—	—
38.8	—	—	—	5.58×10^{4}	3.15×10^{4}	1.78	9.00×10^{6}	7.76×10^{6}	1.16			
50.5	7.38×10^{2}	3.52×10^{2}	2.10	9.10×10^{3}	6.28×10^{3}	1.45	9.41×10^{5}	7.92×10^{5}	1.19	—	—	—
59.0	1.01×10^{2}	5.15×10^{1}	1.96	1.46×10^{3}	1.03×10^{3}	1.42	1.73×10^{5}	1.53×10^{5}	1.13	2.64×10^{6}	2.50×10^{6}	1.06
70.8	8.94	4.75	1.88	1.65×10^{2}c)	1.23×10^{2}	1.34	1.86×10^{4}	1.71×10^{4}	1.09	3.32×10^{5}d)	3.12×10^{5}	1.03
73.0	5.40	3.24	1.67	—	—	—	1.49×10^{4}	1.29×10^{4}	1.16	2.52×10^{5}	2.42×10^{5}	1.04
75.5	4.03	2.30	1.75	—	—	—	8.18×10^{3}	6.85×10^{3}	1.20	—	—	—
79.1	1.62	1.07	1.51	1.98×10e)	1.59×10	1.25	3.30×10^{3}	3.20×10^{3}	1.03	4.60×10^{4}	—	—
85.2	2.92×10^{-1}	1.92×10^{-1}	1.52	—	—	—	6.40×10^{2}	6.40×10^{2}	1.0a)	2.22×10^{4}d)	2.04×10^{4}	1.09
88.4	1.28×10^{-1}	6.92×10^{-2}	1.85	—	—	—	2.92×10^{2}	2.72×10^{2}	1.07	—	—	—
92.0	4.17×10^{-2}	2.7×10^{-2}	1.55	1.17c)	1.05	1.11	1.00×10^{2}	0.96×10^{2}	1.04	—	—	—
96.3	7.82×10^{-3}	—	—	—	—	—	2.62×10	2.26×10	1.16	9.62×10^{2}	—	—
98.6	2.3×10^{-3}	—	—	—	—	—	4.02	4.0b)	1.005	2.05×10^{2}	—	—
Average:			1.77			1.44			1.16			1.05

The error in these data is least in the range 30–80% humidity.
The data apply to a single Thread or Twisted Pair Sample.
A description of these samples and also their resistances at 100 volts, was given in a previous paper.[1]

* The resistance at 50 volts equals that at 40 within the possible error.

a) Error large on account of insensitivity of the galvanometers.

b) Too high on account of rapid polarization.

c) Voltage 50.

d) Voltage 100.

that at 400 volts is less the greater the electrode separation and the smaller the amount of electrolytic material in the samples. The ratio of the resistance at 40 volts to that at 400 volts appears to be approximately constant over the whole range of humidity, i.e., the variations in the ratio are small as compared with the change with humidity in the resistivity of the cotton. The curves in Fig. 2 indicate that in the range 20–80% humidity the insulation resistance of cotton samples may be expressed as a function of humidity and applied voltage by

$$\text{Log}_{10} R = -8.5 \times 10^{-2} H + A,$$

where R is the insulation resistance in megohms, H the relative humidity in percent, and A a constant whose value depends on the applied voltage as well as on the dimensions of the sample, the amount of electrolytic material in the textile, the temperature and other factors. For example, for Twisted Pairs I, A has the value 7.2 at 40 volts, 7.0 at 100 volts and 6.9 at 400 volts.

A large number of tests were made during this investigation to determine whether an increase in voltage always produced a decrease in insulation resistance. When the influence of polarization was taken into account, no exceptions to this were found. At high humidities polarization was extremely rapid, especially for 400 volts, and the initial decrease in resistance on applying the higher voltage was quickly effaced if the current was left on. Evershed considered that the resistance became independent of voltage when the moisture content of the samples was very high. The present results suggest that this finding was due to the error caused by polarization, although there may be a real decrease in the magnitude of the effect at high humidities.

Table IV shows that the insulation resistance for a given voltage can be lowered temporarily by increasing the applied voltage momentarily to a higher value. This change in resistance is opposite to that which would be produced by polarization.

TABLE IV

After-Effect of the Application of a High Voltage

Twisted Pairs I at 30% Humidity		Twisted Pairs I at 70.8% Humidity	
Applied Voltage	Ins. Resistance (megohms)	Applied Voltage	Ins. Resistance (megohms)
38.3	2.95×10^4	37.6	8.90
383.	1.57	376.	4.75
38.3	2.50	37.6	7.40

The measurements were made in the above order.

On the assumption that a textile connecting two electrodes acts as an electrolytic cell, the increase in the conductivity of textiles with increasing applied voltage can be partially explained by Wien's[5] discovery that the conductivity of electrolytic solutions increases with increasing applied voltage, but the rate of increase does not appear large enough to explain more than a small part of the Evershed effect. To explain the Wien effect Joos and Blu-

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[5] M. Wien: Ann. Physik, **83**, 327 (1927); Physik. Z., **28**, 834 (1927).

mentritt[6] have extended the Debye-Hückel theory of the effect of electrostatic forces between free ions in solution, and have obtained agreements with the experimental data. Another indication of the nature of the Wien effect has been obtained by Gyemant,[7] who found that while the conductivity in the direction of the applied field increases with voltage that normal to it is constant. His explanation of this phenomenon involves the association of ions to form ion-pairs.

These theories of the Wien effect are based upon electrostatic forces between the ions in the solution. There are also electrostatic forces between a solid-liquid boundary and ions which are near it, and it seems possible that these forces would have an effect on the conductivity of the layer of electrolyte near a solid-liquid interface similar to that of the forces between the ions themselves on the conductivity of the bulk of the solution. Where the volume of electrolyte is large as compared with the area of the solid-liquid interface such an effect would not be important, but in textiles it is probable that the conducting water paths permeate the textile material in such a way that the interfacial area would be large as compared with the volume of liquid. The ions adsorbed by the solid-liquid interface of the conducting water paths may therefore contribute appreciably to the conductivity of the textile, and the amount of this contribution may be an increasing function of the applied voltage. Evidence that adsorbed ions contribute to the conductivity of cellulose appears to be given by Briggs'[8] discovery that the surface conductivity of cellulose fibres immersed in water (i.e., the conductivity of the water near the solid-liquid boundary) is considerably higher than that of the bulk of the liquid. Data are not available to show how this surface conductivity varies with voltage. There appears however to be sufficient indirect evidence to warrant the suggestion that the Evershed effect may be partly caused by a modified Wien effect operating in the layer of electrolyte close to the solid-liquid interface of the conducting water paths of the textile, due to the forces of adsorption acting on the ions in this layer. The number of adsorbed ions moving in the conduction current, or their velocity, may vary with voltage in such a way as to make the conductivity of the textile increase with applied voltage.

The experimentally determined relationships appear to be reasonably consistent with this explanation. The ratio of the resistances of a sample of cotton as measured at two different voltages remains fairly constant over nearly the whole range of humidity. This would be expected if the ratio of interfacial area to volume of water in the water paths does not change much with humidity, as appears probable. The magnitude of the Evershed effect increases with decreasing electrode separation, i.e., with increasing voltage gradient. This seems reasonable to expect if the adsorbed ions are

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[6] Joos and Blumentritt: Physik. Z., 28, 836 (1927).
[7] A. Gyemant: Physik. Z., 29, 289 (1928).
[8] D. R. Briggs: J. Phys. Chem., 32, 641 (1928).

distributed as a diffuse layer whose density diminishes gradually with distance from the interface, as proposed by Gouy[9] to explain other facts.

The property of increasing conductivity with increasing electric field strength appears to be a very common characteristic of electrolytic conduction, for it occurs in electrolytic solutions, both aqueous and non-aqueous, in textiles and other moisture absorbing dielectrics and in other solid dielectrics such as glass.[10,11] It seems possible that electrolytic polarization and electrostatic forces between ions are involved in all cases.

The conclusion from the present investigation is that at low voltages the Evershed effect is due to the back-e.m.f. of electrolytic polarization, and that at voltages above about 40 the ions adsorbed by the solid-liquid interfaces of the conducting aqueous solutions in the textile may contribute to the increase of conductivity with voltage in a manner similar to the mutually attracting ions involved in theories of the Wien effect. No data were obtained which definitely show whether the redistribution of water in the electric field, as proposed by Evershed, is or is not also a factor.

Residual Electromotive Forces in Cotton

In common with other imperfect dielectrics cotton has the property of absorbing a residual charge, which causes a "residual e.m.f." This residual e.m.f. or charge is an important effect for it is the main difficulty in defining and measuring the resistivity and capacity* of such dielectrics and is also responsible for part of the power loss in alternating electric fields. It has been frequently investigated and many theories have been proposed to explain it,[12] such as inhomogeneity of the dielectric, viscous dielectric displacement or polarization, and electrolytic polarization or ionic space charge.[13,14,15] In the present investigation of cotton a few measurements were made which show the general way in which the characteristics of the residual e.m.f. vary with the moisture content of the cotton. The results lead to the conclusion that at humidities above 20–30% the residual e.m.f. in cotton is caused by the products of the electrolysis of the aqueous solutions which it contains; at humidities lower than this other factors may predominate.

The method used for measuring the residual e.m.f. is essentially the same as that used by Richardson[16] in measuring the "internal e.m.f. of polarization" in quartz. The measurements were made with the circuit sketched in

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[9] G. Gouy: Ann. Phys., 7, 129 (1916).

[10] H. H. Poole: Phil. Mag., 42, 488 (1921).

[11] H. Schiller: Ann. Physik, 81, 137 (1927).

* This term is used loosely in these papers to mean the effective dielectric constant of the material, or a quantity proportional to it.

[12] These theories have been reviewed by E. R. v. Schweidler: Ann. Physik, 24, 711 (1907); L. Hartshorn: J. Inst. Elec. Eng., 64, 1152 (1926); and J. B. Whitehead: J. Am. Inst. Elec. Eng., 45, 515 (1926).

[13] A. Joffé: Ann. Physik, 72, 481 (1923).

[14] S. Mikola: Z. Physik, 32, 487 (1925).

[15] H. Schiller: Ann. Physik, 81, 32 (1926).

[16] S. W. Richardson: Proc. Roy. Soc., 107A, 102 (1925).

Fig. 3-B of the first paper of this series.[1] The applied voltage could be varied continuously from a small fraction of a volt to about 180 volts; several other voltages up to 415 were also available. The residual e.m.f. tends to cause a galvanometer deflection in the opposite direction to that which the applied voltage would produce, and therefore when the applied voltage was greater than the residual e.m.f. the galvanometer was deflected in one direction and when less in the other. By adjusting the applied e.m.f. the deflection could be brought to zero, and the applied e.m.f., as read from the voltmeter, was then equal to the residual e.m.f.

At high humidities the residual e.m.f. could be determined readily to a small fraction of a volt but at low humidities the precision was not as great owing to the high resistances of the samples. Another difficulty at low humidities was the disturbance of the steady galvanometer deflection by the transient currents which flowed through the capacities of the circuit whenever the applied voltage was changed as required by the method of measurement.

To confirm the order of magnitude of the values obtained by this method some measurements were also made by a different method. An air condenser was charged by means of the residual e.m.f. and then discharged through a galvanometer. The circuit was calibrated by repeating this process after charging the condenser to known voltages. In charging the measuring condenser the e.m.f. being measured may be appreciably reduced, unless maintained by a large supply of energy, and measurements made by this method therefore only indicate that the residual e.m.f. is not less than the value which it indicates.

If a voltage which has been applied to a short length of cotton thread exposed to a high humidity is removed and the thread connected to a galvanometer it is found that a current of the order of 10^{-3} ampere flows for several minutes, decreasing gradually with time. The rate of decrease is so slow that even after several hours or a day a current due to the residual e.m.f. in the cotton can be detected. The quantity of energy stored in the cotton appears to be too great to permit the explanation of this effect as a residual electrostatic charge. The rate of discharge also is slower than would be expected of an electrostatic charge in view of the relatively low resistance of the thread (less than its resistance when dry by a factor of 10^6 or more).

No residual e.m.f.'s greater than about 2 volts have been observed at humidities above about 30%, even though voltages of the order of 400 were applied in some cases for several hours. This characteristic would be expected if the residual e.m.f. is due to electrolysis of the aqueous solutions present in the textile. The chemical changes produced at the electrodes by electrolysis cause a difference of potential which opposes the applied e.m.f. These changes are of such a nature that in general they tend to remain after the applied e.m.f. is removed, producing a residual e.m.f. It is evident that residual electromotive forces of this kind should not exceed the back-e.m.f. of polarization; and since the magnitude of the back-e.m.f. of polarization is determined by decompositon potentials and over-voltages it would be expected that residual electromotive forces in cotton due to this cause would not exceed the order of magnitude of these quantities, i.e., about 2 or 3 volts.

If the direction of a current through a cotton sample is reversed the residual e.m.f. produced by it reverses its sign during the discharging process, the first part of the discharge corresponding to the last current and the last part to the first current.[17] For example: an e.m.f. of 374 volts was applied for 4 minutes to a Cotton Thread sample at 70.8% relative humidity; this was followed by 100 volts applied for 2 minutes and finally by −100 volts applied for 2 minutes. The applied e.m.f. was then removed and the resultant residual e.m.f. varied with time in the following way:

Time	1	3	5	7	10	15	minutes
Residual E.M.F.	150	40	10	1	−3	−5	arbitrary units of deflection

The galvanometer deflections for the first 7 minutes correspond to predominance of the residual e.m.f. produced by −100 volts, and those for 10 and 15 minutes to predominance of that produced by +100 and +374 volts. This effect was also observed at 19.5% humidity by charging an air condenser by means of the residual charge. It is a general property of dielectrics which absorb a residual charge. While it may not be an electrolytic effect in cotton at low humidities, it appears to be undoubtedly so at high humidities. The following is a possible explanation: Since the products of electrolysis presumably first make their appearance at the electrode surfaces, it is probable that, when the current direction is reversed, the new products push the products of the first current away from the electrode as a layer, and that there are then at each electrode two layers of electrolyte of different chemical composition, the one layer being composed of anode products and the other of cathode products. The reason for the reversal of sign is evident if the residual e.m.f. is chiefly due to the difference in the chemical composition of the products formed at the anode and cathode respectively; if the process of discharge is the inverse of that of "charging," the layers move up to the electrode surfaces and become discharged (in the sense of being made incapable on producing further current) in the inverse order to that in which they are formed.

The characteristics of the residual e.m.f. in cotton at low humidities differ from those at high humidities, as is evident from Table V. Below about 25% humidity the residual e.m.f. becomes a function of the applied voltage and attains values greater than 100 volts when the applied voltage is of the order of 400 volts. These characteristics are incompatible with the explanation which has been given for the residual e.m.f. at high humidities. They are the usual characteristics of dielectrics which absorb a residual charge. Thus at humidities above 20–30% a piece of cotton in contact with electrodes functions essentially as a secondary cell as regards its residual e.m.f. (i.e., the residual e.m.f. is due to the products of electrolysis), while

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[17] Cf. J. Granier: Bull. Soc. franç. Elect., 3, 335 (1923).

TABLE V

Residual E.M.F. in Cotton at Different Times after the Removal of an E.M.F. of 390 volts which had been applied for Two Minutes

Twisted Pairs			Threads		
Relative Humidity, Percent.	Time, Minutes	Residual E.M.F. in volts	Relative Humidity Percent.	Time, Minutes	Residual E.M.F in volts
2	1	>100	19.5	1	0.0
10	1	>100	30.0	1	0.0
	5	100			
	10	<100	59.0	1/2	1.7
				1	1.0
19.5	1	8.2		5	0.4
	5	4.1			
	8	1.8	76.0*	1	0.5
59.0*	1	0.8	98.6	1	0.75
	4	0.7		5	0.55
	6	0.6			
	8	0.5			
	15	0.45			
89.0	1	1.0			

* The applied voltage was 100 in these cases.

at humidities below this it acts as a dielectric which absorbs a residual charge which is apparently electrostatic in nature. In the preceding paper it was shown that the alternating-current capacity and conductivity change with humidity in a similar way, i.e., that at humidities above 20–30% the textile acts chiefly as an electrolytic cell, but that at lower humidities the dielectric properties become more prominent.

From the general properties of conduction in cotton it would be expected that the following factors would contribute to its residual charge at low humidities. The resistivity-moisture content relationship indicates that part of the energy should be stored in the same way as at high humidities. The residual charge may also be partly due to a regularly distributed capacity associated with the water paths in a way suggested in a previous paper[2] to account for other facts; i.e., electrostatic charges may be distributed through the textile due to its inhomogeneity and consequent non-uniformity of conductivity and dielectric constant, essentially in accordance with Maxwell's theory of absorption in non-homogeneous dielectrics. The residual charge may also be due in part to a viscous dielectric polarization as in Pellat's theory. It is also possible that there is a thin high resistance layer of large capacity at one or both of the electrodes due to polarization.[18]

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[18] Joffé (loc. cit.) has shown that in some crystals almost the whole potential drop is concentrated over a very thin layer at one of the electrodes when current has flowed for some time.

At low humidities, where the residual e.m.f.'s are large, their effect on the apparent resistance (the ratio of applied e.m.f. to current) can be made evident by any change in the applied e.m.f. The current through a cotton insulation appears to be determined by the algebraic sum of the applied e.m.f. and the residual e.m.f. If the applied voltage is reduced there is an instantaneous increase in apparent resistance followed by a slow decrease as the residual e.m.f. becomes reduced to the value corresponding to the lower voltage; if the applied e.m.f. is equal to the residual e.m.f. the apparent resistance is infinite. Increasing the applied voltage causes an instantaneous decrease in apparent resistance followed by a slow increase. Reversal has a similar effect: the apparent resistance is at first abnormally low but gradually increases as the residual e.m.f. decreases to zero and changes sign.

In the range of humidities above about 30%, where cotton acts essentially as an electrolytic conductor, the true resistance of a cotton sample is given by $R = (V - P)/I$, where V is the applied e.m.f., P the e.m.f. of polarization (i.e. the initial value of the residual e.m.f.) and I the current. Since P is of the order of 2 volts and V usually over 100 this correction is small. However, at humidities where cotton acts as a dielectric which absorbs a residual charge, the value taken as the true resistance depends on which of the theories of the residual charge is adopted. When an e.m.f. is applied to a cotton sample at a low humidity (or to any other dielectric which absorbs a residual charge) the current decreases with time, and when the applied voltage is removed a residual e.m.f. remains. According to theories such as those of Maxwell, Pellat or v. Schweidler the initial current includes the anomalous, or residual charging current, and the final steady current therefore is the normal conduction current which should be the basis of the calculation of the true resistivity. On the other hand, according to theories based upon ionic space charge or electrolytic polarization, the initial current (not including the normal charging current) is the normal conduction current which should be used for the calculation of the true resistivity; and the final current corresponds to an abnormal condition of the material due to the formation of a back-e.m.f. of polarization or to a change in the resistance of the sample. Joffé[13] has found that for certain materials a resistance defined by $R = (V - P)/I$ obeys Ohm's law and that the formation of the back-e.m.f. of polarization P is accompanied by a change from uniform to non-uniform distribution of potential in the dielectric. Sinjelnikoff and Walther[19] define the true resistivity of a dielectric on the basis of the initial current and have obtained experimental support for this view. Richardson[16] expresses the current in a dielectric by:

$$i = dQ/dt + (V - P)/R,$$

where dQ/dt is the rate at which charge is accumulating in the dielectric and $(V-P)/R$ is the conduction current. His experiments on quartz provide experimental support for this equation. In measuring the resistivity of

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[19] Sinjelnikoff and Walther: Z. Physik, 40, 786 (1927).

sulphur and other dielectrics Neumann[20] has defined the resistivity on the basis of v. Schweidler's theory of dielectric absorption, taking the final steady current as the basis for the calculation of the resistivity. Thus there appears to be no generally accepted definition of the true resistivity of a dielectric which absorbs a residual charge.

The chief difficulty in defining the true resistivity of dielectrics which absorb a residual charge lies in the fact that it is difficult to distinguish between a residual charging current and a conduction current which decreases with time. For example, the fact that the resistance of a sample of material obeys Ohm's law does not necessarily imply that the observed resistance is based on the conduction current alone, for the residual charging current may be proportional to the applied e.m.f.[21] Further, though non-uniformity of the distribution of potential or resistance in the sample indicates that the observed resistance is unsuitable for calculating the resistivity of the material, uniformity of potential distribution does not exclude the possibility of the observed resistance being based partly on anomalous charging currents, since the residual capacity may be uniformly distributed. Consequently, it does not seem possible to decide from available data whether the apparent resistivity of textiles at low humidities is or is not appreciably affected by residual charging currents. The definition of the true resistivity at humidities above 20–30% is, however, reasonably certain.

Effect of Current on the Distribution of Resistance in Textiles

It is a well-known fact that the resistance of a moisture absorbing dielectric changes with time while direct current is flowing through it. This is of considerable importance in the measurement of the resistance of textiles, for their resistance may be changed by an appreciable amount in certain circumstances by the process of measuring it. Granier[22] has found that the prolonged application of a direct voltage greatly increases the resistance of certain moisture absorbing materials. This also occurs in paper,[23] transformer oil[24] and other dielectrics. The increase of resistance has frequently been attributed to the formation of a high contact resistance between the electrode and the insulating material, to drying of the anode region by the electrosmotic movement of water away from it, to drying by Joule heating, or to the formation of a back-e.m.f. in the material. In the present investigation measurements were made which show the resistance of the contact between an electrode and a cotton thread and the effect of current on the distribution of resistance in the thread. The results are not in agreement with the explanations mentioned above, but can apparently be explained by the probable effects of the products of electrolysis on the conductivity of

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[20] H. Neumann: Z. Physik, **45**, 717 (1927).

[21] Cf. E. R. v. Schweidler: Footnote 12.

[22] J. Granier: Bull. Soc. franç. Elect., **3**, 480 (1923).

[23] Delon, Capdeville and Douchet: Bull. Soc. franç. Elect., **5**, 842 (1925).

[24] Schrader: Elec. J., **16**, 334 (1919).

the aqueous solution through which conduction in the textile takes place. The bearing of the results on electrical breakdown in moisture absorbing dielectrics is also briefly discussed.

In order to determine whether the change in resistance takes place in the cotton itself, or is caused by the formation of a high resistance coating on the electrode surfaces, the following experiment was performed. The two ends of a cotton thread about 4 cm. long were clamped in electrodes A and B, Fig. 3A. The thread also made contact at its middle point with a cylindrical rod C which served as a common electrode; contact with C was maintained by a slight tension in the thread. The resistances AC, BC and AB were measured in the initial state; then an e.m.f. was applied for several hours between electrodes B and C, and the resistance measurements repeated. During this "polarizing"* process C was made positive in some cases and negative in others.

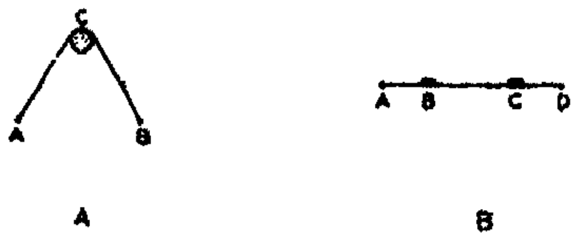

FIG. 3
Arrangement of Auxiliary Electrodes.

The results of these measurements are given in Table VI for brass electrodes and in Table VII for platinum electrodes. The difference between the resistance of the whole thread AB and the sum of the resistances of the sections AC and BC, when divided by 2, is the resistance of the contact of the thread with electrode C. These tables show that the resistance of the contact between a cotton thread and a brass or platinum electrode forms less than 3% of the total resistance of the thread under the conditions of these measurements. This is the case both before and after polarizing the thread, and both when the electrode was a cathode and when it was an anode during the polarizing. This result shows that the increase in resistance takes place in the thread itself rather than at its contact with the electrode. No current flowed in the AC section during the polarization of the BC section. It would therefore be expected that its resistance would be unaffected. However the data show that for brass electrodes the resistance of the AC section is more than doubled by a current flowing in the BC section when C is an anode, while it is slightly decreased when C is a cathode. This implies that the current increases the resistance of cotton in the region around a brass anode, and decreases it in the region around a brass cathode, the change produced in the cathode region being considerably smaller than in the anode region. This result is confirmed by the experiments which will be described next.

To determine the distribution of resistance in a cotton thread both in its initial state and after current had flowed through it for some time, auxiliary electrodes (narrow bars covered with gold or platinum foil) were brought into contact with the thread at different points along its length (at the points B and C in Fig. 3B). The resistances of the sections of thread between each pair of electrodes were measured, thus eliminating algebraically the contact

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* The terms "electrolyzing" or "electrification" could be used instead of "polarizing."

resistances of the auxiliary electrodes. As a further confirmation of the validity of these measurements, the potential distribution in the thread was also measured. Two methods were used. In one of them an insulation resistance circuit was adapted to act as a potentiometer in a manner evident from Fig. 4A. When the galvanometer deflection is brought to zero by varying the applied voltage with the potential-divider, the voltmeter reading is

TABLE VI

Resistance of the Contact between a Brass Electrode and a Cotton Thread in the Normal Condition and the Polarized Condition. (See Fig. 3A)
Resistances in megohms. Humidity 88.4%. Temp. 25°C.

	Thread 1		Thread 2		Thread 3		
	Normal	Polarized[a]	Normal	Polarized[b]	Normal	Polarized[b]	Oppositely Polarized[c]
Resistance of,							
A–B (whole thread)	840	2340	785	8550	577	7180	12700
A–C section	304	300	393	879	256	624	242
C–B section	492	2130	373	7750	318	6420	12700
Sum	796	2430	766	8629	574	7544	12942
Resistance of Contact, R_c	−22	45	−9.5	39	−1.5	182	121
R_c percent of A–B*	−2.6	1.9	−1.2	0.4	−2.6	2.5	0 9

[a] Polarized by applying 90 volts between B and C for 4 hours with C negative.

[b] Polarized by applying 384 volts between B and C for 18 hours with C positive.

[c] Polarized by reversing the direction of the applied e.m.f. (384 volts) for 48 hours: C negative.

* These contact resistances are all less than the experimental error (3%).

TABLE VII

Resistance of the Contact between a Platinum Electrode and a Cotton Thread in the Normal, and in the Polarized Condition.

The data are the resistances as a function of time of application of 370 volts between B and C, Fig. 3A. Resistances in megohms. Humidity 88.5% Temp. 25°C.

Section of Thread:	BC	AC	BC+AC	AB	Contact Resistance	Contact Resistance percent
Time						
0*, C anodic	272	437	709	726	−8.5	−1.1
0, C cathodic	274	452	726	725	0.5	0.7
30 min. C anodic	336	457	793	772	10.5	1.4
3 h. 30 min. ”	1158	447	1605	1562	21.5	1.4
8 h. 0 m. ”	1980	444	2424	2420	2	0.0
10 h. ”	2440	437	2877	2920	−21.5	0.7
23 h. ”	4170	414	4584	4650	−33.	0.7
59 h. ”	7500	384	7884	7820	32.	0.4[a]

* These resistances are for the thread in its normal condition.

[a] These contact resistances are all within the experimental error.

equal to the potential difference between the points where the auxiliary electrodes touch the thread. The essentials of the second method are evident from Fig. 4B: an air condenser was charged to the potential of different points on the thread through the auxiliary electrodes, and then discharged through a galvanometer. Calibrations were made by charging the condenser to known voltages. It was found that these three methods indicated the same distribution of resistance.

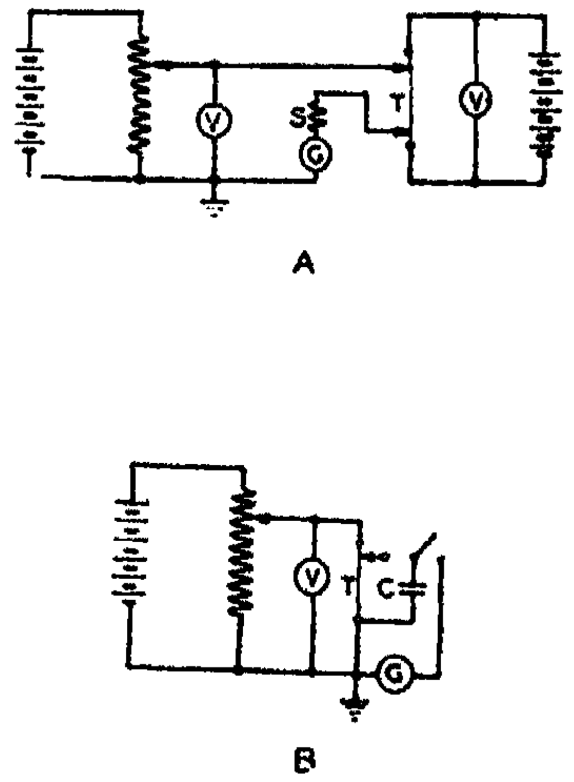

Fig. 4
Methods of determining the Potential Distribution in Cotton Threads.
V—Voltmeter
T—Thread
G—Galvanometer
S—Standard Megohm

The resistance of a cotton thread is approximately uniformly distributed along its length in its normal condition, but after a current has passed through it for a time depending on the intensity of the current, the humidity, and possibly other factors the resistance becomes non-uniformly distributed, as is shown in Table VIII for brass electrodes and in Table IX for platinum electrodes. Comparison of the data in these two tables shows that the distribution of resistance after prolonged polarization (i.e. electrification) depends on the nature of the electrode material. Table VIII shows that for brass electrodes the resistance of the whole thread is increased by a large factor by polarization and most of the resistance is concentrated in the anode section. By reversing the direction of the polarizing current the high resistance region can be transferred from one end of the thread to the other; the resistance of the CD section was 41 megohms when D was cathodic and 31,200 megohms when it was anodic. For platinum electrodes the high resistance portion appears in the middle of the thread.

The distribution of resistance which results when cotton is polarized with platinum electrodes would be expected to differ from that obtained with brass electrodes because different electrode reactions are involved and consequently the effect of the products of electrolysis on the conductivity of the aqueous solutions in the cotton would be different in the two cases. Another evidence of the effect of the difference in electrode reactions is given by measurements of tensile strength. When cotton threads are polarized for a day or so with platinum electrodes the tensile strength in the anode region is reduced by about one-half, while a similar polarization with copper electrodes produces no apparent change in tensile strength. The reduction in tensile strength is probably due to the formation of an appreciable amount of acid at the anode as one of the products of electrolysis; this might tend to prevent the resistance of the anode region of the thread from becoming very high.

The data given in Tables VI to IX are in disagreement with some of the explanations frequently offered for the increase in the resistance of moisture-absorbing dielectrics with time of application of a constant voltage. It has been shown that the resistance of the contact between the textile and the electrode is only a very small fraction of the total resistance of the textile even after current has passed through the textile for some hours. This excludes the possibility of explaining the phenomenon as an increased re-

TABLE VIII

Distribution of Resistance in a Cotton Thread polarized with Brass Electrodes:

Effect of Reversing Polarizing Current

Humidity 88.4%. Temp. 25°C. Polarizing Voltage 380. Resistance in Megohms

Section of Thread (See Fig. 3B)	AB	BC	CD	AD
Initial condition	(Potential distribution uniform)			116
Polarized with A anodic (18 hours at 380 volts)	11,800	—	41	13,600
Polarized with A cathodic (2 hours at −380 v.)	1,580	—	—	2,710
Polarized with A cathodic (46 hours more at −380 v.)	1,370	2,140	31,200	35,200

TABLE IX

Distribution of Resistance in a Cotton Thread as a Function of Time of Polarization with Platinum Electrodes; Time of Recovery. Humidity 88.5%. Temperature 25°C. Resistance in megohms. Polarizing Voltage 370. A is the anode and D the cathode.

Section of Thread (See Fig. 3B)	AB	BC	CD	AB+BC+CD	AD	Difference
Time of Polarization						
0	35.8	63.5	32.6	131.9[a]	174	−42
1 h. 0 m.	363.0	178.0	377.0	918.	893	25
3 30	457.	1343.	201.0	2001.	1990	10
5 30	400.0	1955.	86.0	2441.	2400	41
18 0	425.	2880	961.	4266.	4280	−12
54 0	742.	4500.	1970.	7212.	7180	32
Time of Recovery						
4 0 m.	584.	3355.	767.	4706.	4770	−64
6 0	490	2920.	482.	3892.	3920	−28[b]

[a] This differs from AD by an amount which is greater than the experimental error, probably because of the Evershed voltage effect.

[b] These differences are within the experimental error. They indicate that the contact resistance at the electrodes did not cause errors.

sistance of the contact between the electrode and the textile unless the conditions are quite different from those of the present investigation. The possibility of the phenomenon being due to drying of the anode region by the electrosmotic movement of water away from it, or to drying of the thread as a whole by Joule heating appears also to be excluded. For it is shown in Table IX that a polarized thread still has a non-uniform resistance distribution even after it has had ample time to return to the same temperature and moisture content that it had before being polarized. The fact that the resistance distribution depends on the electrode material is also in disagreement with the drying hypothesis. A polarized thread has approximately the same resistance for both directions of current flow; this would not be the case if the increase in resistance were caused by a back-e.m.f.; however this statement only applies to humidities above 20–30%. It is concluded therefore that none of these explanations is in agreement with the present experimental data. These results, however, appear to be consistent with the following mechanism: The passage of a current through the aqueous solutions in a textile is accompanied by electrode reactions which change the composition, and hence in general the conductivity of the solutions; the conductivity of the solutions determines that of the textile when other factors are constant. Owing to the possibility that the rate of diffusion of ionizable substances in a textile may be very slow on account of the manner in which the water is distributed, differences in the conductivity of the solutions in different parts of the textile may persist for some time; this would explain the persistence of a non-uniform distribution of resistance in textiles for many hours after the removal of the voltage by which it was produced.

The mechanism outlined above also affords a possible explanation of the changes in resistance which follow the reversal of the direction of a current flowing in a textile which is exposed to a high humidity. These changes are sometimes very complicated, particularly when the current direction has been reversed several times, but in most cases they fall into two classes: the resistance decreases and passes through a minimum, or it rises instantly to a value two or three times as great as the original value and then gradually falls. An illustration of the first type of behavior is given by the following figures, which are for the resistance at 50 volts of a Twisted Pair sample at 98.6% humidity; the current direction was reversed at time 0:

Time:	0	10	20	30	40	100 seconds
Resistance:	.46	.36	.35	.40	.42	.50 megohms

If reversing the current creates two electrolyte layers of different composition at each electrode (as already suggested to explain the reversal of the residual e.m.f. at high humidities), the one being of anodic products and the other of cathodic products, and if, as indicated by the data given in this section, the anodic layer is of high resistance (for brass electrodes), two possible effects would be expected. If the anodic and cathodic products do not mix up for some time, the resistance of the cotton would be increased because of the presence of a high resistance layer at both electrodes instead of only one. On the other hand, if they mix quickly and neutralize each other's effects, the resistance would be expected to pass through a minimum. The first type of behavior would explain the sudden increase in resistance sometimes observed after reversing the current direction in a textile, while the second would explain the behavior illustrated by the above figures.

The rate of increase of the resistance of cotton with time of application of a constant voltage varies between wide limits. In general, any factor which increases the current density in the cotton also tends to increase the rate of change of resistance with time: the rate is greater the higher the applied e.m.f.; it increases rapidly with humidity (at least for high humidities); it is greater for samples of small electrode separation than for those of large electrode separation; and it is less the smaller the amount of electrolytic material in the cotton. An example is given by Fig. 5 of the rate of change under conditions where polarization is neither very slow nor very rapid. At humidities of the order of 100% the rate of change of resistance may be so rapid in some cases that an increase by a factor of 10 or more may take place in a few seconds. On the other hand, no detectable change takes place in 1 or 2 minutes in the range 20–70% humidity for Twisted Pair samples or in the range 10–85% for Thread samples. The apparent resistance again increases with appreciable rapidity at humidities below 10 and 20%; this increase is associated with the formation of large residual e.m.f.'s, as discussed in the preceding section.

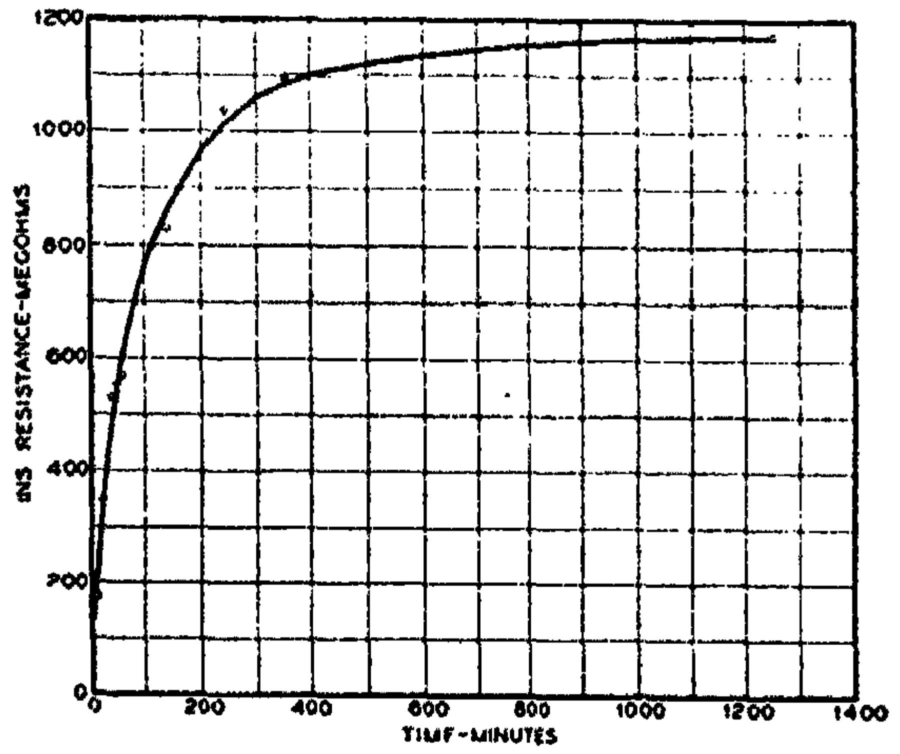

Fig. 5

Variation of Insulation Resistance with Time of Application of 275 volts. The sample is a cotton thread. Humidity—92.6%.

When a galvanometer of long period is used for insulation resistance measurements the resistance must be based on the value of the current at a standard time of the order of one minute after the application of the voltage.

Where polarization is rapid the values so obtained represent the resistance of the textile when it is in a "polarized" condition, i.e., when its resistance is non-uniformly distributed. At humidities above 75 to 95% (for cotton) this "polarized resistance" may differ considerably from the normal resistance, i.e., the value obtained when the distribution of resistance in the textile is uniform.

The polarized resistance of a textile sample varies with the applied voltage in a different way from the normal resistance because its value depends on the amount of polarization which takes place while the voltage is applied and this increases as the voltage is increased. Fig. 6 shows that the resistance corresponding to application of the voltage for a standard time of 1 minute passes through a minimum as the applied voltage is increased. The decreasing branch of the curve is the normal voltage effect and is due to the back-e.m.f. of polarization. The increasing branch is due to the formation of a high resistance layer at the anode at a rate which increases with the voltage. The normal resistance of these samples would give a curve without a minimum (cf. Fig. 1).

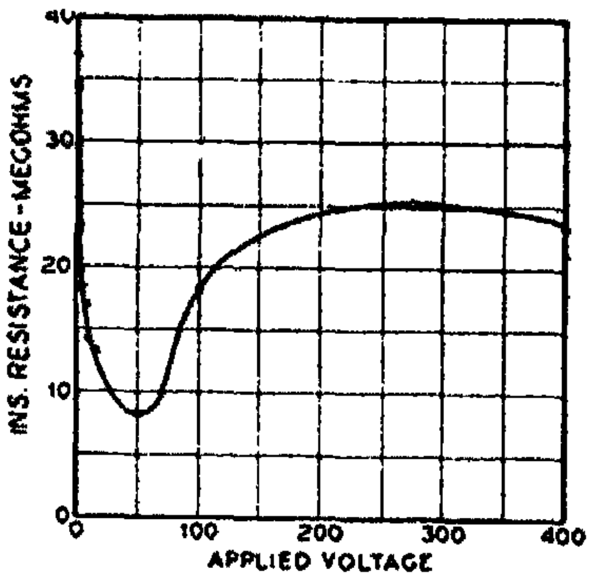

Fig. 6

"Polarized" Resistance of Cotton as a Function of Applied Voltage. The data are for a twisted pair of low electrolyte content. *Humidity—89%.*

At humidities between 98 and 100% the resistance of cotton samples of small electrode separation increases very rapidly with time of application of the voltage, and the resistance corresponding to application of the voltage for 30 seconds or more may increase more rapidly than the applied voltage. An example of this is given in Table X. On increasing the applied voltage from 10 to 412 the current through the cotton, as measured by a galvanometer of 30 seconds period, decreased slightly instead of increasing by a factor of 41.2. This indicates that the resistance of the cotton had increased by a factor of over 40 in less than 30 seconds. The change of resistance with time was too rapid to be observed with the galvanometer, but could be observed when the measurements were made with a milliammeter, or when the rate of polarization was reduced by using a sample of greater electrode separation. Under these extreme conditions it appears that a final constant resistance corresponding to equilibrium between the polarizing and depolarizing processes is reached in a few seconds. Reversing the direction of the applied voltage changed the final polarized resistance by less than 3%. The final value of the polarized resistance corresponding to a given voltage appears under these conditions to be almost independent of the magnitude or direction of previously applied voltages. Somewhat similar behavior is observed in electrolytic cells with valve metals as electrodes and is attributed to the rapid formation of a high resistance layer at one of the electrodes.[25]

The voltage at which breakdown of an insulating material takes place may be regarded perhaps as one of the characteristics of electrical conduction in the material. The possible bearing of the present results on the electrical breakdown of moisture-absorbing insulations will therefore be briefly indicated. *It has been shown that the passage of a current through a* textile tends to produce a non-uniform distribution of its resistance. This results in a non-uniform potential gradient, and in some circumstances practically the whole potential drop may be concentrated over a thin layer at one electrode. As the voltage is increased this layer would break down first. Schiller[26] has suggested that, in dielectrics in which such a concentration of potential drop takes place, breakdown may be due to the formation and breakdown of such layers, so that with each layer the breakdown penetrates further into the dielectric. Schwaiger[27] has found that the breakdown voltage of paper, which has electrical properties similar to those of cotton, is a decreasing function of humidity. From the above considerations it appears that this might be explained by the fact that the rate of polarization increases with increasing humidity. The breakdown voltage might then be more characteristic of the rate of polarization than of the material as a whole. Further, it has been shown that gaseous ionization plays a considerable part in the electrical breakdown of some solid dielectrics.[28] And since some of

TABLE X

Current and Resistance as a Function of Applied Voltage where Polarization is very Rapid

The data are for a cotton thread .5 cm. long between Pt electrodes.
Humidity 98.6%. Temp. 25°C.

Applied Voltage	Current, microamps. × 10^3	Ins. Resistance megohms after 1 min. electrification
.05	1.73	29 (increasing)
.10	4.7	21.3
.20	1.94×10	10.3
10.0	3.34×10^3	3.0
412.0	3.26×10^3	126.5
100.0	9.50×10^3	10.5
50.0	10.2×10^3	4.9
12.5	3.38×10^3	3.7
6.0	1.72×10^3	3.14
10.0	3.03×10^3	3.3
275.0	4.37×10^3	63.0

These measurements were made with a galvanometer of 30 seconds period and in the above order.

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[25] Cf., for example, de Bruyne and Sanderson: Trans. Faraday Soc., **23**, 50 (1927).
[26] H. Schiller: Z. techn. Physik, **6**, 588 (1925); Ann. Physik, **81**, 79 (1926).
[27] A. Schwaiger: Archiv Electrotech. **3**, 332 (1915).
[28] J. B. Whitehead: J. Am. Inst. El. Eng., **42**, Dec. (1923).

the products of the electrolysis of the water present in hygroscopic insulating materials must be gaseous, gas bubbles would tend to form on the electrode surfaces; this might facilitate electrical breakdown.

Discussion

As mentioned earlier, the anomalous phenomena which have been described tend to complicate the interpretation of resistance measurements on textiles and other moisture-absorbing dielectrics. The conclusions which may be drawn from the present results regarding the interpretation of resistance measurements on textiles are briefly as follows: The current used in measuring the resistance may produce a non-uniform distribution of resistance in the textile, accompanied by an increase in the total resistance. The tendency for this to take place is greater the higher the humidity, the smaller the electrode separation, the higher the applied voltage and the longer the time for which it is applied. Changes produced by the current in the resistance of the textile can be detected by determining the resistance or potential distribution by means of probe electrodes, or by determining the resistance as a function of applied voltage and time of its application; since the normal effect of an increase in voltage appears to be to reduce the resistance, an increase in resistance with voltage indicates that the resistance of the textile is being changed by the current. The residual e.m.f. can be measured and the observed resistance corrected for it. The error due to the back-e.m.f. of electrolytic polarization (the initial value of the residual e.m.f.) decreases as the applied voltage is increased. However, since the conductivity of the textile itself apparently increases with increasing voltage, the resistivity at high voltages may correspond to a somewhat abnormal condition of the textile due to the effects of the electrical stress, and the resistance at some intermediate voltage would be more representative of the normal condition of the material.

The above considerations apply to humidities above 20–30% for cotton; at lower humidities the residual e.m.f. causes an increase or decrease of appreciable magnitude in the current through the cotton depending on whether it is in the same, or opposite direction to the applied voltage, and therefore affects the apparent resistivity in corresponding senses. But on account of the difficulty of distinguishing between a conduction current which decreases with time, owing to an increase in the resistance of the material, and a residual charging current which also decreases with time, the true resistivity of a material such as cotton cannot be calculated at humidities below 20–30% on the basis of available data.

In previous papers the characteristics of the d.c. resistivity and a.c. capacity and conductivity of textiles were explained in terms of a mechanism consisting of a conducting aqueous solution distributed in a solid dielectric in such a way that the internal structure of the solid determines the geometric form of the conducting water-paths but is not otherwise involved in the conduction process except as regards the dielectric displacement current. The phenomena described in this paper have also been explained in terms of this mechanism by making the additional assumptions that the distribution of water in the solid dielectric would tend to make the adsorption of ions at the interface between the aqueous electrolyte and the solid dielectric an appreciable factor in conduction; that the conductivity of the layer of electrolyte in which adsorption forces are effective may increase with increasing applied voltage due to liberation of ions or to a modified Wien effect; and that concentration differences in different parts of the electrolyte may persist longer after the removal of the applied voltage than would be the case in ordinary electrolytic cells, because of the geometric form of the conduction paths in a textile.

Summary

In the investigation of the Evershed effect in cotton the following results were obtained: The insulation resistance is a decreasing function of the applied voltage under all conditions. The ratio of the resistances corresponding to any two voltages, such as 40 and 400, is approximately constant over nearly the whole range of humidity, though the resistances themselves varied by a factor greater than 10^8. The ratio of the resistance at 40 volts to that at 400 volts is greater the smaller the electrode separation; it is decreased by a small amount if the amount of electrolytic material in the cotton is reduced. At low voltages the current-voltage curve for cotton closely resembles that of an electrolytic cell; and it is concluded that for voltages lower than about 40 the decrease of insulation resistance with increasing voltage is caused by the presence of a back-e.m.f. of electrolytic polarization in the textile. It is suggested that for voltages greater than about 40 the decrease of resistance with increasing voltage may be largely explained by consideration of the ions adsorbed by the cellulose-water interface in the aqueous conducting paths in cotton; these ions may make a greater contribution to the conductivity the higher the applied voltage due perhaps to a modified Wien effect. These results are more complete than those upon which Evershed's original interpretation of the effect was based and do not appear to lend support to his interpretation.

The residual e.m.f. which remains in cotton after the removal of an external e.m.f. was measured at several humidities. It was found that its characteristics vary considerably with humidity; at high humidities the observed residual e.m.f.'s do not exceed the order of magnitude of decomposition potentials and overvoltages but at humidities lower than 20–30% they are dependent upon the voltages by which they were produced. These results are interpreted as meaning that at high humidities the residual e.m.f. is due to the back e.m.f. of polarization caused by the electrolysis of the aqueous solutions which form the conducting paths in the textile, while at humidities below 20–30% it may be largely due to an anomalous dielectric polarization, though part of its energy should be due to the same cause as at high humidities.

In general the passage of a current through a textile tends to increase its resistance. The rate of change is rapid above 70–80% humidity but slow between 20% and 70% for cotton. The increase of resistance takes place in the textile itself, not at the contact between it and the electrode. The current tends to cause a non-uniform distribution of the resistance of the textile. The distribution depends on the nature of the electrode material; for brass electrodes it becomes concentrated in the anode region, while for platinum electrodes the largest resistance occurs in the middle. This non-uniform distribution may remain for many hours after the removal of the applied voltage. These facts are in disagreement with some of the explanations which have been given for the increase of resistance with time of application of voltage, but can be explained by the effects of the products of electrolysis on the conductivity of the aqueous solutions through which conduction on the textile takes place. The fact that almost the whole potential drop in a textile may become concentrated over a relatively thin layer at the electrode is considered to be of possible significance in the determination of the electrical breakdown voltage of moisture absorbing materials.

The bearing of the results on the measurement of the resistivity of textiles and other moisture absorbing materials is discussed.

The general conclusion from the results is that the anomalous properties of conduction in textiles can be explained in terms of essentially the same mechanism by which the characteristics of the d.c. resistivity and a.c. capacity and conductivity were explained in previous papers, namely, that at humidities above 20–30% (for cotton) a textile acts as an electrolytic cell whose characteristics are somewhat modified by the distribution of the electrolyte in the interior of a solid dielectric.

In concluding the author wishes to thank Dr. H. H. Lowry, who has encouraged him throughout this work and contributed many valuable suggestions.

Bell Telephone Laboratories,
New York.

THE DECOMPOSITION OF TRIPHENYLACETIC ACID BY SULPHURIC ACID*

BY HARRY R. DITTMAR**

Triphenylacetic acid was observed by Bistrzycki and Reintke[1] to decompose quantitatively into carbon monoxide and triphenyl-carbinol when dissolved in concentrated sulphuric acid. The sulphuric acid after the decomposition was orange-yellow in color, due to the triphenylcarbinol which remained dissolved and which was precipitated as a white solid upon diluting the acid with water. The reaction can be represented by the following equation:

$$(C_6H_5)_3C\ COOH \rightarrow (C_6H_5)_3COH + CO$$

A study of this reaction was undertaken in order to compare this decomposition with others involving the action of sulphuric acid which had been investigated and explained by considering the sulphuric acid as a dehydrating agent only. Bredig and Lichty[2,3] quantitatively studied the decomposition of oxalic acid by sulphuric acid, and concluded that the reaction was essentially one of dehydration. Schierz[4], after investigating the action of sulphuric acid on formic acid, reached the same conclusion in regard to the mechanism of the reaction. The action of sulphuric acid on malic acid was studied by Whitford[5] who concluded from his observations that the sulphuric acid did not function by merely extracting water from the malic acid and suggested a more complex reaction mechanism based upon the formation of a hypothetical intermediate compound between the two reactants.

The decomposition of triphenylacetic acid by sulphuric acid although similar to the decomposition of oxalic, malic, and formic acids, could not possibly be connected with the dehydrating property of sulphuric acid because water is not a product of the reaction. A study of this reaction was undertaken with the object of discovering the mechanism of the decomposition, and from a comparison with the action of sulphuric acid on oxalic, formic, and malic acids, to show whether these latter reactions were dependent upon the dehydrating property of sulphuric acid or whether the sulphuric acid functioned in a different capacity.

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* This communication is an abstract of the thesis submitted to the Graduate School of the University of Wisconsin by Harry R. Dittmar in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This investigation was conducted under the supervision of Professor J. H. Walton.

** Contribution from the Laboratory of General Chemistry, University of Wisconsin.

[1] Bistrzycki and Reintke: Ber., 38, 839 (1905).

[2] Bredig and Lichty: Z. Elektrochemie, 12, 450 (1906).

[3] Lichty: J. Phys. Chem., 11, 225 (1907).

[4] Schierz: J. Am. Chem. Soc., 45, 447 (1923).

[5] Whitford: J. Am. Chem. Soc., 47, 953 (1925).

Experimental

Preparation and Purification of Materials.

Triphenylacetic Acid. The triphenylacetic acid was prepared by the method of Schmidlin[6] which involves the action of carbon dioxide on an ethereal solution of the organo-magnesium halide formed from magnesium and triphenylchlormethane. The product, which was recrystallized twice from glacial acetic acid, melted with decomposition at 264° (uncorrected). The triphenylchlormethane used in this synthesis was prepared by the Friedel and Craft's synthesis from benzene and carbon tetrachloride.[7]

Sulphuric Acid. The hundred per cent sulphuric acid was prepared by adding C.P. ninety-five per cent sulphuric acid to a given quantity of fuming sulphuric acid until the resulting solution melted at 10.41°. This melting point agreed well with the values obtained by other investigators. A chemical analysis was also made. Samples weighed by means of a weighing pipette were dissolved in water and precipitated as barium sulphate. The results of two determinations gave values of 100.08 and 100.15%.

Sodiumtriphenylacetate. The sodium salt of triphenylacetic acid has not been described although Elbs and Tolle[8] and Gyr[9] in their study of triphenylacetic acid mentioned the preparation of the ammonium and potassium salts. The sodium triphenylacetate was prepared by dissolving the acid in dilute sodium hydroxide, and evaporating the solution until white crystals began to appear. The solution was allowed to cool, after which the compound was filtered and carefully washed and dried. When so prepared, the compound was obtained in small, white needle-like hydrated crystals. Upon analysis the per cent of water was found to be 5.48 per cent and 5.39 per cent whereas the theoretical amount of water in the monohydrate is 5.49 per cent. The sodium was determined by dissolving a weighed sample in water, and precipitating the free triphenylacetic acid by acidifying the solution with sulphuric acid. The triphenylacetic acid was identified by its melting point of 264°. The filtrate which contained sodium sulphate was evaporated in a weighed two inch porcelain crucible, and fumed several times with sulphuric acid after which the crucible was dried at a dull red heat to constant weight. The per cent of sodium in two samples was found to be 7.16 and 7.19 per cent. The theoretical per cent of sodium in the monohydrate of sodium triphenylacetate is 7.01 per cent. From these results the formula was concluded to be $(C_6H_5)_3CCOONa.H_2O$.

The salt was somewhat efflorescent. If the solution of triphenylacetic acid in sodium hydroxide was allowed to evaporate very slowly over the course of several days, beautiful, transparent, plate-like crystals separated from the solution. They were extremely efflorescent and from some preliminary experiments, appeared to be a higher hydrate.

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[6] Schmidlin: Ber., 39, 634 (1906).

[7] Gomberg: Ber., 33, 3147 (1900).

[8] Elbs and Tolle: J. prakt. Chem., 32, 622 (1885).

[9] Gyr: Ber., 41, 4308 (1908).

Triphenylcarbinol. The triphenylcarbinol was prepared by hydrolyzing triphenylchlormethane by boiling it with water for ten hours under a reflux condenser. The triphenylchlormethane was prepared as described previously. The triphenylcarbinol so obtained melted at 162° (164.2° corrected).

Acetic Acid. The glacial acetic acid was recrystallized several times after which it was fractionally distilled. The fraction boiling between 116.9°-117.5° (745.5 mm) was used. This acid melted at 16.45°.

Phosphoric Acid. A solid preparation of orthophosphoric acid was used which contained less than one per cent of moisture.

Phenol. Phenol of C.P. quality which melted at 40° was employed.

Acetone. Acetone was fractionated several times. The fraction boiling between 56° and 56.6° (738 mm) was taken.

The other substances were the purest obtainable from reliable sources. The materials were carefully protected from moisture at all times. The p-cresol which was used was labeled "practical".

Apparatus and Method of Procedure

The rate at which the triphenylacetic acid was decomposed by sulphuric acid was followed by measuring the volume of carbon monoxide which was evolved in various time intervals. The decompositions were made in twenty-five cc Pyrex round bottom flasks of special design which were supported in a mechanical agitator. Both the reaction flasks and the agitator were of the type designed by Walton.[10] The reaction flasks were connected by means of capillary glass tubing to glass burettes of 10 cc. capacity. Since the water in the burettes was saturated with carbon monoxide, it was not necessary to apply a correction to the observed volume of gas.

In the decompositions the sulphuric acid was placed in the reaction flask while the triphenylacetic acid was contained in a small glass capsule supported in the neck of the reaction flask which could be allowed to fall into the reaction mixture at any desired time. In order to obtain very efficient stirring and consequently prevent supersaturation, small beads made from a glass rod were also added to the reaction flask.

In the first attempts to study the decomposition, triphenylacetic acid was added to the sulphuric acid, but in cases where the sulphuric acid was more dilute than ninety-five per cent, the triphenylacetic acid was not wet by the former acid. This led to the use of sodium triphenylacetate which was readily wet by the sulphuric acid. In the quantitative decompositions, a seventy milligram sample of sodium triphenylacetate was moistened with 0.3 cc of 90.38% sulphuric acid, which insured a more rapid solubility of the compound. The acid which was used to moisten the compound was so dilute that no decomposition resulted from its use. This amount (0.3 cc) of 90.38% sulphuric acid was considered in calculations for the dilution of the one hundred per cent sulphuric acid.

In preparing dilute solutions of sulphuric acid of definite concentrations, a predetermined weight of one hundred per cent acid was diluted with a

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[10] Walton: Z. physik. Chem., 47, 185 (1904).

calculated weight of 90.38% sulphuric acid. Solutions of anhydrous sodium and potassium sulphates in one hundred per cent sulphuric acid were made by adding calculated weights of the sulphates to sixty cc. glass-stoppered bottles into which were weighed definite quantities of one hundred per cent sulphuric acid. The bottles were then tightly sealed and kept at a temperature of sixty to seventy degrees until the sulphates had dissolved, which usually required from one to ten hours. After solution had taken place, the acid was allowed to attain room temperature after which fifteen cc. of the solution was taken for each determination. The solutions of the various organic compounds in sulphuric acid were made in the same manner.

Results.

Completeness and Order of Reaction. In order to check the statement of Bistrzycki and Reintke[1], regarding the completeness of decomposition of triphenylacetic acid in concentrated sulphuric acid, seventy milligram samples of sodium triphenylacetate were added to 10 cc. portions of one hundred per cent sulphuric acid. Two samples decomposed at 12° and 736.4 mm gave 5.11 cc and 5.05 cc of carbon monoxide respectively. Under these conditions the theoretical volume of carbon monoxide from sodium triphenylacetate monohydrate should have been 5.08 cc. Two other samples decomposed at 12° and 740.6 mm gave 5.01 cc and 5.13 cc of carbon monoxide, while the theoretical volume was calculated as 5.05 cc. Several other decompositions gave equally satisfactory results showing that the decomposition was a quantitative one.

The data obtained from a typical run are given in the following table:

TABLE I

A Typical Decomposition

Temp. 12° : H_2SO_4 is 95% : a = 3.76 cc : B.P.—744.6 mm

Time in Minutes	Volume of CO (cc)	x	(a−x)	$K \times 10^3$
0	1.18	0.00	3.76	—
2	1.40	0.22	3.54	30.6
4	1.61	0.43	3.33	30.7
6	1.81	0.63	3.13	30.7
8	1.99	0.81	2.95	30.9
13	2.42	1.24	2.52	31.1
18	2.78	1.60	2.16	31.0
23	3.09	1.91	1.85	30.9
28	3.34	2.16	1.60	30.5
38	3.73	2.55	1.21	29.9
150	4.94	3.76	0.00	
			Av.	30.7

When the data obtained from these decompositions of triphenylacetic acid, were substituted in the equation for a monomolecular reaction—$K = (2.303/t) \log a/(a-x)$—the values of K for any one decomposition were found to be constant. In these decompositions the total volume of carbon monoxide in cubic centimeters was substituted for a and the volume liberated at the end of time, t, as x. That the true speed of decomposition and not the speed of solution was measured is shown by the fact that the velocity constants were not affected by the volume of sulphuric acid. In decompositions by ninety-five per cent sulphuric acid the velocity constant was unaffected by using ten, fifteen, or twenty cc. of sulphuric acid.

The value of $K \times 10^3$ for any particular run was taken as the average value of the velocity constant between twenty-five and sixty per cent decomposition. After sixty-five to seventy per cent decomposition, the value of the velocity constant began to gradually decrease. The values of the velocity constant given in the subsequent tables represent the average constant of from two to six determinations except in a few cases where the scarcity of a particular solute prevented duplicate runs.

Effect of Water. After preliminary observations had shown that water acted as an inhibitor in the reaction between sulphuric acid and triphenylacetic acid, a quantitative study was made on the effect of varying amounts of water. The dilute sulphuric acid was made by adding a calculated weight of 90.38 per cent sulphuric acid to a definite weight of one hundred per cent sulphuric acid. The decomposition could be studied only with sulphuric acid of concentrations between ninety-three and ninety-seven per cents, for at lower concentrations, the reaction rate was exceedingly slow; while at higher concentrations the speed of decomposition was too rapid to permit accurate measurements.

In order to decrease the speed of decomposition as much as possible, the reaction was carried on at 12.0°. Lower temperatures were out of the question since the melting point of one hundred per cent sulphuric acid is 10.41°. Table II gives the influence of water at 12.0°. Each value of the velocity constant is the average of from two to six determinations. The molality of solute refers to the number of mols of solute dissolved in one thousand grams of solvent—sulphuric acid in this case.

TABLE II

The Effect of Water on the Rate of Decomposition of Triphenylacetic Acid by Sulphuric Acid at 12.0°

Per cent of Water	Molality of Water	$K \times 10^3$	$\log K \times 10^3$
3.09	1.77	134	2.13
3.30	1.90	113	2.05
3.65	2.11	82.0	1.91
4.09	2.37	60.9	1.78
5.00	2.93	32.0	1.51
5.03	2.94	31.3	1.50
6.00	3.54	15.8	1.20
7.00	4.18	6.66	0.823

Although the effect of the addition of very small amounts of water can not be ascertained from these data, it can be seen that the inhibitory effect of water decreases as the per cent of water increases. This same phenomenon was observed by Lichty in his study of the decomposition of oxalic acid by sulphuric acid, by Schierz in his study of the decomposition of formic acid, and by Whitford in a similar study with malic acid.

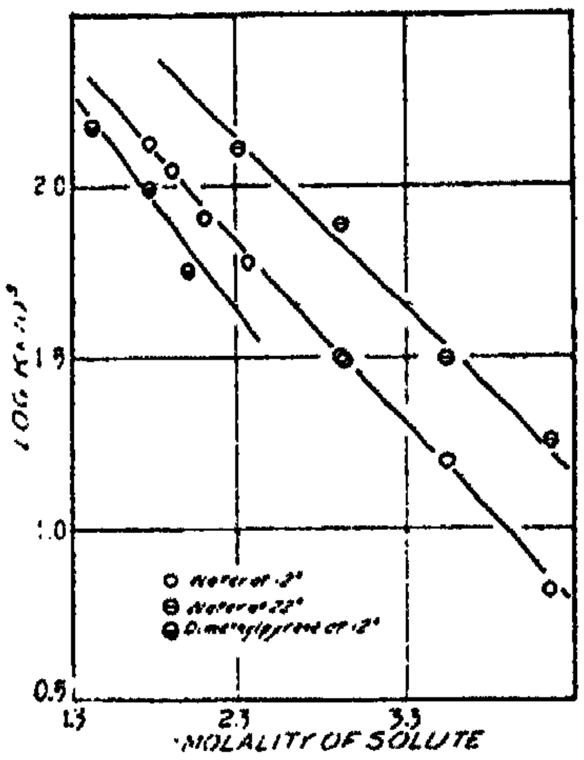

Fig. 1

Effect of Water and Dimethylpyrone upon the Reaction Rate

The effect of less than three per cent of water on the reaction was determined from the equation of the curve produced upon plotting the data of Table II. On plotting the logarithms of $K \times 10^3$ as ordinates, and the corresponding molalities as abscissas a straight line was obtained. (Fig. 1).

The equation of this line was found to be

$$\log K \times 10^3 = -0.540M + 3.076$$

where M is the molality of added water and K the velocity constant. Substitution in this equation gave values which agreed very well with the experimentally determined constants.

That the decomposition of triphenylacetic acid in one hundred per cent sulphuric acid is extremely rapid is shown by calculating the value of $K \times 10^3$ from the above equation when M (molality of added water) is zero. When this was done, $K \times 10^3$ was found to be 1190. The value of the velocity constant ($K \times 10^3$) calculated for 99.90% sulphuric acid (molality of added water: .0555) was found to be 1112. This shows the marked effect of water at the high concentration of sulphuric acid.

From these results it can be seen that water acts as a very marked inhibitor in this reaction. The inhibitory effect of water is comparable to its effect in the decomposition of oxalic acid by sulphuric acid as determined by Lichty, and of formic acid as studied by Schierz. Table III summarizes the influence of water in these cases.

When the molalities of added water were plotted as abscissas and the corresponding logarithms of the velocity constants as ordinates, a straight line was obtained (Fig. 1). The equation for this line was found to be

$$\log K \times 10^3 = -0.544M + 3.4688$$

where M is the molality of water and K the velocity constant. The calculated velocity constant ($K \times 10^3$) for one hundred per cent sulphuric acid was 2943.

Effect of Temperature. The values of the velocity constants at 12.0° and 22.0° were used to calculate the temperature coefficients as well as the critical increments from the Arrhenius equation.

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}$$

which in integrated form can be written

$$E = \frac{1.99\ T_2T_1 \times 2.303 \log K_2/K_1}{T_2 - T_1}$$

The temperature coefficients and the values of E in calories are summarized in Table V.

Table III

Comparison of the Effect of Water in the Decomposition of Oxalic, Formic, and Triphenylacetic Acids by Sulphuric Acid

Acid Studied	Investigator	3–15% H_2O			1.5–3% H_2O		
		$K \times 10^3$ 3% H_2O	$K \times 10^3$ 15% H_2O	$\frac{K (3\%)}{K (15\%)}$	$K \times 10^3$ 1.5% H_2O	$K \times 10^3$ 3% H_2O	$\frac{K (1.5\%)}{K (3\%)}$
		98°	98°		70°	70°	
Oxalic	Lichty	23.65	0.73	32.4	3.15	0.94	3.35
		25°	25°		25°	25°	
Formic	Schierz	185	1.73	106.8	395	185	2.13
		12°	12°		12°	12°	
Triphenylacetic		134	0.061	2200.0	418	134	3.12

The effect of water at 22.0° was also determined with the following results:

Table IV

The Effect of Water on the Rate of Decomposition of Triphenylacetic Acid by Sulphuric Acid at 22.0°

Per cent of Water	Molality of Water	$K \times 10^3$	Log $K \times 10^3$
4.00	2.31	126.	2.10
5.00	2.93	77.9	1.89
6.00	3.54	31.6	1.50
7.00	4.18	18.4	1.264

Table V

Temperature Coefficients and Critical Increments for the Decomposition of Triphenylacetic Acid by Sulphuric Acid Solutions between 12.0° and 22.0°

Per cent of Water	Molality of Water	$K \times 10^3$ 12.0°	$K \times 10^3$ 22.0°	Temp. Coeff. 12.0–22.0°	Crit. increment in calories
4.00	2.31	60.9	126	2.07	12,200
5.00	2.93	32.0	77.9	2.43	14,850
6.00	3.54	15.8	31.6	2.00	11,590
7.00	4.18	6.66	18.4	2.79	17,260
0.00	0.00	1190(calc)	2943(calc)	2.47	15,120

The temperature coefficients for different concentrations of sulphuric acid do not check. Schierz[4], in the study of the decomposition of formic acid found irregularities. Lewis[11] states that in cases of solvent catalysis, E may vary with the solvent and the composition of mixed solvents. This investigator cites the case of the transformation of acetophenoneoxime into acetanilide by sulphuric acid[12] where the value of E increased from 21,720 calories for 94.6 per cent acid to 24,670 calories for sulphuric acid of 93.6 per cent.

From a consideration of the results obtained, no conclusions can be drawn from the temperature coefficients obtained except that irregularities were observed and the temperature coefficients were not abnormally high as was observed in the decomposition of oxalic and malic acids.

In connection with the critical increment it is of interest to note that in the case of malic acid, Whitford[5] found a value in calories of approximately 24,000 calories between 20°-30° or 30°-40° when the decomposition was affected by one hundred per cent sulphuric acid. Schierz[4] in studying formic acid found a value of 19,000 for the average of three determinations for the temperature interval 15°-25° where the concentrations of sulphuric acid varied between 92 and 98%. In this investigation of triphenylacetic acid 14,000 was found to be average value of the critical increment between 12 and 22° when the concentrations of the sulphuric acid employed varied between 93 to 96%. From the data given by Lichty[3] on the decomposition of oxalic acid, it was possible to calculate one critical increment from the fact that for a solution of 0.6% water in 100 grams of sulphuric acid, K × 10³ was 0.5746 at 45.0°, while K × 10³ increased to 18.14 when the temperature was increased to 70.0°. These data gave a critical increment of 29,960 calories. The comparisons of the critical increments of these four reactions will be discussed more in detail in another part of this paper.

Effect of Sodium and Potassium Sulphates. Sodium sulphate was studied at 12° and 22°. The results are shown in the following table:

TABLE VI

Effect of Sodium Sulphate on the Decomposition of Triphenylacetic Acid by 100% Sulphuric Acid at 12° and 22°

Per cent Na_2SO_4	Molality	K × 10³ 12°	log K × 10³ 12°	K × 10³ 22°	Temp. Coeff. 12°-22°
15.00	1.24			124	
14.00	1.15	57.4	1.76	171	2.98
13.00	1.05	64.3	1.81		
12.00	0.960	91.2	1.96		
11.00	0.870	109.8	2.04		

Determinations of the velocity constant of fifteen per cent sodium sulphate could not be made at 12° due to the fact that at this temperature the solution was supersaturated and crystallization took place during a decom-

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[11] Lewis: Trans. Faraday Soc., 17, 575 (1922).

[12] Lobry de Bruyn and Sluiter: Proc. K. Akad. Wet. Amsterdam, 6, 773 (1904).

position. The solutions of concentrations lower than fourteen per cent could not be used at 22° because the speed of decomposition was immeasurably rapid. The temperature coefficient of the fourteen per cent solution between 12° and 22° was 2.98. The critical increment calculated from this value gave 18,300 calories.

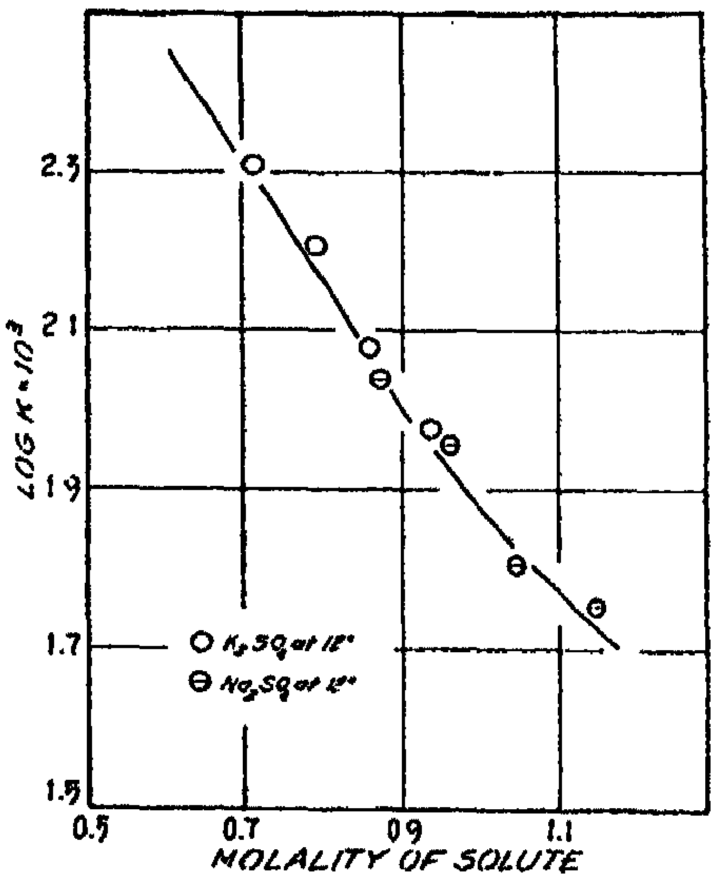

Fig. 2

Effect of Sodium and Potassium Sulphates upon the Reaction Rate

The influence of potassium sulphate is given in Table VII.

TABLE VII

Effect of Potassium Sulphate on the Rate of Decomposition of Triphenylacetic Acid in 100% Sulphuric Acid at 12.0°

Per cent K_2SO_4	Molality	$K \times 10^3$	$\log K \times 10^3$
14.00	0.935	95.0	1.98
13.00	0.858	119.5	2.08
12.00	0.788	160.9	2.21
11.00	0.710	202.6	2.31

Both potassium and sodium sulphates inhibited the reaction to a marked degree, even more than water. For instance, at 12.0° sodium sulphate (molality 1.05) decreased the value of $K \times 10^3$ to 64.3; while the molality of added water which decreased $K \times 10^3$ to 60.9 was as high as 2.37. In this connection it is interesting to note that Kendall and Landon[13] have isolated the following compounds between sodium and potassium sulphates and sulphuric acid — $K_2SO_4.3H_2SO_4$; $K_2SO_4.H_2SO_4$; $2Na_2SO_4.9H_2SO_4$; $Na_2SO_4.2H_2SO_4$; $Na_2SO_4.H_2SO_4$.

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[13] Kendall and Landon: J. Am. Chem. Soc., **42**, 2131 (1920).

The effect of other sulphates could not be determined because they were not soluble enough in one hundred per cent sulphuric acid to decrease the speed of decomposition of triphenylacetic acid to the point where the velocity constant could be measured.

When the logarithms of $K \times 10^3$ were plotted against the corresponding molalities of dissolved sulphates a curve was obtained, Fig. 2, which deviated somewhat from a straight line. It is interesting to note that both salts give points which lie on the same line.

Effect of Hydrogen Chloride. Schierz[1] stated that hydrogen chloride greatly increased the speed of reaction between formic and sulphuric acids. For this reason the effect of this solute was studied on the reaction under investigation.

Sulphuric acid of 1.84 specific gravity was saturated with dry hydrogen chloride. When this acid was used in the decomposition of triphenylacetic acid, the carbon monoxide which was evolved carried with it some hydrogen chloride which was not dissolved by the water in the burette rapidly enough to keep the total volume of gas below that required by the carbon monoxide alone. It was necessary to insert a ten centimeter tube filled with "ascarite" between the decomposition flask and the burette to absorb the hydrogen chloride which was carried with the carbon monoxide.

Four decompositions made in this manner at 12.0° gave velocity constants which averaged 40.4. The results of several decompositions by the sulphuric acid which did not contain dissolved hydrogen chloride gave a value of 42.4. The effect of hydrogen chloride, then, was negligible, although it must be kept in mind that the amount of hydrogen chloride which dissolved in sulphuric acid of 1.84 specific gravity at room temperature was small.

Effect of Various Acids, Alcohols, and Ketones.

Acetic Acid. In studying the effect of acetic acid, decompositions could not be made at 12.0°, for at this temperature a part of the acetic acid separated from the solution. Consequently the influence of this solute was observed at higher temperatures only. The results of the decompositions which were made at 22.0° are given in Table VIII.

The value of $K \times 10^3$ for a solution of twenty per cent acetic acid at 32.0° was 61.2. The temperature coefficient between 22°-32° for the decomposition by a solution of twenty per cent acetic acid in sulphuric was 1.61. The critical increment calculated from this temperature coefficient gives 8,522 calories.

TABLE VIII

Effect of Acetic Acid on the Rate of Decomposition of Triphenylacetic Acid by Sulphuric Acid at 22°

Per cent Acetic Acid	Molality	$K \times 10^3$	$\log K \times 10^3$
15.00	2.94	126	2.10
17.00	3.41	75.5	1.88
20.00	4.17	38.1	1.58
23.00	4.98	18.9	1.28

In Fig. 3 the molalities of acetic acid are plotted as abscissas and the corresponding logarithms of $K \times 10^3$ as ordinates. In the same figure the curve for the effect of water at 22.0° was inserted for comparison. The acetic acid acted as a pronounced negative catalyst although its inhibitory effect was not as great as water under the same conditions. Whitford in his study of the decomposition of malic acid by sulphuric acid found a similar effect. In regard to the negative catalytic effect of acetic acid in this reaction, it is worthy of notice that James Kendall* has shown the existence of an addition compound between sulphuric and acetic acids.

Dimethylpyrone. The influence of dimethylpyrone was studied at 12.0° with the results given in Table IX.

These data are plotted in Fig. 1. The dimethylpyrone was as effective in inhibiting the decomposition as water, a fact which agrees with the results obtained by Whitford in his study of malic acid. Addition compounds between dimethylpyrone and sulphuric acid have been isolated and described by Kendall and Carpenter.[14]

Phenol. The influence of phenol on the decomposition rate of triphenylacetic acid in one hundred per cent sulphuric acid was determined. Table X gives the results.

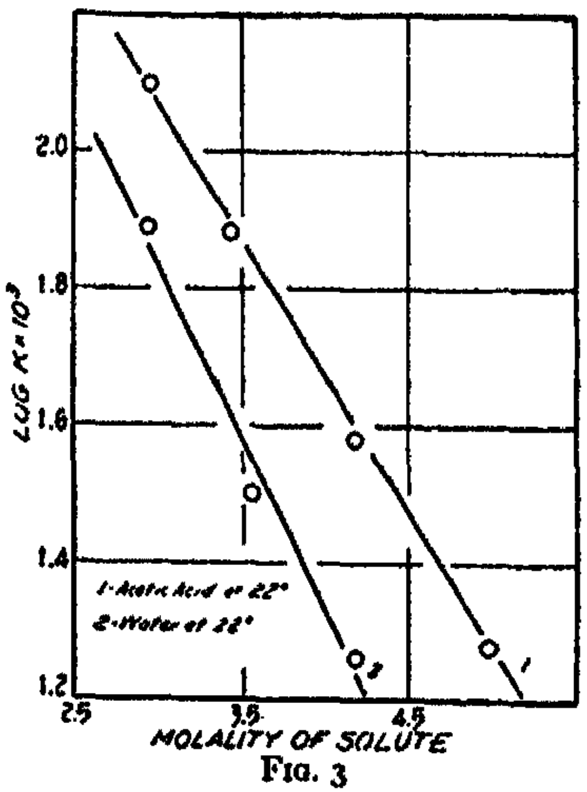

FIG. 3
Relative Effects of Water and Acetic Acid

TABLE IX
Effect of Dimethylpyrone on the Rate of Decomposition of Triphenylacetic Acid by Sulphuric Acid at 12°

Per cent of Dimethylpyrone	Molality	$K \times 10^3$	$\log K \times 10^3$
15.00	1.42	150	2.176
18.00	1.77	101	2.004
20.00	2.02	58.4	1.766

TABLE X
The Effect of Phenol on the Rate of Decomposition of Triphenylacetic Acid by Sulphuric Acid at 12.0°

Molality	$K \times 10^3$	$\log K \times 10^3$
2.50	1.45	0.16
2.00	6.97	0.84
1.50	20.8	1.32
1.00	76.8	1.89
0.50	255	2.41

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* Personal communication.

[14] Kendall and Carpenter: J. Am. Chem. Soc., 36, 2498 (1914).

Two decompositions made at 32.0° in which the molalities of phenol were 3.00 and 2.50 gave values of K × 10^3 which were 2.00 and 6.01 respectively. This gave an increase of the velocity constant for a solution of phenol of 2.50 molality from 1.45 at 12° to 6.01 at 32°. These data when used in the determination of the critical increment gave a value of 12,280 calories. Phenol is consequently a far more effective negative catalyst in this reaction than water. It might be noted at this point that phenol has been shown by Kendall and Carpenter[14] to form a stable addition compound with sulphuric acid composed of two molecules of phenol and one molecule of sulphuric acid. Fig. 4 contains the curve formed by plotting the molalities of phenol as abscissas against the logarithms of K × 10^3 as ordinates.

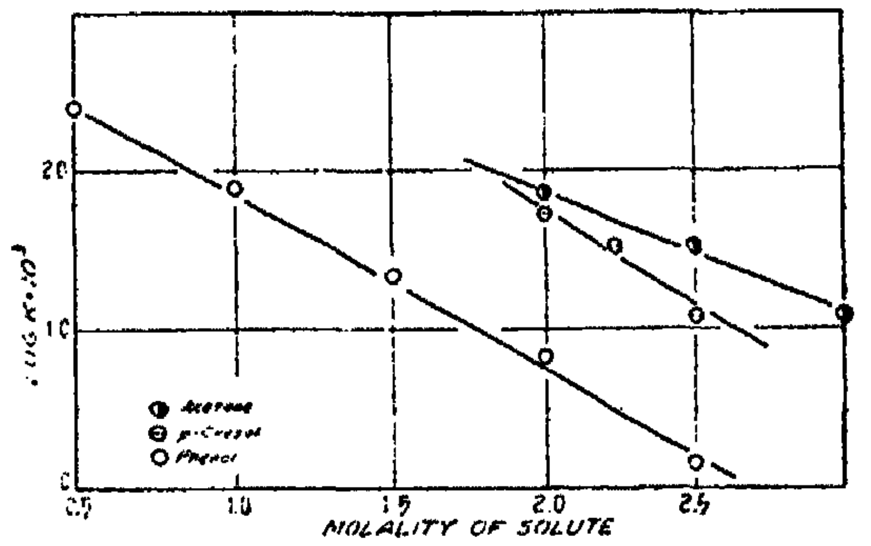

FIG. 4
Effects of Acetone, p-Cresol, and Phenol upon the Reaction Rate

Acetone. The results obtained from studying the influence of acetone at 12.0° are tabulated in Table XI.

TABLE XI
The Effect of Acetone upon the Rate of Decomposition of Triphenylacetic Acid by Sulphuric Acid at 12.0°

Molality of Acetone	K × 10^3	log K × 10^3
2.00	74.5	1.87
2.50	33.9	1.53
3.00	12.3	1.09

Acetone was another solute which decreased the velocity of decomposition rather pronouncedly. Again a straight line was obtained upon plotting molalities of solute against logarithms of the velocity constant in Fig. 4.

Para Cresol. The influence of this solute was studied at 12.0°. The results are tabluated below.

These data which are plotted in Fig. 4 show that p-cresol is an inhibitor to the reaction in which connection it should be noted that Kendall and Carpenter[14] obtained stable addition compounds between p-cresol and sulphuric acid.

TABLE XII

The Effect of p-Cresol upon the Rate of Decomposition of Triphenylacetic Acid by Sulphuric Acid at 12.0°

Molality	$K \times 10^3$	$\log K \times 10^3$
2.50	12.00	1.08
2.26	33.6	1.53
2.00	53.5	1.73

Various Acids, Alcohols and Ketones. Of the inhibitors of the reaction which have been described, water, sodium and potassium sulphates, dimethylpyrone, phenol, and p-cresol form addition compounds with sulphuric acid. In order to determine whether compound formation and inhibition are related, the influence of several more solutes was studied. Since most of the compounds used were not available in quantities large enough to permit decompositions at several concentrations, results at one definite concentration only were obtained. The results are given in Table XIII. In cases where the solute and sulphuric acid have been known to form addition compounds, the formula of the compound and the investigator are inserted.

All of the solutes mentioned in the table act as definite inhibitors except phosphoric acid, the negative catalytic effect of which is not marked. It is of interest to note that phosphoric acid has not been shown to form a compound with sulphuric acid. Ethyl alcohol and acetone are both effective in decreasing the speed of the reaction, although no addition compounds between sulphuric acid, ethyl alcohol or sulphuric acid and acetone have been isolated. Both ethyl alcohol and acetone, however, form addition compounds with other strong acids. Compounds of acetone with hydrochloric, hydrobromic, and hydriodic acids were prepared and described by Archibald and McIntosh.[15] McIntosh[16] has isolated equimolecular addition compounds between acetone and nitric acid and ethyl alcohol and nitric acid. No results were obtained with sulphuric acid because at the low temperatures which were employed the sulphuric acid became extremely viscous. If acetone and ethyl alcohol formed compounds with these other strong acids, it is reasonable to assume that the same tendency toward molecular compound formation should exist in solution between sulphuric acid and ethyl alcohol and acetone. From a consideration of all of the results obtained, it is safe to say that the inhibition of the decomposition of triphenylacetic acid by sulphuric acid and the tendency of sulphuric acid to form molecular addition compounds with these inhibitors are two phenomena which are very intimately related. This point will be discussed more in detail in another part of this paper.

Concentration-Temperature Study of the System Triphenylcarbinol-Sulphuric Acid. The pronounced influence of triphenylcarbinol on the reaction rate suggested the existence of one or more addition compounds between triphenylcarbinol and sulphuric acid. No such compound was found re-

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[15] Archibald and McIntosh: J. Chem. Soc., **85**, 919 (1904).

[16] McIntosh: J. Am. Chem. Soc., **27**, 1013 (1905).

TABLE XIII
Effect of Various Solutes upon the Rate of Decomposition of Triphenylacetic Acid in Sulphuric Acid

Solute	Molality	Temperature	K × 10³	Compound between solute and H_2SO_4	Investigator isolating addition compound
Phosphoric Acid	4.76	12°	30.5		
" "	7.78	12	4.99		
Ethyl Alcohol	3.00	12	33.5		
" "	2.50	12	57.0		
Benzoic Acid	1.50	12	214.0	$C_6H_5COOH . H_2SO_4$	Kendall & Carpenter[1]
" "	2.00	12	161.0		Hoogewerff & Van Dorp[2]
" "	1.50	22	431.0		
" "	2.00	22	427.0		
Acetophenone	2.83	12	19.3	$2(C_6H_5COCH_3) . H_2SO_4$	Kendall & Carpenter[1]
"	2.83	22	49.5		
Benzophenone	1.71	12	145.0	$C_6H_5COC_6H_5 . H_2SO_4$	Kendall & Carpenter[1]
p-Nitrophenol	1.50	12	decomposition		
Crotonic Acid	2.50	12	74.4	$C_3H_5COOH . H_2SO_4$	Kendall & Carpenter[1]
Coumarin	2.50	12	39.7	$C_9H_6O_2 . H_2SO_4$	Kendall & Carpenter[1]
m-Nitrophenol	2.50	12	191.0	$2(C_6H_4NO_2OH) . H_2SO_4$	Kendall & Carpenter[1]
o-Toluic Acid	2.50	12	142.0	$C_7H_7COOH . H_2SO_4$	Kendall & Carpenter[1]
Triphenylcarbinol	1.06	12	75.1	$(C_6H_5)_3COH . 4H_2SO_4$	Present Investigator

[1] Kendall and Carpenter: Ref. 14.

[2] Hoogewerff and Van Dorp: Rec. Trav. chim., **18**, 211 (1899).

ported in the literature. The tendency toward compound formation between sulphuric acid and triphenylcarbinol was an important factor not only from the standpoint of the relation between compound formation and inhibition, but also because triphenylcarbinol was one of the decomposition products of triphenylacetic acid. For this reason an attempt was made to obtain evidence of such a molecular complex.

A temperature-concentration study of the system was made by observing the effect of triphenylcarbinol on the melting point of sulphuric acid. Twenty-five grams of one hundred per cent sulphuric acid was placed in a Beckmann freezing point apparatus. Pure dry triphenylcarbinol was then added through a side arm and the freezing point of the solution taken after the carbinol had dissolved. The cooling baths used to obtain the low temperatures were salt-ice and solid carbon dioxide-ether mixtures. The following data were obtained:

TABLE XIV

Variation of Melting Point with Concentration of the Binary System, Triphenylcarbinol-Sulphuric Acid

Per cent triphenyl-carbinol	Temp.	Per cent triphenyl-carbinol	Temp.
0.00	10.47°	30.00	−3.0
0.24	10.41	31.00	4.0
1.11	9.8	33.30	18.0
2.25	8.6	35.45	27.8
3.52	7.2	37.47	35.0
4.88	5.5	38.50	36.0
6.50	3.4	39.37	38.0
8.08	0.8	41.00	38.0
9.50	−1.6	41.15	39.0
11.01	−4.5	42.78	38.0
12.11	−6.8	43.24	37.5
14.00	−11.8	44.42	34.3
15.45	−15.0	45.31	35.0
17.00	−20.0	45.92	38.5
19.60	−25.0	47.38	50.5
21.01	−32.5		
23.01	Set to glass		

The melting point was taken as the temperature at which the last crystals disappeared. The temperature at which the crystals disappeared was often very difficult to obtain with an accuracy greater than one degree due to the dark ornage color of the solution and the small air bubbles which were stirred into the acid. When the concentration of triphenylcarbinol was above forty-seven to forty-eight per cent, the melting point had increased to the temperature where decomposition took place and no further readings could be made. For the same reason the curve could not be studied from the triphenylcarbinol side. Sulphonation (recognized by the rapid liberation of water) proceeded very rapidly near the melting point of triphenylcarbinol (162°) and more slowly at temperatures as low as 80°.

The data are shown graphically in Fig. 5, with the per cent composition of the solution as abscissas and the corresponding melting point temperatures as ordinates. The maximum in the curve represents a compound and corresponds to a composition of forty-one per cent of triphenylcarbinol. The inclination of the curve at the point where it was discontinued indicates the formation of another compound. The crystals which separated from solution at this point were very well defined with a surprisingly sharp melting point of 39.0°. When allowed to crystallize slowly, the compound solidified in beautiful long, very fine, needle-like crystals often two inches in length.

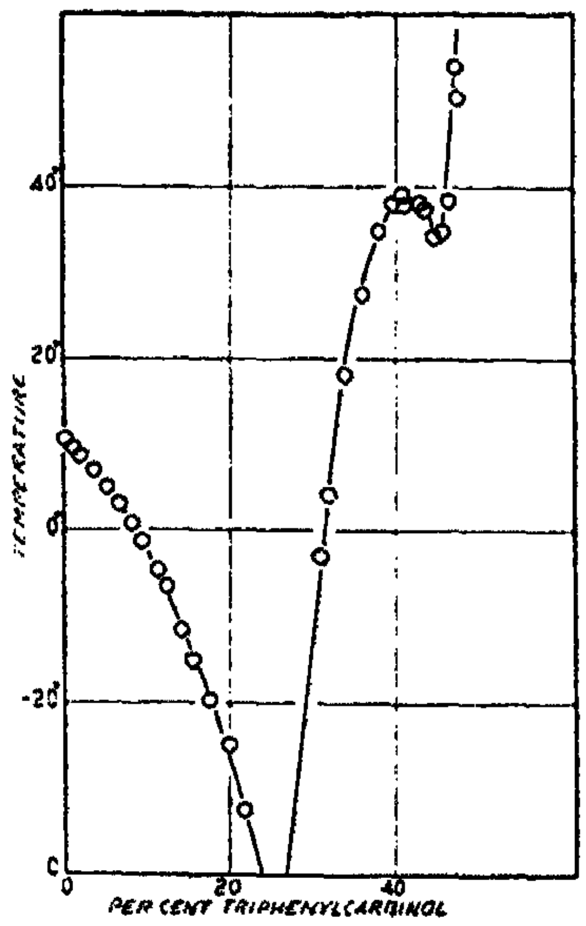

FIG. 5
Sulphuric Acid-Triphenylcarbinol

In order to check the composition of the compound by chemical analysis, some of the solid phase was taken from the half-melted mixture, pressed between porous plates, and allowed to stand in a desiccator for two days. The dried crystals were orange in color and very hygroscopic. They were quickly transferred to a weighing bottle from which weighed samples were added to water and hydrolyzed into triphenylcarbinol and sulphuric acid by boiling for thirty minutes. After filtering off the triphenylcarbinol, the sulphuric acid was titrated with a standard solution of sodium hydroxide with methyl orange as an indicator. The results of two determinations gave a sulphuric acid content of 59.72 and 58.86 per cents which corresponded to a triphenylcarbinol content of 40.28 and 41.14 per cents respectively. These values agree well with the 41 per cent as determined from the curve. This per cent of triphenylcarbinol corresponds to the compound $(C_6H_5)_3COH.4H_2SO_4$ of which the theoretical content of triphenylcarbinol is 39.88 per cent.

These results again show that the inhibitor is a solute which forms a compound with the active catalyst.

Evidence of Compound Formation between Sulphuric and Triphenylacetic Acids. Many catalytic reactions have been shown to depend upon the formation of intermediate compounds between the catalyst and one or more of the reactants. So many substantiations of this theory have been pointed out that it has become of outstanding importance to the study of catalysis. In the reaction under investigation an attempt was made to obtain evidence of compound formation between sulphuric and triphenylacetic acids. Knox and Richards[17] showed that it was possible to demonstrate the existence of molecular addition compounds between acids in solution by solubility determinations. Their method was to determine the solubility of one acid at a particular temperature in solutions of increasing concentration of the second acid. The solubility of the acid at first continually diminished with increasing concentration of the solvent acid in accordance with the effect of a common ion; but as the concentration of the solvent acid became greater this influence was offset by the second influence, namely, compound formation between the acids, and the solubility of the solute acid increased with the increase of concentration of the solvent acid. In cases where the solvent acid was extremely weak, the common ion effect was less pronounced and no minimum was obtained, but only a gradual increase of solubility where compounds were formed in solution. This method furnished a very convenient way of determining compound formation in solution.

The attempt was made to employ this method with sulphuric acid and triphenylacetic acid by measuring the solubility of triphenylacetic acid in sulphuric acid solutions of increasing concentrations. An increase of solubility as the normality of sulphuric acid was increased would be an indication of compound formation. Due to the very low solubility of triphenylacetic acid in solutions of sulphuric acid up to concentrations as high as seventy per cent (at which point decomposition slowly took place) together with the fact that triphenylacetic is an exceedingly weak acid, the experimental difficulties involved in the determination of the dissolved triphenylacetic were so great that no reliable results were obtained.

If triphenylacetic acid forms a compound with sulphuric acid, one could reasonably expect compound formation with hydrochloric and nitric acids as well. The solubility of triphenylacetic acid was the same in sixty-eight per cent nitric acid and in twenty-five per cent hydrochloric acid as in water, namely, five milligrams per one hundred cc. When the concentration of nitric acid was increased above ninety per cent, the solution readily dissolved triphenylacetic acid to form an orange-brown colored solution; one hundred per cent nitric acid was an extremely good solvent, but at that concentration, a reaction took place for solution was accompanied with the liberation of heat and nitrogen dioxide. This was further substantiated by the fact that upon diluting the resulting solution with water, a white substance was precipitated which melted with decomposition at 115°, whereas the melting point of triphenylacetic acid was 246°.

The solubility of triphenylacetic acid was qualitatively determined in liquid hydrogen chloride at the boiling point of liquid hydrogen chloride. Twenty cc. of liquid hydrogen chloride, which was prepared by cooling dry hydrogen chloride by liquid air, was saturated with triphenylacetic acid. The excess solute was filtered from the liquid, which had become yellow in color, by means of glass wool. The filtrate was but slightly turbid. Upon

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[17] Knox and Richards: J. Chem. Soc., **115**, 508 (1919).

allowing the liquid to evaporate, approximately 0.39 gm. of a white residue remained which from its melting point of 264° proved to be triphenylacetic acid.

The tremendous increase in the solubility of triphenylacetic acid in hydrochloric acid when the concentration was increased from twenty-five to one hundred per cent demonstrates compound formation between solute and solvent. In the case of nitric acid the increase of solubility when the concentration is increased above ninety per cent points to the same conclusion, although a complication arises from the fact that the process of solution is accompanied by chemical reaction (probably nitration). Since the solubility does not become pronounced until the concentration of solvent acid is near one hundred per cent, it can be argued from analogy, that with sulphuric acid the increase of solubility, and hence compound formation, takes place only where the sulphuric acid is very concentrated. It is of interest to note that the decomposition of triphenylacetic acid in ninety per cent sulphuric acid is extremely slow, and assuming that the speed of decomposition is proportional to the amount of compound formation, this fact would tend to support the contention that the formation of an addition compound takes place only when the concentration of sulphuric acid is above ninety per cent. The fact that finely powdered triphenylacetic acid is not as readily wet by ninety per cent sulphuric acid as by ninety-five per cent acid again points to the fact that triphenylacetic acid is more soluble in the higher concentrations of sulphuric acid. In this same connection it should be noted that Knox and Richards[17] showed that hydrochloric acid formed an addition compound with both phenyl and diphenylacetic acids. To summarize, the evidence obtained tends to show that triphenylacetic and sulphuric acids form an addition compound when the sulphuric acid is above a concentration of ninety per cent even though such a compound was not isolated.

Solubility of Triphenylacetic Acid in Acetic Acid. If the diminution of the speed of decomposition of triphenylacetic acid by certain solutes was due to molecular combination between one of the reactants—sulphuric acid—and the solute, then, likewise, there would exist the possibility of the solute combining with the triphenylacetic acid to form a molecular complex. Triphenylacetic acid, however, is an exceedingly weak acid and would only tend to combine with those solutes which were quite acidic in nature. Kendall[18] in a discussion of the molecular combinations formed from organic acids in pairs, stated that the tendency toward the formation of addition compounds was dependent upon the difference in acidic strengths of the two components. Again in discussing the addition compounds formed between phenols and trichloracetic acid, Kendall[19] pointed out that the more acidic phenols did not give compounds with trichloracetic acid, whereas more weakly acidic compounds did. In general, the more diverse the chemical characteristics of the components, the greater is the tendency for the formation of molecular

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[18] James Kendall: J. Am. Chem. Soc., 36, 1722 (1914).

[19] James Kendall: J. Am. Chem. Soc., 38, 1309 (1916).

addition compounds; while the tendency decreases as the chemical characteristics of the components become more similar in nature. From this standpoint triphenylacetic acid might be expected to show an inclination for molecular compound formation in solution with the more acidic solutes such as phosphoric or acetic acids, but not with phenol or ethyl aclohol which would be more similar to triphenylacetic acid itself.

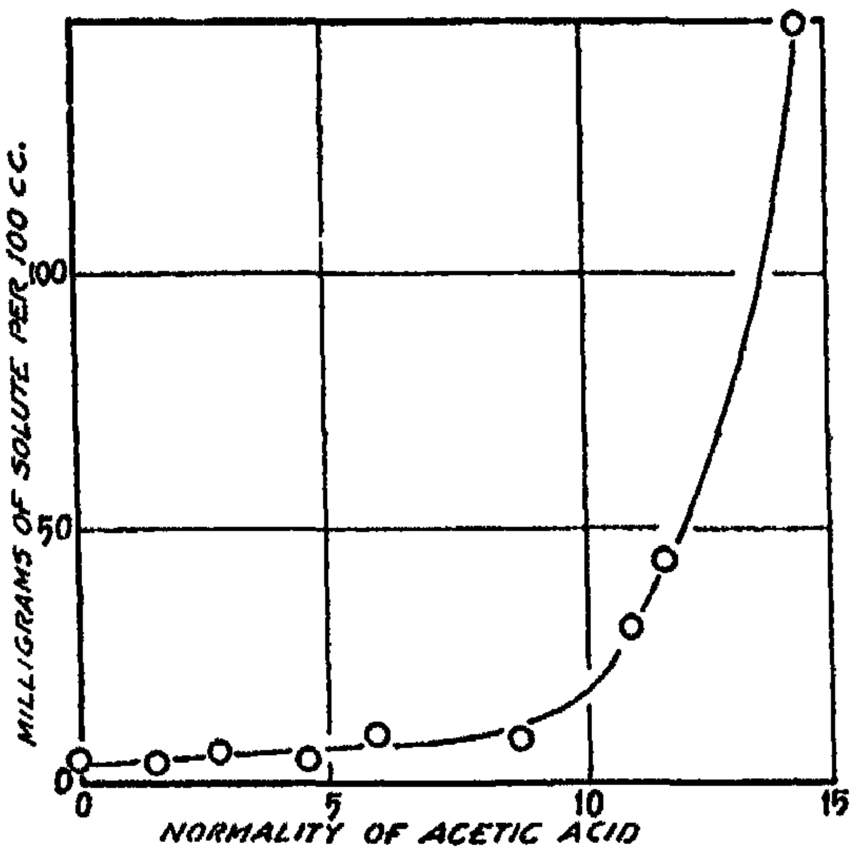

Fig. 6
Solubility Curve of Triphenylacetic Acid in Acetic Acid at 25°.

The solubility method as described by Knox and Richards[17] was used in the attempt to establish compound formation between triphenylacetic acid and acetic acid. The solubility of triphenylacetic acid was determined in acetic acid solutions of various concentrations from zero to seventeen normal Acetic solutions were saturated with the solute at 30° and subsequently cooled to 25° and twenty cc. aliquots were then evaporated to dryness in two inch porcelain crucibles and dried at 105° before being weighed. The results are given in Table XV. Each value represents the average of two or more determinations.

Table XV

Solubility of Triphenylacetic Acid in Acetic Acid at 25°

Normality of Acetic Acid	Grams of Triphenylacetic per 100 cc.	Normality of Acetic Acid	Grams of Triphenylacetic per 100 cc.
0.000	0.0050	8.824	0.0090
1.529	0.0045	10.912	0.0305
2.875	0.0060	11.661	0.0440
4.590	0.0045	14.433	0.1500
5.923	0.0100	17.365	0.6105

The solubility curve is given in Fig. 6. Since triphenylacetic acid is a very weak acid, the decrease of solubility due to the common ion effect is not marked. The solubility begins to raise at a normality of ten and continues to increase very pronouncedly, indicating the formation of a molecular addition compound between the two acids.

Discussion of Results

Mechanism of the Reaction. The results obtained in the study of the reaction between sulphuric and triphenylacetic acids lead to an explanation based upon intermediate compound formation between the two reactants. The evidence for the existence of such a molecular compound has already been given.

The molecular addition compound formed between the sulphuric and triphenylacetic acids can be looked upon as being an unstable oxonium complex which decomposes into carbon monoxide and the molecular complex of triphenylcarbinol and sulphuric acid which has been shown to exist. In triphenylacetic acid either the oxygen of the hydroxyl group or the oxygen of the carbinol group, or both, can be looked upon as being the point where combination with the sulphuric acid molecule (or molecules) takes place. James Kendall and his co-workers[13, 14, 15, 19] have given the structure of the addition compounds which they isolated from esters, acids, aldehydes, and alcohols as oxonium compounds. Likewise, Knox and Richards[17] in their study assumed oxonium complexes. As a matter of fact, the only logical point of attachment between two acid molecules of this type is between the oxygen atoms.

The instability of this complex may be due to a distortion of the electronic configuration of the molecule by the large sulphuric acid molecule resulting in the formation of the triphenylcarbinol-sulphuric acid complex and carbon monoxide. The fact that the addition compound formed between sulphuric acid and the carbinol is more stable than that formed from sulphuric acid and triphenylacetic acid may contribute its share to the rearrangement of the molecule.

The decomposition can be represented by the following equations:

$$y\ (C_6H_5)_3C\ COOH + x\ H_2SO_4 \rightleftarrows y\ (C_6H_5)_3C\ COOH\ .\ x\ H_2SO_4$$
$$y\ (C_6H_5)_3C\ COOH\ .\ x\ H_2SO_4 \longrightarrow y\ (C_6H_5)_3COH + y\ CO + x\ H_2SO_4$$

The velocity of decomposition of triphenylacetic acid would depend upon the number of activated molecules of the intermediate addition compound which in turn would be governed by the concentration of the reactants and the factors which influence activation. The speed of formation of the molecular complex would probably not be an influencing factor, for Kendall[20] states that the speed of formation of oxonium complexes is rapid.

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[20] Kendall and Booge: J. Am. Chem. Soc., 38, 1719 (1916).

The similarity of this decomposition to the decomposition of oxalic, formic, and malic acids suggests the same mechanism for each. In regard to the formation of an addition compound, it is of interest to note that Knox and Richards have actually shown that sulphuric acid forms a compound with oxalic acid in solution, a fact which is in accord with the suggested mechanism.

The critical increment is a measure of the energy which is necessary to activate the molecules to the energy level where reaction takes place. The smaller the critical increment the more readily a reaction would be expected to take place. This relationship holds true in the decompositions of oxalic, malic, formic, and triphenylacetic acids where the readiness of decomposition increases in the order in which the acids are named. The average values of the critical increments in calories of the above reactions under the conditions previously stated is: oxalic acid—29,960; malic acid—24,000; formic acid—19,300, and triphenylacetic acid—14,200. The readiness of decomposition is in the order which would be expected from the critical increments. Again, considering the tendency of compound formation of sulphuric acid with another acid as being dependent upon the difference of acidity, and assuming that this tendency to form a molecular complex is proportional to the velocity of decomposition, then the the case of oxalic, malic, formic, and triphenylacetic acids, the weakest acid would most readily form an intermediate compound with sulphuric acid, and the speed of decomposition would be greatest. The order of decreasing acidity of these four acids is: oxalic, malic, formic, and triphenylacetic. The velocity of decomposition increases in the same order from oxalic, to malic, formic, and lastly triphenylacetic which decomposes most rapidly.

Action of Inhibitors. It has already been emphasized that the solutes which acted as inhibitors in this reaction were all substances which formed molecular addition compounds with the sulphuric acid. This suggests an explanation for the pronounced effect of these substances, namely, that by molecular combination with the sulphuric acid they disturb the equilibrium of the reaction by which the unstable triphenylacetic acid-sulphuric acid intermediate complex is formed by decreasing the concentration of sulphuric acid, which, in turn, diminishes the amount of the intermediate compound, and consequently, the reaction velocity. The influence of some of the inhibitors is very pronounced. For instance, phenol, the molality of which was 0.5, decreased the value of $K \times 10^3$ from 1190 to 255. This concentration represents one mol of phenol to every twenty mols of sulphuric acid. It is difficult to see why such a small amount of phenol would exert such a marked effect on the reaction velocity. Sulphuric acid, however, is a very highly associated liquid. Aston and Ramsay[21] have concluded from the results of surface tension measurements that sulphuric acid which corresponds to the formula $12H_2SO_4.H_2O$ has at room temperature a formula of $(H_2SO_4)_{32}$. It is probable that only certain points in this large associated molecule are free to combine with the inhibitor so that the effective concentration of the catalyst is not represented by the number of mols present.

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[21] Aston and Ramsay: J. Chem. Soc., **65**, 170 (1894).

It was shown that acetic acid which acted as a negative catalyst not only formed an addition compound with sulphuric acid but with triphenylacetic acid as well, and in so doing some of the inhibitor was prevented from combining with the sulphuric acid, a fact which might diminish the inhibition; although the effect could not be very marked. The mechanism of inhibition is then very involved, the actual speed of reaction depending upon three equilibria:

(1) $y(C_6H_5)_3CCOOH + xH_2SO_4 \rightleftarrows y(C_6H_5)_3CCOH \,.\, xH_2SO_4$

(2) $aH_2SO_4 + b\text{ Inhibitor} \rightleftarrows aH_2SO_4 \,.\, b\text{ Inhibitor}$

(3) $c\text{ Inhibitor} + d(C_6H_5)_3CCOOH \rightleftarrows d(C_6H_5)_3CCOOH.c\text{ Inhibitor}$

In cases where the inhibitor was more nearly equal to the triphenylacetic acid in acidity, the possibility of compound formation between them would be negligible and the third equilibrium reaction would be eliminated. In most of the cases of inhibition only the first two equations would be involved. Some of the inhibitors were more effective than others. Since the inhibitor functions by combining with the catalyst, the effectiveness of an inhibitor would depend upon the tendency toward compound formation and the stability of the addition compound.

If the difference in the acidity of the two components is taken as a measure of the tendency towards compound formation, then the negative catalyst which is least acidic in character would be most effective, assuming the stability of addition compounds between inhibitor and catalyst to be equal. In Table XVI the ionization constants of several of the inhibitors are given with their corresponding effects upon the velocity of decomposition.

Table XVI

Relation of Acidity to the Effectiveness of Inhibition at 12.0°

Inhibitor	K	K × 10³	Molality of Inhibitor
Phosphoric Acid[1]	1.1×10^{-2}	30.5	4.75
o-Toluic Acid[2]	1.2×10^{-4}	142	2.50
Benzoic Acid[2]	6×10^{-5}	161	2.00
Crotonic Acid[2]	2.14×10^{-5}	74	2.50
m-Nitrophenol[3]	1.0×10^{-8}	191	2.50
Phenol[4]	1.15×10^{-10}	1.45	2.50
p-Cresol[5]	0.67×10^{-10}	12.0	2.50
Water[6]	1.1×10^{-14}	60.9	2.37

[1] Abbot and Bray: J. Am. Chem. Soc., 31, 760 (1909).

[2] Ostwald: Z. physik. Chem., 3, 241 (1889).

[3] Holleman and Wilhemy: Rec. Trav. chim., 21, 432 (1902); Centralblatt, 74I, 509 (1903).

[4] Walker: Z. physik. Chem., 32, 137 (1900).

[5] Boyd: J. Chem. Soc., 107, 1538 (1915).

[6] Calculated from conductivity of water—Kohlrausch: Z. physik. Chem., 14, 317 (1894).

Acetic acid was not included since its effect was not studied at 12°.

The relationship is fairly good in the first four cases, but in the last four it does not hold. Meta nitrophenol and water do not inhibit the reaction enough to conform to the generalization, while the difference between phenol and para cresol, though not marked, is enough to show an inconsistency.

The stability of the addition compound between sulphuric acid and the inhibitor would also affect the efficiency of the inhibitor. An idea of the stability of a compound which has been shown to exist by a phase rule study, that is, a temperature concentration diagram, can be obtained from the maximum which indicates the existence of the compound. If the maximum in the curve is sharp and well defined, the compound is stable, whereas if the maximum is not pronounced, dissociation of the addition compound is indicated. Since Kendall and his co-workers have established the existence of the addition compounds between sulphuric acid and many of the inhibitors of this reaction, a study of those curves gives an indication of the stability of the compound whose existence they established. In connection with the inhibition of the reaction studied it follows that the solutes which form the most stable complexes with sulphuric acid are those which should show the most pronounced inhibition. A study of these phase rule diagrams between sulphuric acid and the inhibitors listed in Table XVI, excluding phosphoric acid, shows that para cresol forms the most stable addition compound with sulphuric acid while the others are of about the same degree of stability.

The results of this study have substantiated the theory advanced by Taylor[22] to account for the mechanism of negative catalysis. Citing the inhibitory influence of water on the decomposition of oxalic acid by sulphuric acid, Taylor explained the pronounced effect by stating that the inhibitor prevented one of the reactants from taking part in the reaction by forming a molecular compound with it. The inhibition in the decomposition of triphenylacetic acid has been shown to depend upon this very fact.

Another theory formulated to explain negative catalysis is due to Christiansen[23] who assumes that chemical reactions are chain reactions and that the negative catalysts breaks a chain reaction by absorbing the energy which would otherwise activate the molecules which had not reacted. Although this theory seems to explain certain types of negative catalysis[24] it hardly seems applicable to the present case. It is difficult to conceive of a chain reaction taking place in the liquid phase such as the sulphuric acid solutions used in the reaction studied.

The fact that the decomposition of triphenylacetic acid by sulphuric acid in so many details bears such a striking resemblance to the dehydrations of oxalic, formic and malic acids by sulphuric acid suggests that the same factors govern all four reactions. Since the decomposition of triphenylacetic acid takes place without the elimination of water, the water formed in the decomposition of oxalic, formic, and malic acids can only be incidental, and

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[22] Taylor: J. Phys. Chem., 27, 322 (1923).

[23] Christiansen: J. Phys. Chem., 28, 145 (1924).

[24] Blackstrom: J. Am. Chem. Soc., 49, 1460 (1927).

the factors which govern the dehydration of these acids are those which affect the concentration and speed of formation of the unstable molecular addition compounds between the acids and sulphuric acid.

The writer desires to express his appreciation to Professor J. H. Walton not only for suggesting this problem but for his kind and helpful guidance during its progress.

Summary

1. The decomposition of triphenylacetic acid by sulphuric acid has been studied quantitatively and found to be an apparent first order reaction.

2. Seventeen solutes were found which act as pronounced negative catalysts to this decomposition among which are water, sodium sulphate, dimethylpyrone, phenol, acetophenone, and crotonic acid.

3. Hydrogen chloride in low concentrations does not affect the velocity of the reaction while phosphoric acid shows a slight negative catalytic effect when present in rather high concentrations.

4. The inhibitory effect of the negative catalysts increases logarithmically with their concentrations.

5. Although the temperature coefficients are affected irregularly by the presence of inhibitors, the value for the ten degree interval between 12° and 22° are approximately 2.0, although at one concentration of sodium sulphate a value of 2.98 was obtained.

6. The substances which retard the speed of the reaction are those which form molecular addition compounds with the sulphuric acid. This substantiates Taylor's theory of negative catalysis.

7. Indirect evidence of an addition compound between triphenylacetic and sulphuric acids has been obtained. This leads to an explanation of the decomposition of triphenylacetic acid by sulphuric acid based upon the formation of an intermediate unstable addition complex.

8. The preparation of sodium triphenylacetate is described for the first time.

9. A concentration-temperature study of the two component system—triphenylcarbinol-sulphuric acid—has been made with the isolation of a molecular addition compound the formula of which is $(C_6H_5)_3COH.4H_2SO_4$.

10. The solubility of triphenylacetic acid in acetic acid at 25° has been determined.

11. The relative ease with which sulphuric acid decomposes oxalic, formic, malic, or triphenylacetic acids is given by the critical increment of the reactions.

12. The similarity of the decomposition of triphenylacetic acid by sulphuric acid to the decompositions of formic oxalic, and malic acids by the same compound has been pointed out with the suggestion that the mechanism of the decomposition in each of the four cases is practically the same.

Madison, Wisconsin.

RENNIN ACTION IN RELATION TO ELECTROKINETIC PHENOMENA*

BY G. A. RICHARDSON AND L. S. PALMER

Introduction

The results of many investigational studies relative to rennin and rennin action have been reported but the literature has recently been so exhaustively reviewed by one of us[1] that its repetition is not essential at this time. Rennin, when added to milk, converts the calcium caseinate to calcium paracaseinate with the ultimate production of a clot. The chemistry of pure casein is almost identical with that of pure paracasein, but synthetic caseinate and paracaseinate "milks" have always shown significant differences especially with regard to their sensitivity toward electrolytes. This latter property suggested the possibility that rennin might reduce the stability of milk by merely lowering the charge on the calcium caseinate micellae in suspension in milk.

An electrokinetic interpretation of the actual clotting has been suggested.[2] "The rule seems to be that the greater the calcium-binding capacity of the (casein) particles is, and the further removed they are from saturation with calcium, the less calcium ions are required to neutralize their electrical charges. This undoubtedly explains in part why sodium ions will clot the calcium paracaseinate formed in milk by rennin action." Palmer, interpreting the base-binding curves of casein and paracasein[1] considers that calcium paracaseinate is relatively much nearer its isoelectric point than the calcium caseinate at a pH between 6.0 and 6.4, since paracasein binds considerably more calcium at that reaction than does casein. Considering the theory advanced by Palmer, it is assumed that lyophobic sols are stabilized by an electrical double layer around each particle. In the case of negatively charged sols, as, for example, calcium caseinate and calcium paracaseinate, when the outer layer of ions is replaced by the divalent calcium ions, the particles will readily precipitate, gelation being determined by the rate of replacement and precipitation. Since the calcium paracaseinate has greater base-binding capacity and, therefore, is less saturated with base at the pH where clotting occurs, fewer calcium ions are needed to neutralize the stabilizing electric charges, and precipitation ensues even when sodium ions replace calcium ions.

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[1] L. S. Palmer: "Fundamentals of Dairy Science, Associates of Rogers," 195-210 (1928).

[2] L. S. Palmer and G. A. Richardson: Third Colloid Symposium Monograph, 112 (1925).

Experimental

Preparation of Casein. The procedure followed in preparing pure casein for the following experimental work was patterned after that adopted by Van Slyke and Baker,[3] advantage being taken of the later modification reported by Van Slyke.[4] Three different batches were made, their differences existing in the methods of purification. In each case fresh separator skim milk was run through a Sharples supercentrifuge at 40° C. operating at 30,000 r.p.m. before the first precipitation of casein.

Casein I. The freshly precipitated and washed casein was suspended in distilled water and the acid mixture was added slowly until a pH of 2.5 was reached. The clear solution was not centrifuged but was brought back to a pH of 4.6 by the slow addition of five per cent ammonium hydroxide. The precipitated casein was washed as before, redissolved at a pH of 2.5, using five per cent hydrochloric acid, again precipitated with ammonium hydroxide, and washed three times with distilled water adjusted to a pH of 4.6 with hydrochloric acid.

Casein II. Freshly precipitated and washed casein was suspended in water and dissolved by the addition of five per cent ammonium hydroxide with rapid stirring until a pH of 6.8 was reached. The undissolved portion was used in the preparation of casein III. The solution was centrifuged in a Sharples supercentrifuge, and the casein reprecipitated from the clear solution by the addition of five per cent hydrochloric acid. The washing, redissolving, and reprecipitating were repeated and the finely divided, snow-white precipitate was given final washings similarly to casein I.

Casein III. The portion of casein II which did not go into solution at pH 6.8 was dissolved by adding ammonium hydroxide until a pH of 9.1 was reached. Further purification was effected as in the case of casein II.

As a means of further purification, electrodialysis was resorted to in the case of caseins I and II. Each casein suspension at a pH of 4.7 was placed in the middle compartment of a three-compartment cell, which compartment was separated from the two outer compartments by heavy canvas fabric. The outer compartments were filled with distilled water adjusted with HCl to a pH of 4.7. Graphite plate electrodes were suspended in the outer divisions and a mechanical stirrer was used to keep the casein suspension in the middle compartment agitated. Electrodialysis was continued for ten hours, the water in the outer compartments being replaced at intervals. Toluene was used as a preservative.

Following this treatment, the casein was allowed to settle and was washed with distilled water until free from chlorides. Each lot was in turn treated with hot, neutral, 75 per cent alcohol to remove the alcohol-soluble protein. Final washings were made with absolute alcohol, ether, absolute ether, and finally with petroleum ether. Each sample was dried in vacuo at a tempera-

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[3] L. L. Van Slyke and J. C. Baker: J. Biol. Chem., **35**, 127 (1918).

[4] L. L. Van Slyke: Chemical Age, **1924**, 163.

ture of about 25°C. A fine, white powder which readily passed through the 100 mesh sieve resulted. The ash content of each lot was extremely low, being less than 0.05 per cent in each case.

Preparation of Pure Paracasein. A method similar to that used in the preparation of casein was used in preparing pure paracasein. After running the warm milk through the super-centrifuge, it was brought to a temperature of 38°C., and a small amount of commercial rennet extract was added. Rapid stirring with the mechanical stirrer was employed to prevent the formation of a clot. The milk, however, did curdle. From this condition, the paracasein was brought to its isoelectric point, and purified by exactly the same method as used in the preparation of casein II. The paracasein was never subjected to a greater alkalinity than a pH 7.0. The paracasein which was obtained was very white and powdery, and passed through the 100 mesh sieve without difficulty. The ash content was low, again less than 0.05 per cent.

Effect of Rennin on Electrical Migration

In dealing with slow coagulation as contrasted with rapid coagulation, Freundlich[5] attributes the former to the lowering of the potential of the particles concerned in coagulation to the first critical potential. It is emphasized that for slow coagulation the charges on the particles are not reduced to zero potential. That the coagulation of milk by rennin is a slow one is beyond doubt.

Freundlich, dealing with cataphoresis and reviewing the literature thereon, sets forth the formula, $\mu = \frac{\zeta H D}{4 \pi \eta}$, from which it will be seen that the velocity of migration is directly proportional to the ζ potential on the particles, provided such factors as the potential gradient, the dielectric constant and the viscosity remain constant. A few preliminary experiments, using the Ostwald pipette and synthetic "milks," confirmed previous reports that rennin does not alter the viscosity of the milk prior to the actual thickening.

Consequently, if rennin does lower the potential of the calcium caseinate particles in milk, it should be possible to recognize this change by means of cataphoretic measurements. However, instead of using whole milk, or even skim milk which contains many constituents not affected by rennin, it should be much preferable to use sols consisting of either calcium caseinate in colloidal dispersion or a mixture of calcium caseinate and calcium phosphate, both of which are in colloidal dispersion.

Two methods fo- determining rates of migration in the electric field were adopted. The first of these was concerned with the actual migration and subsequent distribution of the protein along a tube after the current had passed for a definite period. This was accomplished by dividing the tube into sections and analyzing each section for protein both before and after

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[5] H. Freundlich: "Colloid and Capillary Chemistry," 244, 432, 435, 582, 700 (1922).

the current flow. The other method was concerned with the linear migration of the column of sol along a tube, measurements being made at definite intervals. In each of these ways it was possible to compare cataphoretic movements in control sols treated with boiled rennin and in sols treated with active rennin under identical conditions.

Cataphoretic Tubes

Several types of tubes were tried, but U-tubes were found to be most convenient. The first satisfactory results were secured using a modification of Burton's cataphoretic tube.[6] This consisted of a glass U-tube to each arm of which was fastened by means of short piece of rubber tubing, a glass tube of the same bore as the U-tube, and being divided into two equal parts by means of a glass stopcock. Thus, by means of the stopcocks and clamps, the tube could be divided into five sections, four of which were of equal capacity (11 cc.), the middle one (the U of the tube) being of considerably greater capacity (16 cc.). The total length of the tube was approximately 75 cm. For the sake of consistency, the sections were numbered consecutively from 1 to 5, the cathode section always being No. 1.

After filling the tube with the solution to be tested, the ends were closed by means of pieces of cellophane securely fastened so as to provide a non-leakable tube. A cup-shaped glass compartment was next attached to the end of each arm by means of a heavy rubber tube. These compartments were made so that they would be in a vertical position when the tube was horizontal. The entire tube, with the exception of the upper part of the outer compartments, was immersed in a water bath, provided with a mechanical stirrer and intake and outlet tube. The outer compartments were then filled with the same solutions as filled the tube itself. Electrical connection was made by means of carbon electrodes which dipped into the solution in the outer compartments. The current used was taken from a 220 volt D.C. power circuit.

A more satisfactory tube and one which was used exclusively in the later experiments was more of the Coehn[7] type. It also was U-shaped, was 66 cm. in length, and was divided into 6 sections of equal volume (9.5 cc.). The same system of numbering was used as in the previous tube. A glass stopcock separated sections 1 and 2; a rubber connection, sections 2 and 3; a glass stopcock (the middle of the tube), sections 3 and 4; a rubber tube, sections 4 and 5, and a stopcock, sections 5 and 6. Thus, it was possible by the proper manipulation of the stopcocks and clamps to empty each section in turn. The same cup-shaped outer compartments were used with this tube as with the former.

In later experiments a change was made in the electrode connections. Whenever the ends of the tube were closed with cellophane, the outer compartment cells were used. Later when carbon rods were made to dip into the

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[6] E. F. Burton: Phil. Mag., (6) 11, 440 (1906).

[7] A. Coehn: Z. Elektrochemie, 15, 653 (1909).

end sections, resort was had to rubber stoppers (through which the electrodes passed) and rubber tubing to provide a non-leaking connection. The rubber tube was partially filled with mercury into which dipped the outside terminals which were also of carbon. This type of connection could be used either in the horizontal or the vertical position, and permitted of the immersion of the tube in either position.

The latter type of tube was used in the studies of the linear migration of the entire column although use was made of only the end stopcocks of each arm. The tube was supported in the vertical position in the bath leaving the upper portion of each arm above the surface of the water, a definite amount of solution was introduced, the column was allowed to come to rest, and the stopcocks were then closed. By allowing distilled water to flow slowly from a pipette down the inside walls of each arm the remainder of each tube was then filled with water, leaving a clear dividing line between the water and the solution in each arm. Before opening the stopcocks the electrodes were inserted into the liquid in the corresponding arm and the rubber connections were clamped tightly to the arms; thus, preventing any migration of the column due to any differences which might arise in surface levels. The stopcocks could then be opened and closed at will without producing any change in the level of the boundary layers.

Methods of Use. Two general methods for comparing migration velocity were used. One consisted of allowing the current to pass for a definite period, with or without reversal, at the end of which time the stopcocks were closed and the rubber tube connections clamped. Each section was then emptied, and analyzed for total protein using the Kjeldahl method. Certain precautions were necessary. In order to obtain representative samples for the nitrogen determinations one drop of concentrated sodium hydroxide solution was added to the solution from each section, and the corresponding section was rinsed once with its alkali-treated liquid. The anode section always contained coagulated protein, which gathered in compact form either on the interior side of the cellophane membrane or on the electrode itself. Extreme care was exercised in order to remove all of this protein and to get it dissolved in the alkaline contents of its corresponding section. Current reversal did assist materially in preventing too close packing at the anode. It was also noticed that the outside of the cellophane membrane at the cathode became thickly coated with protein.

The second method of making linear measurements of the migration of the boundary layer between a solution and the superimposed column of pure water when a current was allowed to pass for definite intervals. In these experiments current reversals were found advantageous. The practice was to allow the current to flow in the forward direction for five minutes, reverse for five minutes, and to flow forward for ten minutes. At the end of this preliminary treatment the position of the meniscus of the boundary layer in the cathode section was considered the zero from which all subsequent readings were made. The current was then allowed to flow forward for forty minutes when a reading was taken. This procedure was continued as long as desirable. Except in one or two cases (chiefly with the calcium caseinate-calcium phosphate sols) clear readings could be made at the end of reversals. In this way, it was feasible to measure the total distance through which the meniscus moved in a definite time.

There was a tendency for bubbles to gather around the cathode electrode, but this difficulty was easily overcome by closing the stopcock in the cathode arm, releasing the electrode, refilling the section with water, and replacing the electrode before opening the stopcock. No change in the position of the meniscus was produced if these precautions were observed.

Rennin Solutions

The rennin solutions used in the various experiments had a common origin in a commercial product, Marshall's Rennet Extract. These solutions varied with respect to purity, and were graded accordingly, solution No. 1 being the least pure, and so on. The methods of preparation were as follows:

Rennin Solution No. 1. The commercial extract was dialyzed for twelve hours in collodion tubes against running distilled water having a temperature of about 4°C. The precipitated material was then removed by centrifuging and the clear, brown supernatant liquid preserved for use by storing in the cooler at 4°C. Owing to its rapid deterioration, this solution had to be used when fairly fresh. This solution was always diluted before use—a 30 per cent solution of Rennin No. 1, for instance, being one in which 30 cc. of the solution was diluted to 100 cc. by the addition of distilled water.

Rennin Solution No. 2. The commercial extract was partially purified by first dialyzing to remove the bulk of the sodium chloride and then condensing in the dialyzing tube by the pervaporation method of Kober,[8] an electric fan being used to hasten the process. When the dialyzed extract had been thus reduced to a very viscous consistency, the rennin fraction was dissolved in 0.3 per cent hydrochloric acid and the suspended material removed by centrifuging. The solution was then neutralized to a pH of 6.4 by the addition of sodium bicarbonate. This latter solution was then quickly concentrated by blowing warm air over a flat-bottomed glass dish containing the solution. The resulting thick fluid was stored at 4°C. and constituted a stock solution. Dilutions were made by adding 1 cc. of the supernatant liquid of this stock solution to 10 cc. of water. The activity of this dilution was such that 1 cc. clotted 100 cc. of fresh skim milk at 40°C in from two to three minutes. Fresh dilutions were made for every experiment.

Rennin Solution No. 3. Freshly dialyzed rennet extract was acidified with hydrochloric acid to a pH of 4.7 at which reaction the flocculent precipitate settled quickly leaving an amber-colored, supernatant liquid. The finer particles were removed by prolonged centrifuging, only a faint cloudiness persisting. Sodium bicarbonate was added until a pH of 7.24 was reached. The resulting solution was very active, 1 cc. clotting 100 cc. of skim

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[8] P. A. Kober: J. Am. Chem. Soc., 39, 944 (1917).

milk at 40°C. in one minute. Four 70 cc. portions were removed, three of which were acidified with hydrochloric acid to reactions corresponding to a pH of 6.90, 6.44 and 5.36, dilutions being made with distilled water such that all four samples would contain the same concentration of enzyme.

Rennin Solution No. 4. A still more highly purified solution was prepared by acidifying a portion of rennin solution No. 3 to a pH of 4.3, centifuging to remove the finely divided suspended material, and again neutralizing with sodium bicarbonate. This solution at a pH of 6.4 was so very active that 1 cc. clotted 100 cc. skim milk at 40°C. in 45 seconds. Three lots of this solution were obtained which by careful addition of sodium bicarbonate were brought to a pH of 6.4, 6.95, and 7.48 respectively.

It was observed that both No. 3 and No. 4 solutions rapidly deteriorated even when kept cold. Experiments, however, were conducted while the solutions were fresh.

Calcium Caseinate and Calcium Caseinate-Calcium Phosphate Sols

Two general types of calcium caseinate, or calcium caseinate-calcium phosphate, sols were used. These sols were milky white especially when warm and their appearance resembled skim milk to a marked degree.

Type A. It was found quite possible to make perfectly stable calcium caseinate sols ranging from a pH of 6.0 to a pH of 8.0 and above. These would easily withstand boiling, the only visible effect of the heating being an increase in the milky appearance. This type of sol was made by triturating pure casein with a saturated calcium hydroxide solution in a mortar until a thick paste was made. The amount of alkali solution necessary to bring a definite weight of casein to any pH was estimated from the base-binding curves of Palmer and Richardson.[1]

The paste was transferred to a wide-mouth glass jar, diluted with the required amount of the calcium hydroxide solution and stirred intermittently with a mechanical stirrer until an equilibrium was reached. If an excess of hydroxide was added the pH was reduced by triturating the sol with more casein. These sols were always allowed to stand overnight in the cooler, which allowed the foam to break and also assured the reaching of an equilibrium. The excess protein, if any, was then removed by centrifuging, and distilled water was added to give the required dilution. The hydrogen ion concentrations, as in all the other determinations, were always measured potentiometrically, using the Bailey electrode. These sols neither coagulate nor clot when rennin only is added, not even under optimum temperature conditions. Check samples of calcium paracaseinate sols were made in essentially the same way.

Type B. The second type of sol was made by dissolving casein in saturated calcium hydroxide solution as previously described and increasing the hydroxyl ion concentration by the addition of the hydroxide solution to a pH of from 7.0 to 7.5 depending upon whether it was desired to add much or little acid to reduce the pH to that desired. In order to increase the hydrogen ion concentration to the desired degree, very dilute phosphoric acid was added very slowly. This was done by adding the estimated amount of acid to the required amount of dilution water and adding this to the sol from a capillary tip held close to a rapidly rotating stirrer, or while pouring the sol repeatedly from one beaker to another. The latter was usually more satisfactory on account of the greater foaming induced by the stirring.

This type of sol would usually clot with rennin at the proper temperature, more especially if the pH had been much greater than 7.5. To prevent this, resource was had to dialysis or to oxalation. Each of these treatments increased the pH, the former only slightly, but it was found that after dialysis the necessary amount of phosphoric acid could be added without danger of subsequent clotting of rennin.

Although more than twenty sols were prepared and studied, only a few of the representative results will be reported. These varied in protein concentration from 1.4 per cent to 3.0 per cent, and in hydrogen ion concentration from a pH of 6.1 to 7.69. The calcium caseinate-calcium phosphate sols were either dialyzed or oxalated before being studied, and all sols were studied while still fresh. No preservatives were used.

All samples were prepared for study in essentially the same manner. Equal volumes of sol were warmed to 40°C. and to each was then added 1 cc. of rennin solution for every 70–100 cc. of sol. They were then allowed to remain at 40°C. for from 15 to 30 minutes, when they were cooled to the temperature of the water flowing through the water bath. In order that the protein content and the conductivity of the controls should not differ appreciably from the experimental samples; boiled rennin was added to the controls instead of active rennin. Both sols were treated in an identical manner. The rennin solutions were always tested for activity with skim milk. The experiments were conducted at the lower temperatures in order that the possibility of proteolysis taking place might be reduced as much as possible under the conditions of the experimental procedure.

The Migration of Protein in the Electric Field

Eight sols were studied under similar, though not identical, conditions and protein analyses were made of the solution in each section of the cataphoretic tubes before and after the current had passed for definite periods. The data obtained are shown in Table I. In all cases, good agreement was found in the experimental results. In every sol, except No. 3, the concentration of protein in the cathode section was reduced to a greater extent in the controls than in those sols which had been treated with active rennin. There was a corresponding increase in the protein concentration in the anode sections although no very definite relationship between the protein lost from the cathode sections and that gained in the anode sections could be determined. However, by computing the number of milligrams of protein in the entire tube at the beginning of the experiment, and in the individual sections of the tube at the conclusion of the experiment, good agreement was usually obtained and practically all of the protein could be accounted for.

TABLE I
Migration of Protein in the Electric Field in Rennin-treated and Control Solutions of Calcium Caseinate.

Sol No.	Sol Type	pH	Duration of flow Hours	Type of tube	Treatment	Protein distribution in sections of tube						
						Original per cent	1 per cent	2 per cent	3 per cent	4 per cent	5 per cent	6 per cent
1	B-dial'd	6.7	2.5	Horiz'l	BR	1.62	1.27	1.63	1.59	1.59	1.78	
				+ memb.	R	1.62	1.31	1.58	1.55	1.58	1.70	
2	B-dial'd	6.63	4	"	BR	1.40	1.02	1.36	1.43	1.44	1.43	1.55
					R	1.40	1.06	1.36	1.34	1.33	1.33	1.49
3	A	7.1	4.75	"	BR	2.29	2.14	1.92	1.99	2.40	2.31	2.63
					R	2.29	2.05	2.09	2.13	2.30	2.32	2.68
4	A	6.6	4.5	"	BR	2.04	1.87	1.95	1.95	2.04	2.08	2.21
			1.5 Rev.	"	R	2.04	1.92	1.93	1.96	1.96	2.02	2.25
5	A	6.61	3	Vertical	BR	2.43	1.81	2.40	2.42	2.41	2.40	2.90
					R	2.40	1.84	2.44	2.49	2.45	2.42	2.82
6	A	6.4	5.33	Vertical	BR	2.47	1.94	2.53	2.55	2.55	2.54	2.80
			1.66 Rev.		R	2.47	2.09	2.49	2.48	2.50	2.50	2.71
7*	A	6.6	5.33	Vertical	Water	2.54	2.50	2.42	2.28	2.30	2.55	3.44
					R	2.65	2.65	2.46	2.05?	2.33	2.57	3.24
7*(a)	A	6.6	4.5	Vertical	BR	2.56	2.46	2.41	2.36	2.40	2.53	3.13
			0.5 Rev		R	2.52	2.54	2.49	2.32	2.07?	2.42	3.14
8	Sodium cas.	6.47	3	Horiz'l	BR	2.49	2.01	2.39	2.47	2.19	2.32	3.44
				no memb.	R	2.49	2.29	2.21	2.37	2.45	2.28	3.08

* 7 and 7(a) are samples of same sol. 7(a) was treated with more dilute rennin than 7; the control of 7(a) was treated with boiled rennin not with water.

B-dial'd = Cal. cas.-cal. phosp. dialyzed.
A = Cal. cas.
Rev. = Reverse
BR = Boiled rennin
R = Rennin

It is very evident that there is usually no very consistent uniformity in the final concentration of protein in the middle sections, especially in those trials in which the tubes were supported in the horizontal position. A plausible explanation for this lack of uniformity is to be found in the fact that the friction offered by the stopcocks and the disturbance in the column attendant on the clamping of the rubber connections would be sufficient to yield considerable experimental error especially in the instance of such dilute protein solutions.

Good agreement between the various results, however, is obtained by considering only the two end sections of the cathode and anode arms. Sufficient justification for the ignoring of the middle sections is afforded considering the experimental conditions under which the samples for analyses were secured.

In sol No. 3, greater migration of the protein took place in the sample to which active rennin had been added than in the control sample. The pH of this sol was 7.1. In this connection it should be remarked that the same tendency was noticed in some preliminary experiments with oxalated skim milk whose pH was between 7.1 and 7.2. The same irregularity was found with sol No. 16 (Table II) whose reaction was similar; namely, pH 7.18. The significance of these latter results will be pointed out later.

Linear Migration by the Boundary Layer Method

In the first set of experiments, eight sols were studied and the data obtained are shown in Table II. In each sol (except No. 19) whose pH was below a value of 6.9, rennin reduced the rate of migration of the boundary layer. No. 19 was a calcium paracaseinate sol, and it is significant that no difference in the rates of migration was obtained between the rennin-treated and the control sols.

In these experiments, it was found impossible to record the movement of the meniscus in the anode arm on account of the fact that coagulation occurred there. On reversals, the column did separate from the coagulum, leaving an intervening space of water-clear liquid. The latter was replaced with sol when the current was again made to flow forward. The repeated reversals caused layers or bands of coagulated protein to be formed in the boundary region of the anode section.

A noteworthy observation was made in the experiment with calcium caseinate-calcium phosphate sols. In these cases, while the current was passing in the forward direction, two menisci were observed to form in the cathode section, the main meniscus being the lower of the two. Between the two, the liquid was only moderately turbid. Upon reversal the two menisci approached each other again, and again separated when the current was righted. In this way the turbid zone became wider and wider as time passed. Much the same observations were made in the anode section, only the conditions were the reverse of the former. This would seem to indicate that in calcium caseinate-calcium phosphate sols, two colloidal suspensions

TABLE II

Migration of Rennin-Treated and Control Solutions of Calcium Caseinate

Sol No.	Type	pH	Temp. °C ±0.5	Treatment	Mm. of migration at end of 40 Min.	60 Min.	100 Min.	120 Min.	160 Min.	180 Min.	220 Min.	Average Velocity u per min.
9	A	6.62	18	BR	8.0	12.0	20.0	24.0	33.0	36.0	44.0	206.3
				R	6.0	9.0	15.0	18.0	25.0			156.3
13	A	7.69	17.5	BR	7.8	9.9	16.7	19.0	27.3			170.63
				R	7.2	9.4	16.1	18.5	26.6			166.3
14	A	6.81	17.0	BR	9.5	13.2	22.4	25.7	35.5	39.0	48.2	219.1
				R	8.7	11.9	20.4	23.9	32.1	35.5	43.7	198.7
15	A	6.63	16.5	BR	9.0	12.0	21.0	25.0	33.5	37.0	45.5	206.8
				R	8.7	11.2	18.6	21.2	28.5	31.8	39.8	180.9
				RH	8.6	11.0	18.6	21.9	29.9	33.2	40.5	189.1
16*	B-oxal'd	7.18	18.0	BR	7.5	—	11.0					183.3
				R	9.3		16.0					266.7
17*	B-dial'd	6.7	18	BR	13.6		21.3		28.0			350
				R	10.7		16.0		22.0		28.3	275
18	B-dial'd	6.47	17.5	BR	12.2	21.4	36.9	47.3	64.2	75.2	91.7	416.8
					11.8	15.3	28.0	32.0	43.0	48.0	58.8	267.3
19	Ca. Paracas	6.45	17.5	BR	5.2	7.2	12.6	14.3	19.7			123.1
				R	5.4	7.2	12.6	14.4	20.2			126.2

*With sols 16 and 17 the readings on reversal were not clear; hence the readings represent the position of the meniscus at the end of the forward periods only.

BR = boiled rennin
R = active rennin
RH = active rennin in heated sol.

exist, one of which migrates in the electric field at a greater rate than the other. The low concentration of the slow-moving colloid coupled with the fact that such behavior was present only in the calcium caseinate-calcium phosphate sols would suggest that this colloid is calcium phosphate rather than calcium caseinate. Further studies will probably verify this assumption.

The results of these experiments substantiated in every respect the results obtained from the group of experiments in which the migration was followed by protein analyses. In every case (except No. 19) when the pH of the milk was below a value of 6.9, less migration was noticed in the rennin-treated milks than in their controls. At a reaction corresponding to a pH of 6.92 the addition of rennin does not appear to exert an appreciable effect on the *migration velocity*.

When, however, the reaction of the sols corresponded to a pH of 7.18, surprising results were obtained. Greater migration was evidenced in the active rennin sols than in the controls.

When the reaction of the sols was still more alkaline, corresponding to pH values of 7.51–7.69, no significant differences were observed between the rates of migration of the control sols and those to which active rennin had been added. If rennin exerts any action on calcium caseinate at these lower hydrogen ion concentrations, such action is not revealed by the migration studies.

Linear Migration in Heated and in Non-heated Sols at Various Hydrogen Ion Concentrations

It is well known that rennin action as determined by the clotting process is considerably retarded in natural milk which has been previously heated even to pasteurizing temperatures. It is also recognized that the hydrogen ion concentration of milk exerts an influence, not only upon the rate at which clotting occurs, but also upon the nature of the clot itself.

The data obtained in the migration studies having shown that one of the fundamental effects of rennin is to reduce the potential of the calcium caseinate micellae, it seemed of interest to determine whether migration velocity studies using synthetic "milks" would also furnish a basis for explaining, in part at least, the influence which the hydrogen ion concentration and previous heat treatment exert on the clotting process of natural milk.

For this purpose a series of three sols was prepared in such a manner that in all samples the casein was exposed as nearly as possible to the same degree of alkalinity. The method of preparation of these sols was fundamentally the same as of the type A sols already described. A three per cent calcium caseinate solution having a pH value of 7.51 was regarded as a stock solution and known as sol 10. Sols 11 and 12 were prepared from this solution by triturating portions with varying amounts of casein, and diluting with water to produce a three per cent solution. Thus, sols numbering 10, 11, and 12 constituted three samples whose protein content was practically identical, but whose pH values were 7.51, 6.92, and 6.14, respectively.

Each sol was divided into two 150 cc. portions, one portion of which was heated in a boiling water bath for a period of one hour. The heating lowered the pH values of sols 11 and 12 to 6.85, and 6.12, respectively, no record being kept of the effect on sol No. 10. Migration studies were made on the heated and non-heated portions of each sol in the manner previously described for linear migration measurements, 1 cc. of rennin solution No. 2 being added to each 70 cc. of solution, boiled rennin being used in the controls. The results are recorded in Table III.

The data indicate very clearly that previous heating not only increased the rate of migration of calcium caseinate micellae, but also that rennin produces a correspondingly greater reduction in the velocity of migration in the heated sols, even though the rate is not reduced to the same level as in the corresponding non-heated sols. In the case of sol No. 10, whose alkalinity corresponded to a pH of 7.51, the action of heat was opposite to that produced in sols 11 and 12. In the alkaline sol, the rate of migration was apparently reduced by heating, although the 2.5 degree difference in the temperature of the bath in the two experiments no doubt was a factor. In addition, some hydrolysis doubtlessly took place at this alkaline reaction during the prolonged boiling. What effect this would have on migration is difficult to forecast.

The action of heat on the sols at the neutral or slightly acid reaction is of greater importance so far as rennin action is concerned than on the sols of abnormal alkalinity. The marked increase in the rates of migration in the heated portions of both 11 and 12 over the non-heated fractions suggests a much greater effect on the lowering of these charges in the case of the heated sols, but in no case was the rate of migration reduced as low as that of the rennin-treated, non-heated samples. These results not only serve to explain the retardation in the clotting process in heated milks, but also lend considerable support in favor of the argument that the effect of heat is on the calcium caseinate itself.

Studies in Migration in Rennin Solutions

In order to find some plausible explanation for the unforeseen differences in migration tendencies of rennin-treated sols above and below a pH of 6.9–7.0, a study was made of the behavior in the electric field of rennin itself at various hydrogen ion concentrations. A preliminary determination had already shown that when the commercial extract at a pH of 7.0 was subject to an electrical current protein migrated to both the anode and cathode.

In view of the fact that rennin dries in straw-colored flakes,[9] that highly concentrated rennin solutions are dark in color, and that during dialysis rennin solutions not only become less active but also lighter in color, it was assumed that the brown or amber color is associated with the enzyme itself. Accordingly it was found easily possible to prepare samples for linear migra-

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[9] F. Fenger: J. Am. Chem. Soc., 45, 1, 249 (1923).

TABLE III

Migration in Relation to pH and Previous Heating

Sol No.	Sol Type	pH	Temp. °C ±0.5	Treatment	Mm. of migration at end of 40 min.	60 min.	100 min.	120 min.	160 min.	180 min.	220 min.	Average Velocity u per min.
10	A	7.51	21	BR	10.5	14.0	23.0	26.3	34.6			216.3
				R	11.0	14.0	22.5	26.0	35.3			220.6
			18.5	BRH	9.0	11.5	18.5	21.3	29.1			181.9
				RH	9.5	12.5	20.2	23.1	30.8			192.5
11	A	6.92	17	BR	8.0	11.0	19.0	22.5	30.0			187.5
				R	8.5	11.3	19.1	22.3	29.6			185.0
		6.85	17	BRH	9.0	12.7	21.9	26.7	36.7			229.4
				RH	9.0	12.3	20.6	24.3	32.5			203.1
12	A	6.14	17	BR	9.0	12.5	21.2	24.9	33.2			207.5
				R	9.0	12.0	19.0	21.8	29.6			185.0
		6.12	17	BRH	9.5	14.0	24.5	29.5	39.5	44.5	55.0	250.0
				RH	8.0	11.5	20.0	24.5	32.5	36.3	44.1	200.5

BR = Boiled rennin
R = Active rennin
BRH = Boiled rennin — heated sol
RH = Active rennin — heated sol

tion studies. The same tube was used. No difficulty was experienced in obtaining clear boundary layers between the rennin solutions and the superimposed columns of water.

In the following experiments the purified rennin solutions Nos. 3 and 4 were used. The four samples of rennin solution No. 3 had hydrogen ion concentrations corresponding to pH values of 7.24, 6.90, 6.44, and 5.36. Three samples of the more highly purified rennin solution No. 4 with respective pH values of 6.40, 6.95 and 7.48 were studied in order to substantiate the findings secured with rennin solution No. 3.

All of the rennin solutions were treated exactly alike, but their behaviors were decidedly dissimilar. The method employed was essentially the same as for the casein sols, 50 cc. of solution being used in each case, the portions of the tube above the surface of each column being filled with distilled water. Clear menisci were always obtained. Because of the tendency for gas to form around the electrode in the cathode arm the current was reversed for 10 minutes at the end of every 20 minute forward period. The water in the tube was replenished as often as necessary, the same precautions being taken to prevent any change in the position of the boundary layer as were used in the experiments with casein.

The migration of rennin above a pH of 7.0. The rennin solution at a pH of 7.24 exhibited a marked tendency to migrate toward the anode. The total distance through which the meniscus travelled during the entire period cannot be stated on account of the fact that readings were too indefinite at the end of each reversal period. However, at the end of 110 minutes during which time the current had been reversed for a total of 30 minutes, the meniscus in the cathode arm had moved toward the anode a distance of 6.9 mm. A grey turbidity had developed at, and penetrated below the meniscus in the anode section. This latter was no doubt due to the acidity developed there, which caused the coagulation of the acid precipitate impurity still remaining in the rennin.

A second solution, a portion of the more highly purified rennin solution No. 4, and which had a pH value of 7.48, was similarly treated. At the end of 80 minutes during which time the current had been reversed for 20 minutes, the meniscus in the cathode section had moved toward the anode a distance of 5.0 mm., which represents a distance of approximately 6.7 mm. in 80 minutes. This figure corresponds closely with the reading of the former rennin solution at the end of the same time. The meniscus in the anode section became somewhat more intensely amber colored and moved toward the anode. Toward the end of the experiment a faint grey ring formed at the meniscus. The temperature in each case was 18.0 ± 0.5°C.

The migration of rennin at a pH of 5.36. This portion of rennin solution No. 3 was treated similarly to the two preceding solutions. The experiment was run in duplicate. In both cases a grey turbidity appeared at and below the boundary line in the anode section. The cathode section presented a sharp contrast with that of the previous experiment. Instead of the boundary moving toward the anode, there was a distinct movement in the opposite direction; the distance of movement not being determinable at first on account of the faintness of the meniscus. However, after the current had passed for a few minutes, a coffee-brown ring formed at the boundary, becoming broader and of a deeper color as time passed. On repeated reversals a series of these coffee-brown rings formed and were pushed together in much the same manner as were the caseinate rings in the anode section in the experiment with casein sols.

The behaviour of rennin at a pH of 6.44. The same procedure was followed as in the previous experiment with much the same results. The meniscus in the cathode section moved toward the cathode for a very short distance, and as the run progressed the coffee-brown ring formed, grew deeper in color, and broadened into a band a few mm. in width as the succeeding rings formed and were pushed together. The cloudy band appeared in the anode section as in the previous experiments. The amber color appeared fainter below the meniscus in the anode section.

In order to repeat this experiment a composite sample was made from portions of rennin solution No. 3, and this was brought to a pH of 6.35. The result was identical with the former, a visible piling up of the brown color occurring around the meniscus in the cathode arm. The procedure was then reversed by reversing the current for 20 minutes and allowing it to flow for 10 minutes in the forward direction. The brown color gradually faded from the former cathode section and a characteristic amber colored layer appeared above the old meniscus in the anode section.

The same results were secured with a portion of the still more highly purified solution No. 4. This sample had a pH value of 6.4, and was a highly active solution (1 cc. clotted 100 cc. of skim milk in 45 seconds).

The migration of rennin at a pH of 6.9–7.0. Three experiments were conducted in which two portions of rennin solution No. 3, which had a pH value of from 6.90 to 6.91, and a portion of solution No. 4, whose pH value was 6.95, were used. All of these solutions were highly active.

In none of these three solutions could any movement of either boundary layer be detected, even though the current was passed for 80 minutes. The only visible indication of the presence of a current was the narrow grey band which formed at the meniscus in the anode section in each case.

The data collected from these experiments with purified rennin solutions of varying hydrogen ion concentrations show that the direction of migration of rennin in the electric field changes within a zone of hydrogen ion concentration corresponding to pH values of 6.90 and 7.0. At a pH of 7.24, for instance, the migration of the rennin solution was toward the anode, indicating that the amber-colored element carried a negative charge. The same result was obtained with the rennin solutions at a pH of 7.48. With the two samples having pH values of 6.90 and 6.95, no movement in the electric field could be observed, which indicated the presence of an equal number of positive and negative charges on the colored particles. This observation would lead to the conclusion that the isoelectric point of rennin lies within the zone of reaction corresponding to these pH values. In order that the definite isoelectric point may be determined, a somewhat more highly refined technique would be required.

In the experiments with rennin solutions on the acid side of pH 6.9, the migration of the rennin was clearly in the direction of the cathode, indicating an excess of positively charged colloid ions.

Discussion

From the results obtained it is quite evident that the action of rennin is related to the electrical charges on the caseinate micellae which action culminates in a lowering of potential differences beyond the point where stability is possible.

Freundlich,[5] discussing slow and rapid coagulation in colloidal solutions by means of electrolytes, distinguishes between two critical potentials. In order for flocculation to be definitely started the first critical potential must be attained. If the stabilizing ζ potential is still further reduced to the point where it becomes zero, the second critical potential is reached. "Slow coagulation takes place between the first and second critical potentials, in a range of concentration of the coagulator which causes a lowering of the potential of the micellae below the original in a range, therefore, in which they are partially but not completely discharged. We are still at some distance from the isoelectric point."

The transformation of a sol into a gel is really the coagulation of the sol under specific conditions. According to Freundlich[5] (p. 700) and Weiser[10] the first prerequisite for the formation of a gel is a sufficient concentration of the micellae; otherwise, flocculi will separate. Furthermore, the micellae must be lyophilic and remain so upon coagulation. Under these conditions, during coagulation, the micellae either bind large quantities of water molecules, or merely envelope them. In this way, only ultramicroscopic layers of the dispersion medium separate the coagulated but still ultramicroscopic small micellae from one another. A gel is formed. That this is exactly what happens when rennin acts upon diluted milk is at once apparent to anyone who has watched the coagulation of the caseinate micellae in the ultramicroscope.

It has already been postulated by Palmer and Richardson[1] that calcium caseinate and calcium paracaseinate in solution at the hydrogen ion concentrations of fresh milk are striking examples of colloidal dispersions intermediate between lyophobic and lyophilic sols, dispersing in water like the latter, yet retaining their visibility in the ultramicroscope and their coagulability by cations.

It is quite evident, then, that if by the addition of rennin to a stable colloidal dispersion of calcium caseinate, a condition of such instability is induced that a lower concentration of precipitating ions would be required for coagulation than for the original solution, then clot formation would occur if

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[10] H. B. Weiser: First Colloid Symposium Monograph, 38 (1923).

sufficient micellae were present, and if the concentration of precipitating ions was such that only a slow coagulation would ensue. In this connection, we have already demonstrated[1] that 4 per cent calcium caseinate solutions to which 20 cc. of 1 per cent calcium chloride solution have been added for every 100 cc. of milk produce typical clots when treated with dilute rennin solutions.

The contention advanced by Porcher[11] that the presence of a second colloid is necessary before gelation will take place is not supported by our findings. With very dilute calcium caseinate solutions the concentration of the micellae is insufficient to permit of a clot being formed, but with solutions as concentrated as 4 per cent, or even 3 per cent, gelation will occur provided precipitation is sufficiently slow.

It is well known in colloidal chemistry that flocculation is induced in lyophobic sols by the addition of small quantities of certain lyophilic sols. For instance, Freundlich[5] (p. 582) has shown that when electrolyte-free gelatin is added in small concentration to a negative lyophobic sol, a condition of greater stability is induced. Flocculation may or may not occur, depending upon the relative concentrations of the micellae and of the electrolytes present as well as upon the charge on the micellae. The decrease in stability in these cases is indicated not only by the change in color of the sols but also by the decrease in the concentration of electrolyte necessary to effect flocculation. This sensitization of lyophobic sols, however, has been found only in the case of lyophilic sols which under the experimental conditions were able to yield oppositely charged colloid ions. It is the opinion of Freundlich, therefore, that albumin, being amphoteric, should provide in neutral solutions sufficient colloidal cations and anions to sensitize both positive and negative lyophobic sols.

The data obtained from the experiments with calcium caseinate sols and with rennin solutions indicate that the clotting of milks by rennin can best be explained on the basis of colloidal reactions. That rennin is a lyophilic colloid is evidenced by its great insensitivity toward electrolytes, and by its homogeneous appearance in the ultramicroscope. Rennin solutions are stable even in saturated sodium chloride solutions. Migration studies have shown it to have its isoelectric point within a zone corresponding to pH values of 6.9–7.0. Above a pH of 7.0 its migration toward the anode indicates that this colloid is negatively charged. Below a pH of 6.9 the migration is in the opposite direction, indicating positively charged micellae. Calcium caseinate micellae at every reaction studied migrated toward the anode.

Consequently, when a dilute rennin solution is added to a calcium caseinate solution below a pH of 6.9, the positively charged rennin ions neutralize part of the negative charges carried by the caseinate micellae. When this happens, if cations are present in sufficient concentrations, then a slow coagulation takes place. Divalent cations being greatly superior to monovalent cations in their precipitating power, a lower concentration of the former suffices to

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[11] Ch. Porcher: Pub. Soc. Chimie biol., 1926, No. 6.

bring about coagulation in the calcium caseinate, or calcium caseinate-calcium phosphate sols. We have previously[1] demonstrated, however, that the addition of relatively small amounts of a saturated sodium chloride solution is sufficient to produce gelation in calcium paracaseinate sols in exactly the same way as does the addition of rennin to calcium caseinate milks under conditions suitable for clotting.

That the addition of rennin to calcium solutions does lower the potential on the micellae in suspension was demonstrated in our experiments in every solution whose pH was less than 6.9. In every case whether the determination was made by actual protein analysis, or by the linear migration of the boundary layer, it was found that the addition of rennin reduced the rate of migration in each type of tube used in the cataphoresis studies.

As was to be expected, different results were obtained in those caseinate sols whose reaction was in the range where clotting does not occur in natural milk. In those sols whose reaction fell within the isoelectric zone of rennin, no significant difference was found between the rates of migration in the treated and control tests. In those sols, however, whose reactions were slightly above a pH of 7.0, the rates of migration were reversed, and rennin appeared to exert a favorable effect on migration. This would indicate that rennin instead of sensitizing a caseinate solution on the alkaline side of neutrality, acts as a protector. This would seem a plausible explanation since at a pH above the isoelectric point of rennin there are present negatively charged caseinate micellae and negatively charged rennin micellae. Under such conditions the rennin micellae could not well sensitize the calcium caseinate.

The sols at the pH value of 7.5 and above behaved the same as those at a pH of 7.0 with the exception that no appreciable difference could be established in the rates of migration of the caseinate and the paracaseinate sols. This is quite in conformity with the accepted ideas that gastric rennin does not act in alkaline reactions.

While the results of the migration studies with calcium paracaseinate sols will not permit of comparison with those with calcium caseinate sols, as far as the actual values for ζ potential are concerned, since we are dealing with individualistic sols, yet they do serve to explain certain characteristics of paracaseinate sols. That they do not clot with rennin is due to the fact that the addition of rennin does not lower the potential on the micellae as is evidenced by the fact that no significant differences in the rates of migrations exist between the rennin-treated and the control tests, even at such an optimum reaction as a pH of 6.45. Thus the addition of rennin does not induce a condition of instability. That paracaseinate sols are more sensitive to the addition of electrolytes, even sodium chloride, than caseinate milks is doubtlessly due to the fact that the electrical charges carried by the paracaseinate micellae are relatively much smaller than is the case with the caseinate micellae. This is very evident when their relative velocities of migration are compared.

The data obtained from the cataphoresis experiments with heated sols are interesting not only because they substantiate the results obtained with non-heated sols, but also because they explain why a higher concentration of calcium ions is necessary to bring about normal gelation in heated milk than in natural raw milk. In every case studied, with the exception of the most alkaline sols, previous heating increased the rate of migration of the micellae.

The action of heat on the synthetic "milk" seems to be one of stabilization, the result of an increase in the ζ potential of the caseinate micellae. These charges are reduced when rennin is added, but the reduction is insufficient to allow the calcium ions present to effect precipitation in the normal time. Either precipitating ions must be added, or a longer time allowed for clotting to occur. What effect an increase in the amount of rennin added would have on the time of clotting of these "milks" has not been studied. The effect of heat is clearly due to its action on the caseinate particles themselves. This interpretation of the effect of heat very definitely overthrows Marui's[12] conclusion that heating increases the protective action of the casein for the calcium phosphate dispersion to such an extent that rennin can not reduce *this power sufficiently to allow the precipitating ions to coagulate the calcium* phosphate. Marui had only indirect evidence in support of his argument. Marui, however, was the first to prove definitely that the effect of heat on milk was due to its action on the caseinate of milk. What the effect was he did not determine.

Conclusions

1. The isoelectric point of rennin as determined by cataphoretic method lies between the pH values of 6.9 and 7.0.

2. The addition of rennin to caseinate solutions having pH values between 6.1 and 6.9 reduces the rate of migration of the caseinate micellae. This indicates that rennin lowers the electrical charge on negatively charged semi-lyophilic micellae.

3. The addition of rennin to caseinate solutions of pH values from 7.0 to 7.25 increases the rate of migration of the caseinate micellae. At the pH values of 7.5 and 7.69 no appreciable change in migration is produced.

4. The addition of rennin to calcium paracaseinate solutions of pH 6.45 does not change the velocity of migration.

5. Previous heating of neutral and slightly acid caseinate solutions results in an increase in the rate of migration which indicates an increase in the charge of the protein micellae. It is well known that a greater concentration of electrolyte is necessary to cause precipitation of casein in heated than in non-heated milks. The effect of heat in this case is clearly on the calcium caseinate.

6. The action of rennin on heated calcium caseinate sols is one of decreasing the velocity of migration in the electric field. Inasmuch, however, as the reduction does not reach the low level which is reached in the rennin-treated but non-heated sols, this explains why the addition of calcium chloride to boiled natural milk facilitates its clotting with rennin.

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[12] S. Marui: Biochem. Z., 173, 363, 371, 381 (1926).

A CRITICAL CONSIDERATION OF SOME SCHEMES OF FRACTIONATION*

BY ARTHUR A. SUNIER**

During the course of another research it was necessary to fractionally evaporate molten cadmium rather extensively in a high vacuum. The difficulty of experimentation made it the more necessary to choose a scheme of fractionation which would give the greatest yield with the least possible effort. A rather careful search of the literature has shown that no thorough study of fractionation schemes has been recorded. Since many different schemes were considered in the course of the experiments mentioned above, it was thought desirable to give the results of these critical considerations, especially since the work was both new and valuable in other fields of research.

It will be every evident to all, that the simplest scheme of fractionation from the standpoint of ease of manipulation is one in which half of the material is evaporated, and thus half is left as residue: such a scheme[1] employs *cuts of two*. All of the schemes to be presented in this paper will be modifications of the general scheme of cuts of two.

Four cases have been recognized in the various schemes to be considered. These are illustrated in Figs. 1A, B, C and D. Comparing these figures it is soon noticed that 1A is characterized by the fact that arrows proceed from the circles of all the zero material formed; this means that all the zero formed has been redistilled and thus reworked into the scheme of fractionation; this case will be referred to as: ZERO INCLUDED. In Fig. 1B, however, the arrows are found to *point to* the circles of the zero material formed, but *not away* from the circles; this shows that the zero material has not been redistilled and hence it has not been reworked into the scheme of fractionation; this case will be referred to as; ZERO NOT INCLUDED. Similarly in Fig. 1 C, the zero and L_1 material has not been redistilled so this case will be called: ZERO AND L_1 NOT INCLUDED. For the case illustrated in Fig. 1 D the name given is: ZERO, L_1 and L_2 NOT INCLUDED. The designations L_1, H_1, L_2 etc. mean simply one arbitrary unit light, one unit heavy, two units light etc. The absolute magnitude of the unit will naturally vary with the material used, but since cuts of two are being considered the conclusions drawn later should be applicable to any material regardless of the magnitude of the unit.

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* Contribution from the Chemical Laboratory of the University of Rochester.

** Presented in part at the Symposium on Physical Chemistry held in Rochester, New York, in January 1923.

[1] Lord Rayleigh (Phil. Mag. (5), **42**, 493 (1896)) and Mulliken and Harkins (J. Am. Chem. Soc., **44**, 37 (1922)) have recognized that cuts of two make for symmetry of the fractions and thus make for a most practical scheme of fractionation.

A closer examination of Fig. 1 A reveals the fact that on working the first row, the yield is 20 grams of L8, for the second row an additional 40 grams of L8 and so on until the sixth row is seen to yield 74.3 grams of L8, nearly four times the yield of the first row. The yield for all six rows is 325.3 grams of L8, a quantity over fourteen times larger than the yield obtained on working the first row alone. The yield obtained in any given scheme of fractionation is of course a very important factor, but there are others which are important too; these will be considered immediately.

In order to obtain the 20 grams of L8 from 5120 grams of zero material (by working only one row), 5100 grams of cadmium must be evaporated; this is obtained by adding up the amounts evaporated in each step which are 2560, 1280, 640, 320, 160, 80, 40, 20. In order to obtain the next 40 grams of L8, on working the second row, only 3780 grams of cadmium must be evaporated; the amounts evaporated in each step are: 1280, 960, 640, 400, 240, 140, 80, 40. The yield per gram evaporated has dropped from 255 to 94.5 (see Table I), a very decided drop and a very important one. Since the rate of evaporation must usually be kept at a minimum it is soon evident how important this factor becomes in any large separation which might be attempted. Several other factors will be discussed later.

The above two paragraphs have dealt with just one case—ZERO INCLUDED (in the production of L8). For the other three cases, Figs. 1 B, C and D should be consulted. In Table I will be found the important quantities such as yield, grams evaporated, and yield in relation to the grams evaporated, for each of the four cases. It will suffice to call attention to Fig. 2 where some of these factors, for all four cases, are compared graphically. Curves with maxima or minima should be studied carefully. For instance in Fig. 2 A it is seen that it would not, in general, be advisable to work more than four rows in the case—ZERO, L1 and L 2 NOT INCLUDED, but for ZERO INCLUDED perhaps some fifteen rows might be worked with great success. The graph, Fig. 2 D, of grams evaporated per gram yield is a very interesting and important one. It will be dealt with later on.

The results of calculations on the production of L10 are presented in part in Fig. 3. A careful study of these figures shows the results are even more favorable than those obtained in the preceding cases. The maxima in Fig. 3A are found to be farther to the right than those in Fig. 2A. For ZERO INCLUDED 38 grams of L10 are produced on working only the sixth row in place of 5 grams of L10, on working the first row—an increase greater than 7 fold. Other very interesting results could be pointed out, but space does not permit.

The results of similar calculations on the production of L6 and L4 will not be presented in detail, since it is felt that the results are not important enough to warrant space for all the data accumulated for these cases.[1]

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[1] Complete calculations may be found in the thesis (Univ. of Chicago 1925) of the author.

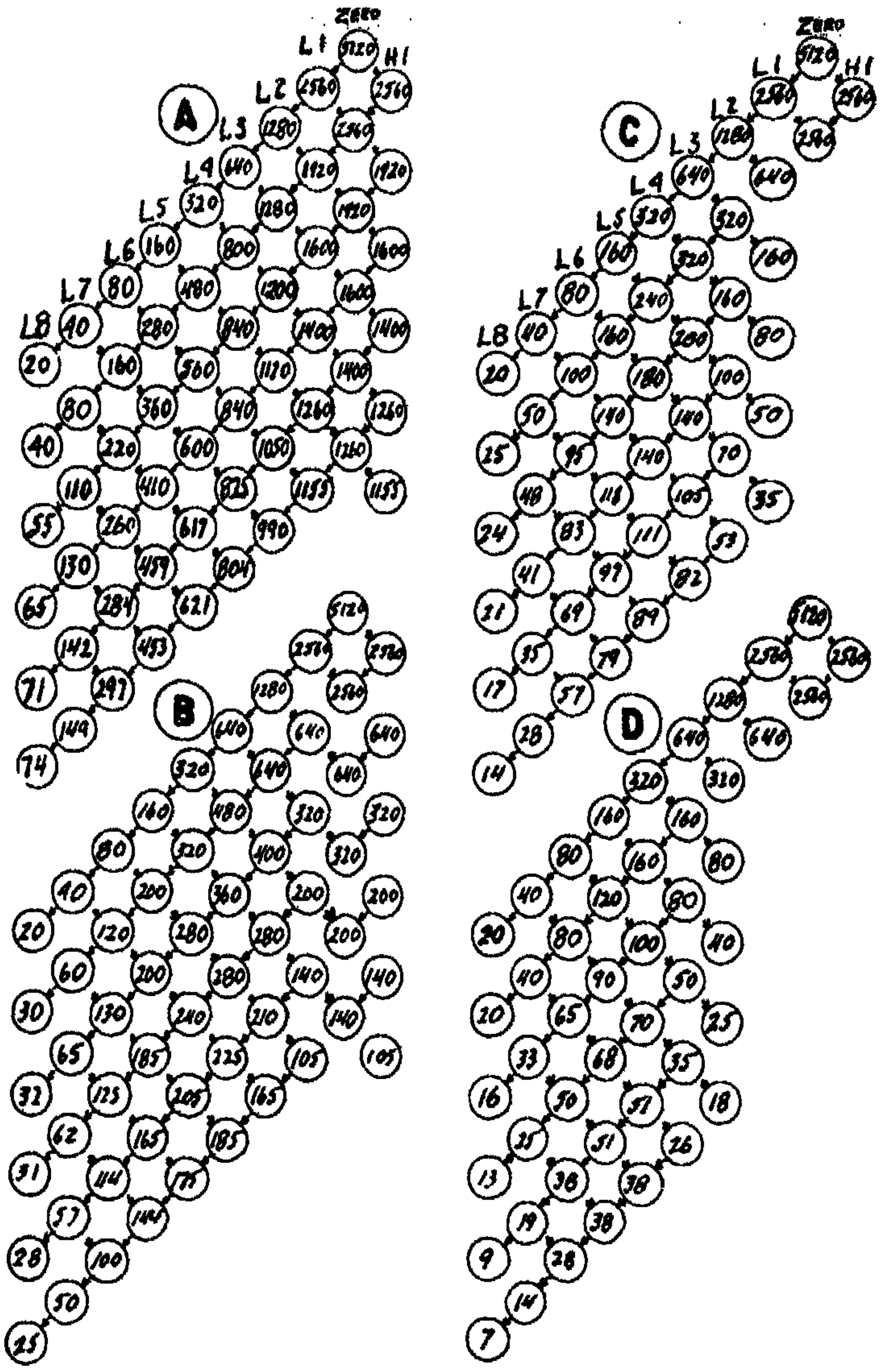

Fig. 1
Illustration of Four Cases in the Production of L8

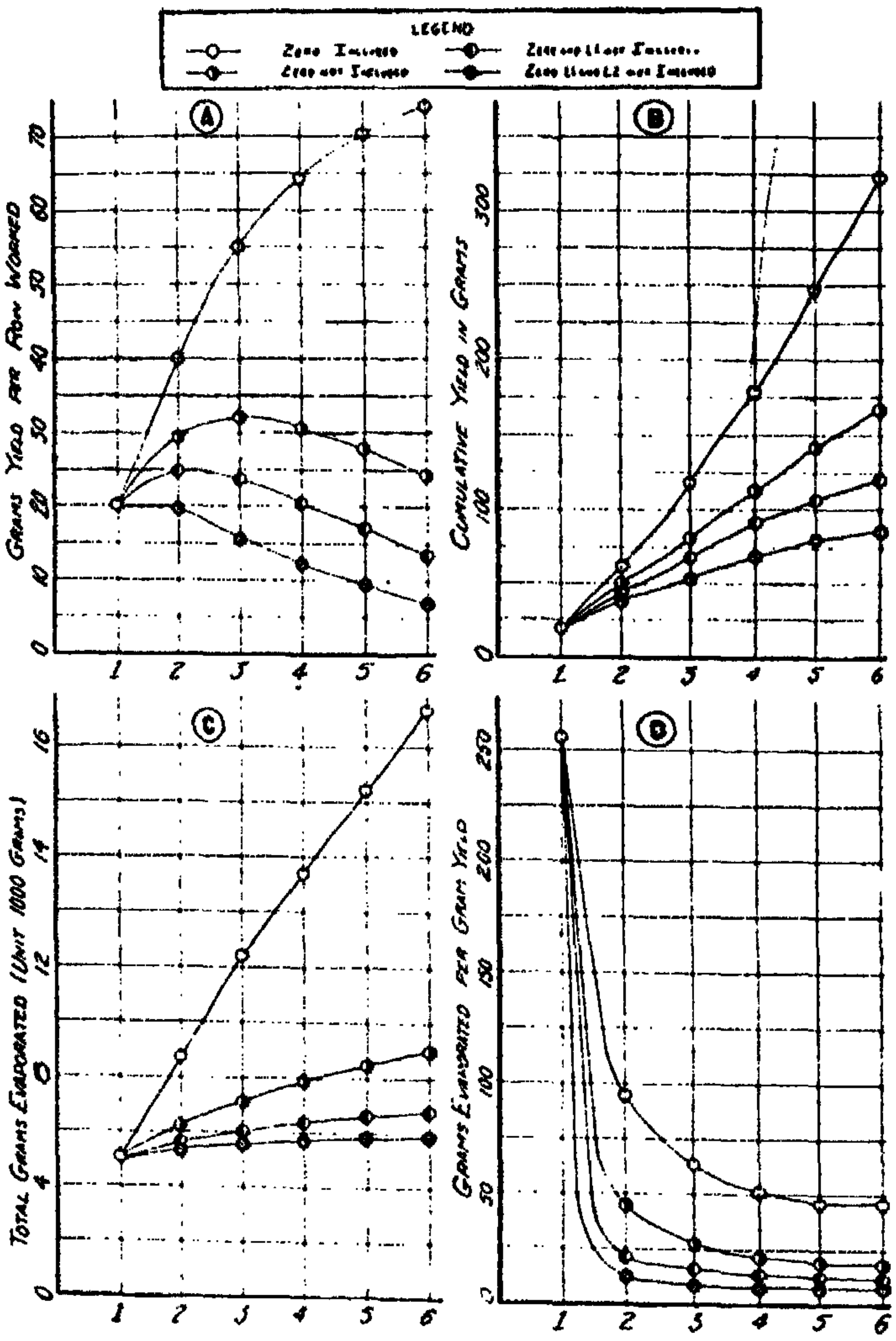

Fig. 2
Graphs of the Production of L8 (abscissae—number of rows worked)

In Fig. 4 one factor, namely yield, is considered for two cases. The results are placed on a common basis; this being that the yield for the first row is called 100%, yields for other rows being figured as percentages of the first row yield. In Fig. 4A the results for L10, L8, L6 and L4 are compared for the case ZERO INCLUDED. The great advantage gained on working several rows for the production of L8 and especially L10 is readily grasped. In Fig. 4B the case ZERO NOT INCLUDED is considered. For this case the yields are not so favorable as in A, but the general shape of the curves is much the same; maxima occur in different places as would be expected. The dotted line in B, extended two more rows, show the course of the curves to eight rows; the calculations will not however, be given at this time. Although for this one factor, yield, the case ZERO INCLUDED is the more favorable case, this will not prove to be true when other factors are considered.

TABLE I

Work on L8

Case	Rows Worked	Yield in Grams for Each Row	Cumulative Yield in Grams	Grams Evaporated for Each Row	Cumulative Grams Evaporated	Grams Evaporated per Gram Yield
Zero Included	1	20	20	5100	5100	255
	2	40	60	3780	8880	94.5
	3	55	115	3405	12285	62.0
	4	65	180	3180	15465	49.0
	5	71	251	3010	18475	42.5
	6	74.3	325.3	2831	21306	41.6
Zero not Included	1	20	20	5100	5100	255
	2	30	50	1230	6330	41.0
	3	32.5	82.5	877.5	7208	27.0
	4	31.2	113.7	686.0	7894	21.9
	5	28.4	142.1	557.7	8452	20.3
	6	25.1	167.2	462.5	8914	18.5
Zero and L1 not Included	1	20	20	5100	5100	255
	2	25	45	595	5695	23.8
	3	23.7	68.7	411.2	6106	17.4
	4	20.6	89.3	310.5	6417	15.1
	5	17.2	106.5	243.2	6660	13.6
	6	14.2	120.7	193.8	6854	13.7
Zero L1 and L2 not Included	1	20	20	5100	5100	255
	2	20	40	280	5380	14.0
	3	16.2	56.2	183.7	5564	11.4
	4	12.5	68.7	131.2	5695	10.5
	5	9.4	78.1	96.8	5792	10.2
	6	7.1	85.2	72.1	5864	10.1

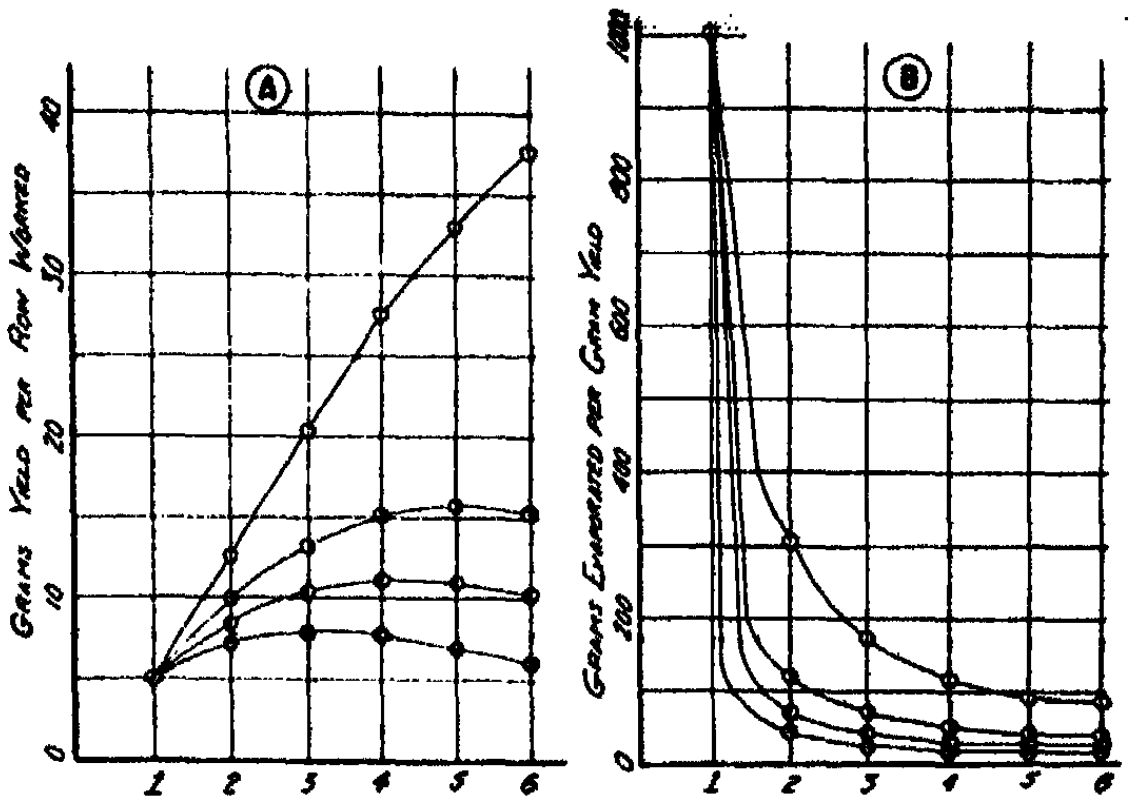

FIG. 3
Graphs of the Production of L_{10} (abscissae—rows worked)

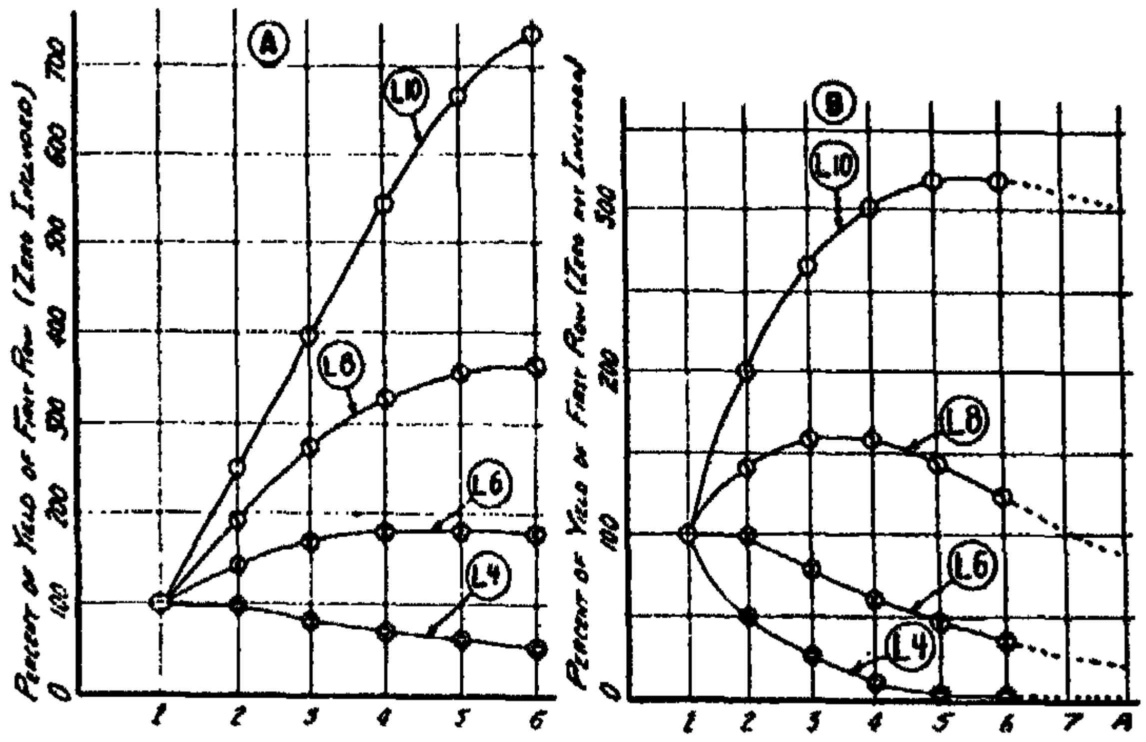

FIG. 4
Comparison of certain cases on the Percentage Basis. (abscissae—rows worked).

In Fig. 5A, the factor, grams evaporated per gram yield is considered. In this graph, the first case (ZERO INCLUDED) is considered 100% and all other data is referred to this. Then too, the results presented are for *all six* rows being worked. The most favorable of the four cases (for any given curve) will be that one which is the lowest point in the curve. It so happens that for the production of L6, L8 and L10, case 2 is the most favorable.[1] The saving in choosing case 2 instead of case 1, for the production of L10 is seen to be very nearly 24%, a quantity by no means to be neglected in a comprehensive scheme of fractionation. Table II gives the data which have been used in Fig. 5A.

In all calculations presented above the distillations were carried out on the light fraction alone (it is assumed, however, that in all cases where the zero material is reworked that the heavy fraction has been carried along also). Usually it is desirable to work on the heavy fraction also, since some saving in time results and of course eventually fractions are obtained which should have just twice the separation that would be obtained on working the light fraction alone. This being true it was thought desirable to consider two factors and two cases involved in the production of a definite quantity of L8 and H8; this quantity was arbitrarily chosen as 100 grams of each. The two factors which are considered are first, the grams evaporated per gram yield, and second, the amount of original material required to give the desired result; the latter factor being a new one and an important one. The two cases presented are ZERO INCLUDED and ZERO NOT INCLUDED. Fig. 5B and Table III should be consulted in this connection. The graph shows that case 1 is the more favorable when considering the factor of original material required, while case 2 is the more favorable when considering the grams

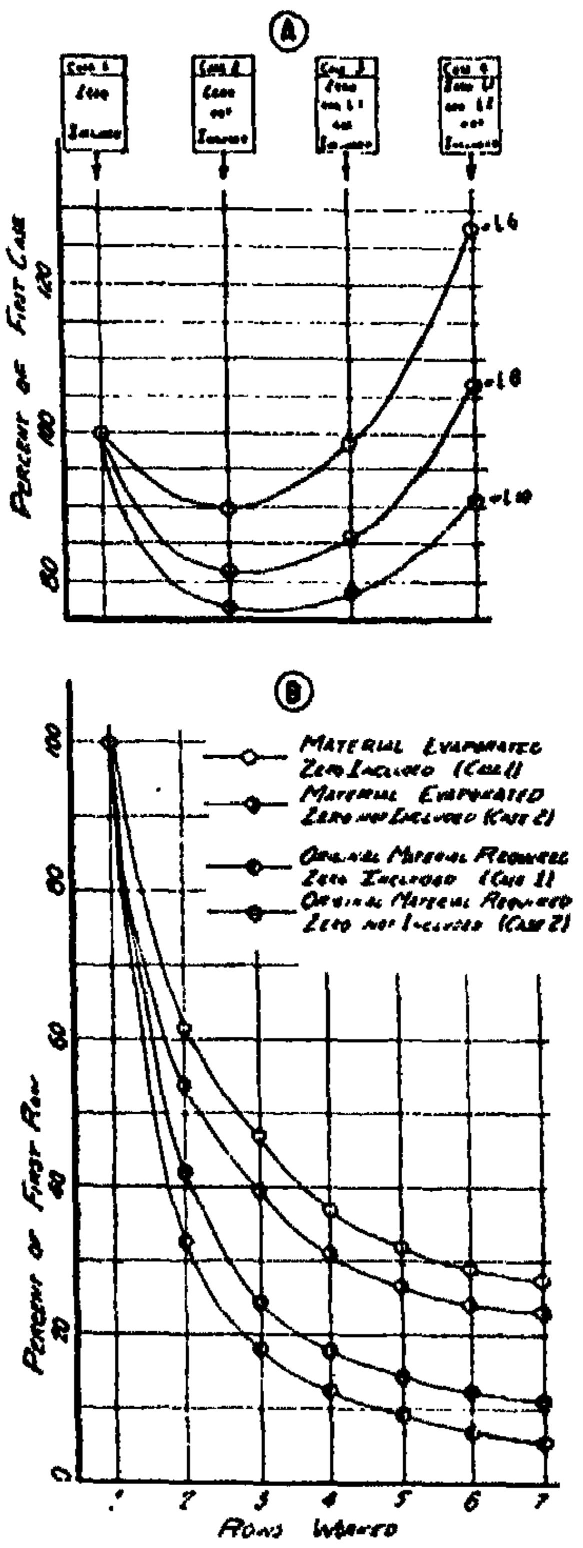

FIG. 5

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[1] It is almost certain, however, that if L16 or L30 were being formed the position of the minimum would be shifted to the right; in other words case 3 or case 4 would be the most favorable. Calculations along these lines have been completed for some time and may be presented for publication in the near future.

TABLE II

	Case	Evaporation per Gram Yield for 6 Rows worked	
		Grams	% of First value
Work on L6	Case 1	27.1	100.0
	Case 2	24.3	89.7
	Case 3	26.6	98.0
	Case 4	34.4	127.0
Work on L8	Case 1	65.5	100.0
	Case 2	53.3	81.5
	Case 3	56.8	86.8
	Case 4	68.8	105.1
Work on L10	Case 1	161.1	100.0
	Case 2	122.8	76.2
	Case 3	126.0	78.2
	Case 4	145.5	96.2

TABLE III

Object: To prepare 100 Grams L8 and 100 Grams H8

Rows worked	Case	Original Material Required		Material Evaporated	
		Grams	% of First Row	Grams	% of First Row
1	Case 1	25600	100.0	38200	100.0
	Case 2	25600	100.0	38200	100.0
2	Case 1	8533	33.3	23200	60.8
	Case 2	10240	40.0	20200	53.0
3	Case 1	4460	17.4	17200	45.0
	Case 2	6200	24.2	14350	37.6
4	Case 1	2842	11.1	14100	36.9
	Case 2	4500	17.6	11640	30.5
5	Case 1	2046	8.0	12200	31.9
	Case 2	3600	14.1	10100	26.4
6	Case 1	1575	6.15	10950	28.6
	Case 2	3060	12.0	9130	23.9
7	Case 1	1280	5.0	10100	26.4
	Case 2	2700	10.5	8480	22.2

that need to be evaporated in order to obtain the desired result. If the material being distilled or diffused is very expensive, case 1 would no doubt be chosen, while case 2 would be chosen if a particular element had to be distilled exceedingly slowly in order to attain a fair separation. It is evident, then that these two factors should be considered carefully before deciding on any scheme of fractionation.

The general conclusions to be drawn from these critical considerations are:

(1) The scheme of fractionation should, in general, be carried outward in both directions as far as possible.

(2) The number of rows worked should, in general, be large.

(3) The more important factors which should be carefully considered in any scheme are: yield, grams evaporated per gram yield, and the quantity of original material needed to give the desired yield. It is hoped that the above considerations and conclusions will prove to be of value in other fields of research, such as rare earth separation, which usually involves many hundreds of recrystallizations.

It is a pleasure to acknowledge that this problem is an outgrowth of another problem suggested by Professor W. D. Harkins, of the University of Chicago.

For an application of the principles laid down in this article the reader is referred to the work published (since this article went to press) by Harkins and Mortimer (Phil. Mag. 6, 601 (1928), especially pages 619 to 623). A printed abstract of the author's thesis, referred to above, has also appeared (Univ. Chic. Abst. Theses. Sci. Ser. 4, 173 (1925-1926).

THE SOLUBILITY OF GALENA AND A STUDY OF SOME LEAD CONCENTRATION CELLS*

BY LESLIE F. NIMS AND WALTER D. BONNER

Various investigators have reported on the solubility of galena in water, but the results they report are not in good agreement with one another. Table I lists the solubilities reported.

TABLE I

	Moles per liter H_2O	t°C	Investigator and Reference
PbS Pp't'd.	3.6×10^{-6}	18°	Weigel: Z. physik. Chem., **58**, 288 (1907)
Galena, Freiberg	1.21×10^{-6}	18°	" " " " " " "
Galena, Artificial	1.21×10^{-6}	18°	" " " " " " "
PbS Pp't'd	1.25×10^{-6}	25°	Hevesey and Paneth: Z. anorg. Chem., **82**, 323 (1913)
PbS	5.5×10^{-6}	18°	Biltz: Z. physik. Chem., **58**, 288 (1907)
PbS	5.1×10^{-8}	25°	Knox: in Mellor: Comp. Treat. Inorg. and Phys. Chem., **7**, 789.
PbS	2×10^{-14}	18°	Treadwell-Hall: Anal. Chem., **1**, 22.

In this investigation the solubility of galena has been determined by a method involving the use of concentration cells containing a liquid junction. In a cell of the type:

$$\mathrm{Pb(Hg)},\ \mathrm{Pb^{++}}(a_1) \vdots \mathrm{Pb^{++}}\ (a_2),\ \mathrm{Pb\ (Hg)}$$

the electromotive force due to the difference in concentration is given by the familiar equation:

$$E_c = \frac{RT}{2F} \ln \frac{a_2}{a_1} \tag{1}$$

and the electromotive force of the liquid junction may be estimated by means of the equation:

$$E_{L}{}^{[1]} = \frac{\frac{\Lambda_C}{V_C} - \frac{\Lambda_A}{V_A}}{\Lambda_C + \Lambda_A} \cdot \frac{RT}{F} \ln \frac{a_2}{a_1} \tag{2}$$

where Λ_C and Λ_A are the ionic conductances of the cation and of the anion respectively and V_C and V_A are the valences of the cation and of the anion.

The experimental work was done on cells which did not have the same anion on both sides of the liquid junction. It was thought necessary, therefore, to show that the electromotive force of the cells could be calculated

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* Contribution from the Chemistry Department, University of Utah.

[1] Noyes and Sherrill: "Chemical Principles," p. 263 (1922).

from equations 1 and 2 if we modified equation 2 so that the term Λ_A was replaced by the arithmetical mean of the two anion conductances, $\frac{\Lambda_{A1} + \Lambda_{A2}}{2}$. To do this, the following cells were studied:

A. $Pb(Hg), PbCl_2$ (Sat) $\|$ $PbBr_2$ (Sat), $Pb(Hg)$
B. $Pb(Hg), PbCl_2$ (Sat) $\|$ PbI_2 (Sat), $Pb(Hg)$
C. $Pb(Hg), PbBr_2$ (Sat) $\|$ PbI_2 (Sat), $Pb(Hg)$

It was found that such a modification would give values in agreement with the measured values.

Next the electromotive force of the cell:

D. $Pb(Hg), PbSO_4$ (Sat) $\|$ PbS(Sat), $Pb(Hg)$

was measured and by means of equations 1 and 2 the activity of the lead sulphide in a saturated water solution was obtained.

Materials and Apparatus

Lead bromide, lead iodide and lead sulfate were prepared from cold dilute solutions of the corresponding potassium salt (Merck's blue label which had been purified by recrystallization) by precipitation with purified lead nitrate. The precipitated lead salts were further purified by washing five times with conductance water. The lead chloride (Kahlbaum's) was further purified by washing with conductance water.

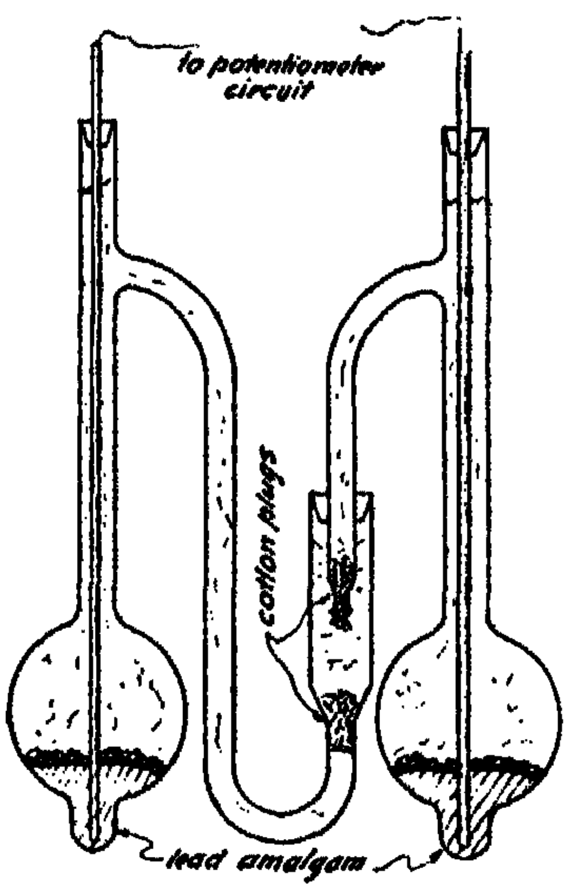

Fig. 1

The galena, from Montezuma, Colorado, was very pure and was washed with a dilute solution of ammonium acetate to remove surface oxidation products.

The lead amalgams were made by electrolysing a 10% solution of pure lead nitrate with mercury as a cathode. The current employed was 20 milliamperes and the amalgams contained 3.3% of Lead.

The cells employed are illustrated in Fig. 1. Cotton plugs were placed at the liquid junctions to prevent the washing of the liquids from one arm of the cell to the other.

The electromotive force of the cells was measured by means of a Wolff potentiometer and a carefully checked Weston standard cell. Each cell was measured after it had stood in a thermostat at 25° ±0.1° a sufficient time to attain equilibrium as indicated by a constant e.m.f. The e.m.f. reported is the mean e.m.f. of at least two and in most cases three cells which differed by less than 1% among themselves. The cells when carefully made proved readily reproducible and would maintain a constant e.m.f. for a period of two days or more after which the e.m.f. would begin to drop due to the diffusion of the electrolyte from one arm to the other.

Experimental Results

The e.m.f. of the cells was measured and also calculated by equations 1 and 2. The constants necessary to carry out the calculations are given in Tables II and III and the results are tabulated in Table IV.

It will be noticed from the above table that the agreement between the calculated and observed valves of the e. m. f. is good when it is remembered that the calculation for the liquid junction potential is only an approximation. The discrepancy in the lead chloride—lead bromide cell may be due to the e. m. f. of the cell itself being small and any extraneous e. m. f's. either at the liquid junction or at the electrodes themselves would consequently be a large part of the total quantity. It must also be remembered that the activities of the lead halides are not accurately known.

A few measurements were made on some lead cells in which the anions present were of different valence. A similar modification of equation 2 as proposed for the case where the anions present were of the same valence did not lead to a good correlation between calculated and measured values of the e.m.f.'s. Hence only the measured e.m.f.'s of these cells are listed in Table V.

TABLE II

Salt	Solubility at 25°C. grams/1000 grams H_2O	Moles/1000 grams H_2O	Activity Coeff. γ	Activity α
$PbCl_2$	10.842[1]	3.913×10^{-2}	0.39[3]	1.576×10^{-2}
PbI_2	0.764[1]	1.657×10^{-3}	0.71[4]	1.177×10^{-3}
$PbBr_2$	9.744[1]	2.655×10^{-2}	0.41[4]	1.089×10^{-2}
$PbSO_4$	0.045[2]	1.44×10^{-4}	0.83[5]	1.196×10^{-4}

[1] Lichty: J. Am. Chem. Soc., 25, 474 (1903).
[2] Beck and Stegmuller: Arb. kais. Gesundh., 34, 446 (1910).
[3] Brönsted: Z. physik. Chem., 56, 645 (1907).
[4] Lewis and Brighton: J. Am. Chem. Soc., 39, 1906 (1917); Lewis and Randall: "Thermodynamics," 424 (1922).
[5] Lewis and Randall: Ibid, 344 Table I.

TABLE III[1]

Ion	Ionic Conductance at 25°C	Ion	Ionic Conductance at 25°C
Pb^{++}	72.8	I^-	76.3
Cl^-	75.2	SO_4^{--}	78.4
Br^-	77.5	S^{--}	91.0

[1] The values in Table III are taken from Noyes and Sherrill: "Chemical Principles," 120, except that for the sulfide ion which was calculated from data presented in "Physikalischen-chemischen Tabellen: Landolt-Börnstein-Roth, 4th Edition pp. 1097 and 1124, Tabellen 240 and 249.

TABLE IV

Cell	Calculated E_c	E_L	$E = E_c - E_L$	Observed E
A	0.00476	−0.00255	0.0073	0.0077
B	0.0333	−0.0176	0.0509	0.0495
C	0.0285	−0.0154	0.0440	0.0420

TABLE V

Cell	Observed E
Pb(Hg), $PbCl_2$ (Sat) ‖ $PbSO_4$ (Sat), Pb(Hg)	0.1030
Pb(Hg), $PbBr_2$ (Sat) ‖ $PbSO_4$ (Sat), Pb(Hg)	0.0955
Pb(Hg), PbI_2 (Sat) ‖ $PbSO_4$ (Sat), Pb(Hg)	0.0530

Determination of the Solubility of Galena

The electromotive force of the cell:—

$$\mathrm{Pb(Hg),\ PbSO_4(Sat)\ \|\ \underset{(x)}{PbS}(Sat),\ Pb(Hg)}$$

was determined to be 0.0670 at 25°C. If we add algebraically equations 1 and 2 we get:

$$E = E_C - E_L \tag{3}$$

$$E = \left[\frac{1}{2} - \frac{\dfrac{\Lambda_C}{V_C} - \dfrac{\Lambda_A}{V_A}}{\Lambda_C + \Lambda_A}\right]\frac{RT}{F}\ln\frac{\alpha}{x} \tag{4}$$

Using the proposed modification to take care of the different anions present, and substituting in equation 4 the constants from Tables 3 and 4 we have:

$$0.0670 = \left[\frac{1}{2} - \frac{\dfrac{72.8}{2} - \dfrac{84.7}{2}}{157.5}\right] 0.05915 \log\frac{1.196 \times 10^{-4}}{x} \tag{5}$$

or

$$x = \frac{1.196 \times 10^{-4}}{\operatorname{antilog}\dfrac{0.0670 \times 157.5}{0.05915 \times 89.7}} \tag{6}$$

Since lead sulphide is very dilute we may assume the activity to be nearly unity. Hence from equation 6 we get the concentration of lead sulphide in a saturated water solution at 25°C., to be $C = 0.9363 \times 10^{-6}$ moles per 1000 grams H_2O which is somewhat less than the value reported by Weigel.

Summary

The e.m.f's. of the following cells have been measured:

	Cell	E at 25°C
1.	Pb(Hg), $PbCl_2$ (Sat) ‖ $PbBr_2$ (Sat), Pb(Hg)	0.0077
2.	Pb(Hg), $PbCl_2$ (Sat) ‖ PbI_2 (Sat), Pb(Hg)	0.0495
3.	Pb(Hg), $PbBr_2$ (Sat) ‖ PbI_2 (Sat), Pb(Hg)	0.0420
4.	Pb(Hg), $PbCl_2$ (Sat) ‖ $PbSO_4$ (Sat), Pb(Hg)	0.1030

	Cell	E at 25°C
5.	Pb(Hg), $PbBr_2$ (Sat) ‖ $PbSO_4$ (Sat), Pb(Hg)	0.0955
6.	Pb(Hg), PbI_2 (Sat) ‖ $PbSO_4$ (Sat), Pb(Hg)	0.0530
7.	Pb(Hg), $PbSO_4$ (Sat) ‖ PbS (Sat), Pb(Hg)	0.0670

The e.m.f. of cells 1, 2 and 3 were shown to agree with the calculated values. We were not able to calculate the e.m.f. of cells 4, 5 and 6. From the observed value of the e.m.f. of cell 7, the solubility of galena was found to be 0.94×10^{-6} moles per 1000 grams of water at 25°C. This value is probably accurate within 30%.

Salt Lake City, Utah,
September, 1928.

THE BOILING-POINTS OF AQUEOUS SOLUTIONS*

BY WILDER D. BANCROFT AND HERBERT L. DAVIS

In the field of physical chemistry probably no generalization has been of greater aid or served to suggest more experimental investigations than the van't Hoff treatment of the osmotic pressure of solutions, with its demonstrations of the relation between this and the other colligative properties of solutions. This was soon followed by the empirical statement of Raoult relating the vapor pressure of an "ideal" solution and its molecular concentration, and then by the Arrhenius Theory of Electrolytic Dissociation to account for the behavior of solutions of electrolytes.

Most chemists have been content to accept these generalizations as adequate or to confine their work to a study of very dilute solutions in which the deviations from the theories are not marked. Of the properties of solutions, the one most suitable for determination is usually held to be the freezing-point, and some very splendid measurements have been made of this property. The boiling-point is the property next in favor but, principally from a fear of the unknown magnitude of superheating, relatively little work has been done on the boiling-points of aqueous solutions of electrolytes. The data that are available do not cover the very dilute solutions nor the concentrated ones, much less show the changes over the whole range.

Boiling-Points at One Atmosphere

A stimulus to this investigation was the very disturbing work of Kahlenberg[1] who showed that many common solutes in water do not behave at all as the ionization theory would require. In dilute solutions the agreement is fair but in concentrated solutions their behavior is most atrocious from the standpoint of a pious adherent to the Theory of Electrolytic Dissociation. Kahlenberg showed that, while electrical conductivities at 0° and at 95° gave values for the degree of dissociation of common salts in qualitative agreement with the theory, the values calculated from the freezing-points and boiling-points of the same solutions were markedly different, indicating in some cases that the solute salt was more than completely dissociated. On the basis of these, as yet, uncontradicted and unexplained results Kahlenberg continues to be one of the most able opponents of the dissociation theory.

This theory has been so valuable in other directions that we feel justified in assuming that possibly other factors have entered to give rise to these apparently anomalous results. Such factors as the displacement of the water equilibrium or abnormal heats of dilution may well account for these phe-

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* This work is preliminary to the programme now being carried out at Cornell University under a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] J. Phys. Chem., 5, 339 (1901).

nomena. At least a restatement of the problem is not amiss since it may finally lead to an explanation of these abnormalities which have been too long ignored.

For many years Professor Bancroft has been proclaiming that the most profitable way of attacking this problem is not by a study of the dilute solution or "slightly polluted water" but by a study of the concentrated solutions. Pragmatically this seemed true since the attack on dilute solutions showed so little progress. An idea of the situation may be gained if one considers a large number of curves of various kinds and of various eccentricities, all tangent to the axis at the origin. A study of the infinitely small portion of each curve near the origin will tell nothing about the true nature of the curve. Only as one considers the extensions of the curves does the specific nature of each become apparent. If we plot properties of solutions against concentrations, only in the concentrated solutions will the specific character of these properties become apparent. It may be admitted readily that the study of concentrated solutions has its own set of difficulties; but when as much time and thought shall have been spent on these as have been expended on the properties of dilute solutions, more light will be enjoyed than we now have.

While we have been most interested in boiling-points, the abnormalities of concentrated solutions are shown also by the freezing-points. These data from a number of authors are given in the tables of Landolt, Börnstein and Roth. In solutions containing from 7.09 to 24.6 grams of potassium chloride in 100 grams of water, the apparent molecular weight of the salt varies between 42.7 and 43.0 so that the curve of molecular weight against concentration is practically a straight line parallel to the concentration axis. For solutions of potassium bromide containing from 0.3 to 45.6 grams per 100 grams of water the values are between 62.5 and 67.7 and for solutions containing more than 8.1 grams the values are between 67.0 and 67.7. The apparent molecular weight of potassium iodide varies from 88.5 to 91.8 in solutions containing from 1.0 to 21.4 grams per 100 grams of water.

It should be noted that the apparent molecular weight and therefore the apparent degree of dissociation of these three salts is practically constant at about 80 percent over a considerable range of concentration. The dissociation theory and the dilution law require that, if the values of the apparent molecular weight or of the degree of dissociation be plotted against concentration of the salt, the apparent molecular weight should give a curve extrapolating to half the value of the formula weight in the infinitely dilute solution and approaching the value of the formula weight in the concentrated solutions. The degree of dissociation extrapolates to 100 percent in the dilute solution and approaches zero in the concentrated solutions. Potassium nitrate and silver nitrate appear to be in qualitative agreement with the theory, although the degree of dissociation of these salts can not be made to fit the simple dilution law.

In the study of these relations, the device was used of plotting M/F (the ratio of the apparent molecular weight, M, to the formula weight, F) against the concentration. This relation is simple and is comparable for all the salts ionizing into two ions. Its connection with α, the degree of dissociation, has been shown by Lewis[1] to be:

$$\frac{M}{F} = \frac{1}{1 + \alpha}$$

In the dilute solutions the apparent molecular weight ought to extrapolate to half the formula weight if the theory be followed.

Before leaving the freezing-point data, reference may be made to the experiments of Flügel[2] and of Roth[3] who have measured the freezing-points of some dilute solutions of common salts. While in every case extrapolation points to complete dissociation of the salts in the infinitely dilute solutions, neither freezing-points nor conductivities can be made to agree with the dilution law. In the more concentrated of their solutions the same appearance of constancy of dissociation with increased concentration is evident, which continues to be marked as really concentrated solutions are reached.

The data on boiling-points reveal a similar state of affairs with the abnormalities greater in most cases. This paper will deal mostly with solutions of potassium chloride, potassium bromide, potassium iodide and potassium nitrate, as common salts showing typical abnormalities. Kahlenberg's results for potassium chloride show that in the most dilute solution (2.122 g in 100 g of water) the apparent molecular weight is 37.7. The next solution (5.124 g) gave 38.1 and then the apparent molecular weight decreased to 33.0 for the solution containing 31.84 g in 100 g of water. For this salt complete dissociation is indicated when the apparent molecular weight is 37.3 while the observed value, 33.0, represents 125% dissociation. Since this is a manifest absurdity, some explanation is called for.

The behavior of solutions of potassium bromide and potassium iodide is similar. In the most dilute solutions of potassium bromide M = 66.0, then 66.1, and then decreases gradually to 55.7 for a solution containing 51.2 g KBr in 100 g of water. The value of M for potassium iodide decreases from 94 to 78.4. In all these cases and in others, the apparent molecular weight decreases to a value which indicates more than complete dissociation instead of increasing toward a value indicating no dissociation as the concentration is increased. In regard to the boiling-points of their solutions silver nitrate and potassium nitrate are again in qualitative agreement with the theory.

After plotting Kahlenberg's data, the question arose as to whether these halide solutions would extrapolate to complete dissociation as at the freezing-point, or to some other value, as appeared possible. The early experiments were designed to confirm those of Kahlenberg and to answer this question.

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[1] "A System of Physical Chemistry," 2, 139.

[2] Z. physik Chem., 79, 577 (1912).

[3] Z. physik. Chem., 79, 599 (1912).

The first apparatus employed was one built by Mr. Ross Babbitt for use in the course in Physical Chemistry. This apparatus has proven quite useful for certain purposes such as following the sucrose inversion by observing the rise in boiling-point, or the determination of the molecular weight of non-electrolytes. The apparatus consisted of a Dewar flask of about 250 cc capacity fitted with a rubber stopper with five holes. Through these holes passed: the Beckmann thermometer; the reflux condenser tube; a small stoppered tube for introduction of solute; and two mercury-filled glass tubes sealed to the platinum heating spiral and supporting, just above the spiral, a Pyrex tube with vigreux tips to break the bubbles as they rise and pump solution around the bulb of the thermometer and out over the tube. Several runs showed the molecular weights of the potassium halides to be considerably higher in this apparatus than those found by Kahlenberg, and to vary widely and irregularly. Some electrolysis of the iodide solution was observed and the temperature readings were quite largely influenced by changes in the depth of solution and position of the thermometer. It was found, however, that if a solution containing about two grams of salt in one hundred grams of water were used as the standard, and elevations of the boiling-point measured from it rather than from pure water, the apparent molecular weights came out nearly the same as found by Kahlenberg.

This phenomenon could be best explained on the assumption that there was marked superheating of the water which decreased as salt was added. This question of superheating is the one that requires more attention than any other in the determination of boiling-points of aqueous solutions. Superheating seems to arise from two principal causes. The first of these is an inherent reluctance of the liquid in contact with the heating surface to form bubbles of vapor. A common remedy for this is the introduction of large roughened surfaces. A second cause is the fact that bubbles formed 3.5 cm. under the surface of water will be about 0.1° hotter than if formed at the surface. The principal problem in the design of boiling-point apparatus is the removal of this superheating, bringing the solvent vapor into equilibrium with the solution under no hydrostatic head. This problem becomes even more important when one considers the work of Gerlach,[1] who showed that the boiling-point of a solution is affected greatly by the material of the vessel used and the character of the heating surface. Furthermore, the effect of various salts on the superheating in a given vessel was quite erratic and unpredictable, certain salts increasing it, certain ones having a constant effect, while in others the superheating decreased with increasing concentration of the salt. If salts do thus change the superheating of a solution in an unknown specific way, it is unsafe to assume this a constant error throughout a set of determinations and the only apparatus that may be used for such experiments is one in which there is no superheating of the pure water, or at least one in which this superheating is completely removed.

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[1] Z. anal. Chem., 26, 413 (1887).

The Washburn-Read[1] modification of the Cottrell apparatus has found much favor and was believed to accomplish this. Some preliminary runs on potassium bromide in this apparatus gave a fairly constant value of M at 65 to 66, thus agreeing with Kahlenberg and others. Then a test for the superheating was devised. If this apparatus really removes superheating, the thermometer ought to read the same whether pure water and steam are being pumped over the bulb, or the bulb is in steam only. Closing the pump tube of the Cottrell apparatus by a stopper caused the thermometer to read from 0.03° to 0.04° lower than when the pump was throwing water and steam over the bulb. This means that the superheating is not completely removed in the Cottrell apparatus and that, in the familiar form, it cannot be used for accurate results in dilute salt solutions. Probably the error introduced is much less in the organic solvents to which its use has hitherto been confined.

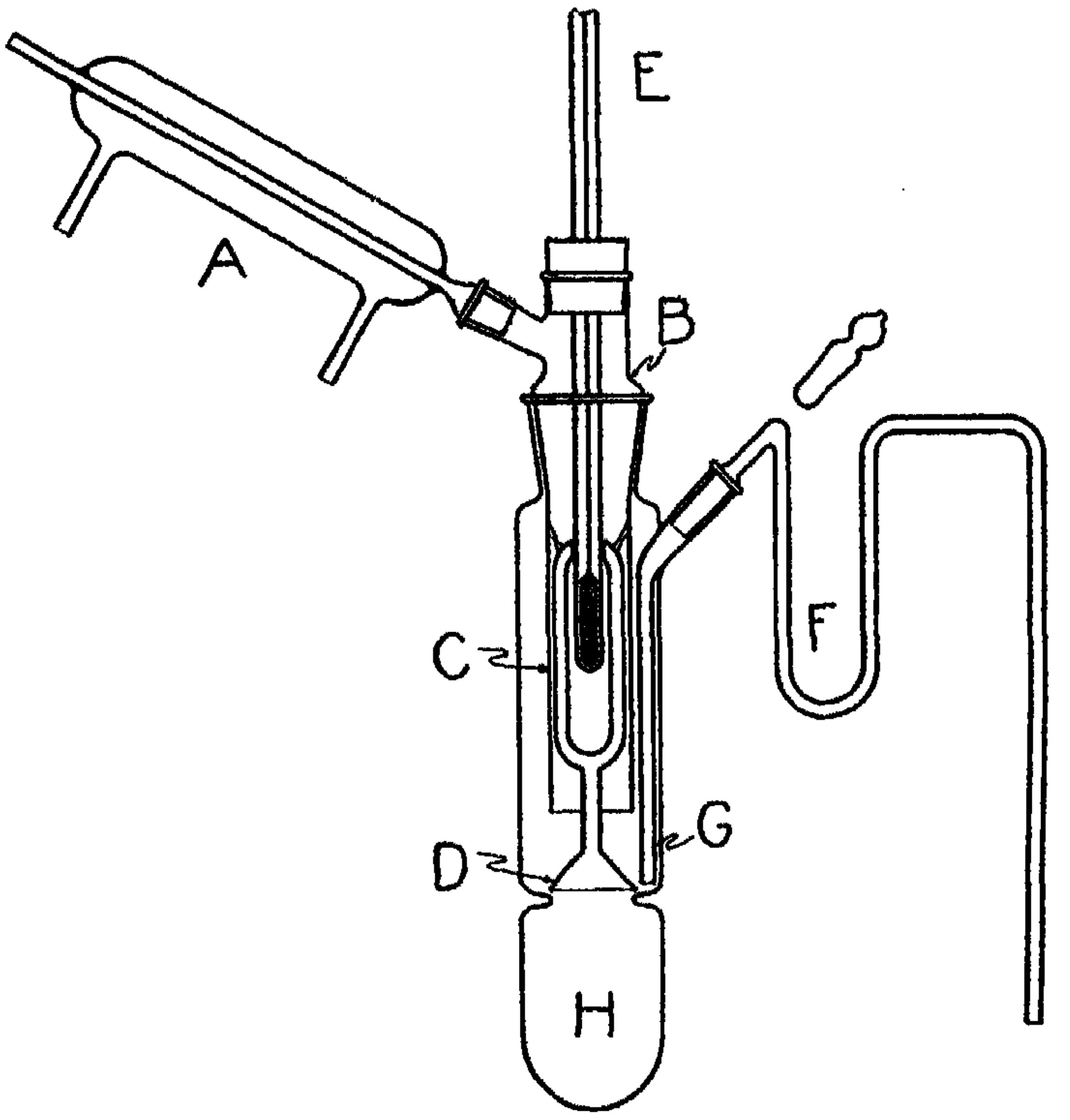

Fig. 1

A similar test with the Babbitt apparatus showed a difference of about 0.4°, to explain the results previously obtained. A modification of the Cottrell apparatus was designed which showed a superheating of about 0.008°,

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[1] J. Am. Chem. Soc., 41, 729 (1919).

which was an improvement; but would still be too large, since the observed rise in boiling-point for the dilute solution might well be half that value.

It was believed that the superheating in the Cottrell apparatus was mostly due to the hydrostatic head under which the bubbles were formed and entered the pump tube. If this large superheating were in part relieved by causing the bubbles to pass freely through a mass of the solution before entering the pump, the rest of the superheating might well be removed in that tube. To this end the pump tube was shortened and the body of the apparatus constricted in such a way that the vapor bubbles after passing upward freely through about half the liquid are deflected into the pump tube.

The new apparatus is shown in Fig. 1 and, in addition to the above, will be found to differ from the Cottrell form in some respects. The new position of the condenser A is more in accord with good theory. In the older form the condenser opened below the large stopper B and outside the sheath C, the main function of the sheath being to protect the thermometer from the cold refluxing water. If the elimination of air around the thermometer in the older form were incomplete, the reading would be too low and would rise as the air was expelled. In this form air is expelled as soon as boiling starts. Practical considerations of construction and operation may make the lower position of the condenser advisable without great sacrifice of accuracy. The present apparatus is made of Pyrex, except the condenser, the withdrawal tube F, and its stopper, which are of ordinary glass. Ground joints for these parts are made very tight by the unequal expansions of the two kinds of glass on heating to the boiling-point. Solute is introduced as pellets down the condenser or as a powder through the condenser opening, boiling being interrupted and the condenser removed. In general the same procedures as given by Washburn should be followed.

The principal advantage of this apparatus lies in the fact that superheating of the pure water is really removed, since the thermometer reads the same whether the pump be operating or not.

Experimental Work on the New Apparatus

Jablcyznski and Kon[1] reported the construction and operation of an ebullioscope in which the thermometer dips into the liquid, superheating being minimized by rapid stirring to produce a whirl which entraps vapor bubbles and brings them into contact with the solution. They admit a superheating of 0.01° and probably have more, but explicitly assume this superheating to be constant. As a test solution they employ boric acid and were able to show that its apparent molecular weight varies irregularly between 61.4 and 61.86 as the concentration increases from 1.87 to 14.5 grams of boric acid in 73 grams of water.

This agrees with the findings of Kahlenberg over a much wider concentration range. In his experiments the molecular weight changed irregularly between 61.2 and 65.2 while the concentration increased from 3.161 to 36.407

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[1] J. Chem. Soc., 123, 2953 (1923).

grams of boric acid in 100 grams of water. The change in molecular weight in both cases is so irregular that it is probably within the experimental error. In Kahlenberg's results the most dilute solution gives 63.2 and the most concentrated 62.9 and there is no sign of a definite trend with concentration.

This property of the constancy of molecular weight is shown by very few solutes in water and may possibly be accounted for on the assumption that these solutes are practically inert toward the solvent water. It certainly cannot be explained by the statement that since boric acid is so weak an acid we would scarcely expect it to be able to show any change on dilution. Nobody postulates any dissociation or change of dissociation with cane sugar and yet its apparent molecular weight changes most abnormally as evidenced by these figures from Kahlenberg.

Boiling-Points of Sugar Solutions

Grams sugar in 100 g water	20.75	29.51	36.15	289.4
Rise in boiling-point	0.30°	0.42°	0.55°	7.10°
Apparent molecular weight	360	366	342	212

The formula weight of cane sugar is 342 and yet the apparent molecular weight decreases regularly from this value to 212.

The volatility of boric acid in steam is well known and it was suggested that this might be affecting the boiling points of its solutions. Since these were used as test solutions, an answer to this question was sought. Koningh[1] found that no appreciable loss of boric acid took place on boiling aqueous solutions, until they were reduced nearly to dryness when a rapid volatilization of boric acid takes place. Skirrow[2] reports the distillation of ten cubic centimeter samples from two liter solutions of boric acid of increasing concentration. The concentration of boric acid in the distillate rises rapidly at first and then flattens to a practically constant value when a solution containing 200 grams of boric acid in a liter gives a distillate containing 0.62 grams of boric acid in a liter. This indicates that the partial pressure of the boric acid is negligible.

Boric acid was used in the new apparatus and gave results which are in agreement with the other investigators.

Boiling-Points of Boric Acid Solutions

Grams acid in 100 g water	2.41	4.82	7.23	9.64	14.44	19.28
Rise in boiling-point	0.207°	.417°	.617°	.817°	1.269°	1.609°
Apparent molecular weight	60.6	60.1	60.8	61.3	59.3	62.3

Solutions of potassium nitrate present an unexpected phenomenon. Data for these solutions are given in Table I. The formula weight is 101.1.

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[1] J. Am. Chem. Soc., 19, 385 (1897).

[2] Z. physik. Chem., 37, 84 (1901).

Table I

Boiling-Points of Potassium Nitrate Solutions

Grams KNO_3 in 100 g Water	Rise in B. P.	M calc.	Grams KNO_3 in 100 g water	Rise in B. P.	M calc.
0.626	0.059°	55.2	10.0	0.813°	64.0
1.260	0.113	57.9	15.0	1.182	65.9
1.910	0.166	59.8	20.0	1.544	67.4
2.541	0.220	60.0	25.0	1.892	68.7
3.175	0.272	60.6	30.0	2.232	70.0
4.434	0.383	60.2	35.0	2.567	70.8
6.350	0.538	61.4	40.0	2.884	72.1
9.827	0.807	63.3	50.0	3.493	74.4

These data are found to lie on a curve similar in form to the dilution law curve, except that between 0.25 and 0.75 molar the values of the degree of dissociation are decidedly higher than would fit a regular curve. This hump in the values of α is accompanied by the observation that for these concentrations in the apparatus the bubbles formed are much smaller and much more numerous, so as to raise perceptibly the level of the boiling solution. This results in the thermometer being heated abnormally by the body of the solution and the rise in boiling-point observed being abnormally high. Above or below these concentrations the appearance of the boiling potassium nitrate solutions is not markedly different from that of pure boiling water. Apparently the salt at these concentrations is having a depolymerization effect on the water.

This tendency of the potassium nitrate solutions to give little change in the apparent degree of dissociation for this intermediate concentration range was found also by Kahlenberg from conductivities at 95°.

A similar phenomenon appears in the boiling-points of the potassium halide solutions. In these, as well as in the potassium nitrate solutions, the values for the dilute solutions have been found to extrapolate to complete dissociation in the infinitely dilute solution. Further work is now being done on these solutions and will probably be communicated later as a complete system.

Consideration of these facts suggested the possibility that at higher pressures and temperatures such solutions as here mentioned might prove to be more or less abnormal than at one atmosphere and 100°. Some preliminary runs were made and are reported in the following sections.

Description of Pressure Apparatus

The water or solution to be studied was put in a Pyrex test-tube A 29 mm in diameter and 150 mm deep, with a capacity of about 100 cc, the test-tube being about three-fourths filled. The test-tube was held in a steel bomb B closed at the top with a heavy-threaded cap which was tightened by a spanner wrench. Making this joint tight proved very troublesome but was finally achieved by machining two ridges on the cap and one on the body of the bomb so that a thin, well-annealed copper gasket was pressed into a "v" and thus closed the joint, Fig. 2.

The bomb was heated in a bath of Crisco, furnished with a motor stirrer and heated partly by a direct gas flame and partly by an electrical resistance wound around the bath just inside the heavy pipe-covering insulation.

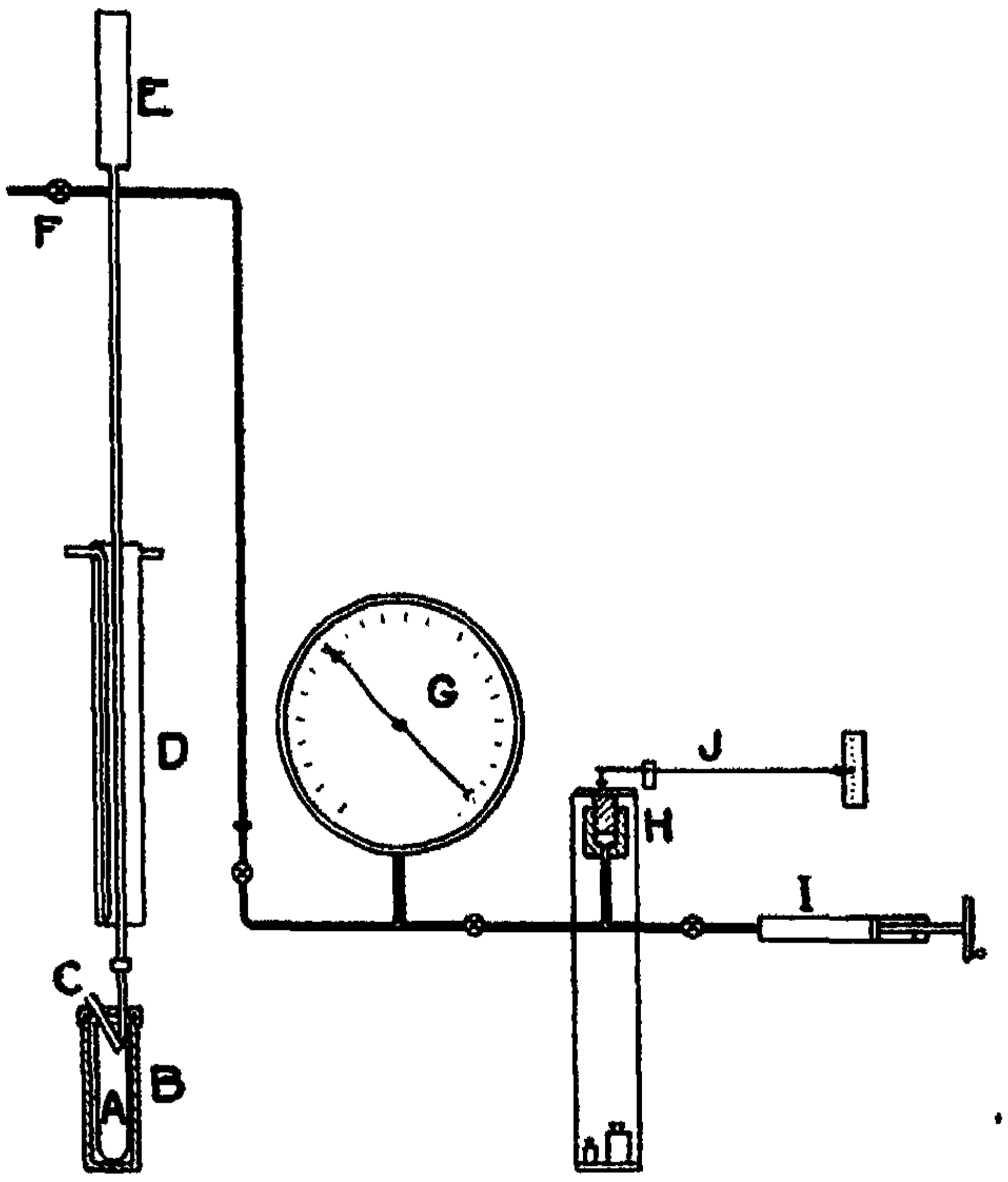

Fig. 2

Dipping into the solution tested was a monel metal thermometer well, C, brazed into the bomb cap. This well was supplied with an extension sleeve to keep the bath liquid from the thermometer and the well was filled with sufficient mercury to immerse the 76 mm immersion Nürnberg thermometer to the mark. This thermometer had a scale from 140° to 230° in fifths of a degree and was calibrated by two Bureau of Standards' thermometers having a common point at 200° and extending, one above, and the other below that point.

Dipping into the solution tested was also the monel metal lower end of the reflux condenser tube, fitted with holes just inside the bomb for the escape of steam, and provided with a beveled lower end to deflect the condensed water from the thermometer well and to cause it to reënter the solution near the side wall of the test tube. In the test-tube glass beads were used to facilitate boiling until it became apparent that they were markedly attacked by the water at the high temperatures; therefore they were replaced by strips of platinum.

The monel metal lower end was attached 9cm above the top of the bomb, by a ground-joint connection, to the quarter-inch brass pipe that made up the rest of the open system. The first vertical length of pipe was surrounded through part of its length by a brass condenser D with the cold water inlet at the lower end to ensure quick condensation.

At the top of this first section of pipe was a capacity chamber E made up of iron pipe of capacity about 300 cc. Here air pressure was applied from an air tank through a Parr needle valve F. The brass pipe was then carried down to the gage. To the height of the piston on the absolute gage this pipe was filled with oil which first actuated a very sensitive Bourdon pressure gage G made by the American Schaeffer and Budenberg Corp. This gage served as first approximation and as an index of pressure changes but was not relied on for the final readings. Beyond this gage, the oil actuated the absolute pressure-gage H built around a piston and cylinder very kindly furnished by Prof. F. G. Keyes and practically of the same design as the gages built and used by him and his associates.[1] A valve between the gage and the Bourdon permitted the use of the Bourdon alone to read pressures and another valve between the gage and the oil injector I permitted the direct contact through the air column between the boiling liquid and the absolute pressure-gage. The motion of the piston was magnified by means of a long pointer J moving over a scale. By observation of the motion of the pointer, an indication was obtained as to whether the weights used on the gage were sufficient to balance the pressures developed. Also variations in pressure caused by the boiling of the liquid were transmitted to the gage and were plainly perceptible by the oscillations of the pointer even though the capacity chamber had been included to minimize this effect. Final readings were always taken under these conditions after they had been shown to be constant for some time.

The piston, yoke, pans, and supports which constitute the fixed load on the piston were weighed and an additional weight prepared so that the total minimum load on the piston was 10,000 grams and this sum was added each time to the removable weights employed. The weights were all calibrated against standards. The constant of the gage as determined by Prof. Keyes was 0.49912 mm per gram load. This meant a total load of about 26,000 grams on the piston when the vapor pressures were about 17 atmospheres. A small motor actuating an oscillator, kept the piston from sticking during a run. The pressures were all converted to mm of mercury and reported as such. The whole apparatus was mounted on a pipe stand raising the gage 117 cm from the floor.

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[1] J. Math. Phys., Mass. Inst. of Tech., 1, 196 (1922); J. Am. Chem. Soc., 41, 589 (1919).

For tightness it was necessary to solder all joints of the apparatus except the brass ground-joint connections. These were coated with a shellac mixture and screwed tight. The bath itself had to be brazed since the temperatures employed are above the melting point of solder. In the earlier part of the experiments, lead washers were used under the monel metal thermometer well and condenser reflux pipe where they screwed into the bomb cover. The hot water soon attacked and rendered these ineffective and brazing had to be resorted to there too. In spite of the fact that, inside the pipe, the steam going to the condenser, was up to 100° hotter than the melting point of solder, the soldered parts of the ground-joint connection, joining the monel metal end and the brass condenser pipe, held fairly satisfactorily. The margin of safety was too small however, and on those occasions when the bath temperature was permitted to exceed 225° or 230°, this solder gave way, necessitating complete tearing down and resoldering. Up to this point, apparently, the condensing water running down the pipe was sufficiently cool to keep the solder from melting. It would probably have been better design to have replaced the two ground joints by one such joint above the condenser, and to have brazed the joint between the monel metal end and the brass condenser tube. Such a single ground-joint would permit the necessary adjustments of the bomb.[1]

Operation of Pressure Apparatus

For purposes of reproducibility, constancy of superheating, etc., the bath temperatures were ten degrees hotter than the bomb temperatures it was desired to measure. The latter temperatures were set arbitrarily at 180°, 190°, 200°, and 210° on the Nürnberg thermometer, which gave from the calibrations, 178.9°, 188.9°, 198.9° and 208.3° respectively as the corrected temperatures. As heating of the bath was started, a slight excess of air pressure was applied above that thought to be necessary for the desired boiling-point. Then as the bomb temperature approached the desired reading, the air pressure was slightly reduced so that the temperature did not too greatly exceed the temperature wished. When a series of readings of temperature and pressure over possibly half an hour indicated equilibrium had been reached, these data were taken as valid. This procedure gave quite satisfactory results with water and probably would with any pure solvent.

But the case of solutions offered another difficulty. In order to avoid local superheating, the bath had been designed to produce fairly uniform heating on the surface of the bomb and rather rapid stirring of the bath made this possible. But since the surface of the liquid in the tube was under slightly less pressure than the main body of the liquid, it was the portion that boiled more readily. As boiling continued and condensation started, the upper portion of the solution became increasingly diluted and the vapor pressure increased, or the temperature fell if the pressure remained constant.

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[1] The authors wish to express their deep appreciation of the very able machine work done on this apparatus by Mr. Harry Bush, the mechanician of Baker Laboratory at Cornell.

Early readings on salt solutions showed this; but the reason for it was not understood until later. Then the device was adopted of stirring the solution by a sudden release in pressure causing a vigorous ebullition with consequent stirring. The pressure was then quickly increased up to about the value expected to be in equilibrium at the desired temperature. The temperature rose readily and a few trials established the proper pressures. The appearance of equilibrium would be maintained for possibly ten minutes or more and then the pressure would increase, or more probably the temperature would fall slightly. Readings thus obtained, were taken as representing the vapor pressures of the solutions studied and the data are here represented.

Before starting the actual runs, it was necessary to discover if the bath temperature affected the readings of the thermometer in its well in the bomb. A special run with water in the tube and with the system above the condenser open to the atmosphere through the safety pet-cock, showed that a thermometer in the well maintained a constant reading of 100° although the bath temperature went as high as 170°. No higher reading than this was shown by the bomb thermometer although the bath was kept at the elevated temperatures for long periods. The conclusion seemed justified that the boiling of the water in the bomb produced sufficient cooling of the thermometer well to balance the heat carried to it by metallic conduction from the bath. It therefore seemed reasonable to assume that temperatures of the bomb, measured when the bath was ten degrees hotter than the bomb, would not be affected by this difference, or, if slightly affected, the error would be a constant one.

Naturally the first runs of the apparatus were made on water. Table II shows the results of two such runs compared with the vapor pressures of water at the same temperatures as given by the Regnault-Smithsonian Tables.

TABLE II

Temp.	178.9°	188.9°	198.9°	208.3°
I	7521 mm	9321	11412	14007
II	7549	9349	11445	14065
Average	7535	9335	11428	14036
Tables	7357	9218	11423	13848

While the agreement with the values of Regnault leaves much to be desired, the agreement of the runs themselves is satisfactory. A possible explanation for the failure of the results to agree with those of Regnault may be found in the calibration of the Nürnberg thermometer. The 200° point was the only point that could be compared directly with the standard thermometers, the other points being interpolation calibrations. At the 198.9° point, the agreement with the values of Regnault is satisfactory.

After water came the study of some solutions in water. As indicated above, boric acid has been found to be a good testing solution and was, therefore, employed in this apparatus.

Before proceeding with the data, it might be well to give the method used for the calculations of the molecular weights at these elevated temperatures. As indicated by Kendall[1] the data of Frazer and Lovelace[2] can be expressed rather well by the equation,

$$\frac{p - p_1}{p} = \frac{n}{N}$$

At the same time, Kendall adds that this is "the dilute solution equation" constituting the limiting case of the more exact equation,

$$\ln \frac{p_0}{p_1} = \frac{n}{N},$$

where p_0 is the vapor pressure of the pure solvent, p_1 that of the solution, and n and N are respectively the number of mols of solute and of solvent in the solution. Since this is the form we have recently shown to be valid,[3] we have used it to calculate the apparent molecular weight of the different solutes. Expressing this equation in terms of solute in 100 grams of water, it becomes $n = 12.78 \log \frac{p_0}{p_1}$. Of course, $n = \frac{g}{M}$ where g is the number of grams of solute in 100 grams of water and M is the molecular weight of the solute.

Solutions were used containing 10 grams and 20 grams of boric acid per 100 grams of water, heating where necessary to cause solution. The solutions were placed in the test-tube in the bomb and run exactly as the water had been run. The pressures and calculations are shown in Table III.

TABLE III

Boiling Points of Boric Acid Solutions

Boric Acid (10 grams per 100 grams of water.)

Temp.	178.9°	188.9°	198.9°	208.3°
Vapor press. water	7535	9335	11428	14036
Vapor press. Solution	7326	9043	11090	13620
Molecular weight	64.08	56.70	60.00	59.87
Average		60.16		

Boric Acid (20 grams per 100 grams of water.)

Vapor Press. Solution	7124	8756	10757	13213
Molecular weight	64.24	56.29	59.55	59.62
Average		59.92		

The formula weight of boric acid is 61.84, and it is evident that the average values here found differ from this value by about three percent. This discrepancy may be accounted for on the very reasonable assumption that 3.5 cc of water were continuously out of solution as vapor and refluxing condensed water.

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[1] J. Am. Chem Soc., 43, 1392 (1921).

[2] J. Am. Chem. Soc., 36, 2439 (1914).

[3] J. Phys. Chem., 32, 1 (1928).

The runs on the potassium chloride solutions proved less satisfactory as the design of the apparatus showed increasing signs of inadequacy. Leaks developed and it became more difficult to recognize and maintain the boiling-point. The data in Table IV show the average values for some runs on solutions containing 20 grains of potassium chloride in 100 grams of water.

TABLE IV

Boiling-Points of Potassium Chloride Solution

Temp.	178.9°	188.9°	198.9°	208.3°
Vapor press. (H_2O)	7535 mm	9335	11,428	14,036
V.P. (solution)	6995	8642	10643	12,964
Molecular weight calculated	48.35	46.71	50.63	45.35

If we may ignore the third value, these data indicate an increase in dissociation with rise in temperature. This is contrary to the findings of Noyes[1] in his high-temperature conductivity measurements in more dilute solutions than this one. On the other hand, Kahlenberg's results at 100° by the boiling-point method give an apparent molecular weight of 35.12.

It is probable that an improved apparatus designed possibly somewhat similarly to that used by Noyes will be capable of giving much more reliable and consistent results in the study of this interesting phenomenon. More recently there appeared an interesting paper by Monrad and Badger[2] who determined the boiling-points of electrolytic caustic solutions under reduced pressures. Their apparatus was of monel metal and included a Cottrell pump and a platinum resistance thermometer. Certain details would have to be altered to permit high-pressure work but the general design seems as well suited for the problem here outlined as it proved for the investigation they made.

Summary

1. A study of the data on the boiling-points of aqueous solutions reveals striking divergences from the commonly accepted theories.

2. The Washburn-Read modification of the Cottrell boiling-point apparatus is shown to be ineffective in removing the superheating of water. The test for this is described.

3. A new modification of the Cottrell apparatus is described and is shown capable of removing the superheating of pure water, thus making possible the determination of the boiling-points of dilute aqueous solutions.

4. Dilute solutions of potassium nitrate and of the potassium halides are found to be completely dissociated in the infinitely dilute solutions.

5. A preliminary study of the boiling-points of aqueous solutions under from ten to twenty atmospheres pressure is described.

6. Results with the pressure apparatus indicate that potassium chloride is as abnormal at the higher temperatures as it is known to be at 0° or at 100°.

Cornell University

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[1] Pub. Carnegie Inst., No. 63 (1907).
[2] Ind. Eng. Chem., 21, 40 (1929).

COLLOIDAL BEHAVIOR OF THE SULFIDES AND HYDROXIDES OF CADMIUM AND ZINC*

BY WILHELMINA DAUS AND OLIN F. TOWER

I. Sulfides

That cadmium and zinc sulfides can be obtained in colloidal form has long been known,[1] but few attempts have ever been made to obtain them as Liesegang's rings in different gelatinous media. In 1904, J. Hausmann[2] prepared a number of metallic sulfides in layers in gelatin. Some of them precipitated in rings, as for example, zinc sulfide, while others as cadmium sulfide formed only a single layer. He used a solution of metallic salt containing five percent gelatin, and after this had set, he added the sulfide ion in the form of ammonium sulfide or sodium sulfide. The zinc sulfide rings resulted only with the former reagent, the latter reagent precipitating the various sulfides in a single layer.

The following experiments were carried out in order to ascertain the best conditions for obtaining both of these sulfides in the form of Liesegang's rings. Three gelatinous media were tried: (a) silica, (b) agar-agar, and (c) gelatin. With all of these jellies, experiments were made both with the sulfide ion in the gel and the metallic ion in the solution above and vice versa, i.e., with the metallic ion in the gel and the sulfide ions above.

Table I

One percent Agar-agar Gel

Conc. in gel. Sodium sulfide (10 cc. of soln. of following concentrations employed)	Conc. above the gel Cadmium chloride	Results
0.1 N	0.5 N	Yellow ppt., no banding
.25 N	.75 N	Faint bands
.3 N	.7 N	Fairly good bands
.4 N	.8 N	Good rings
.5 N	.8 N	Rings obtained
.5 N	N	Fairly good bands
.6 N	N	Good rings
.75 N	N	" "
.75 N	1.5 N	" "
.75 N	2.0 N	" "
N	1.5 N	Best rings of this group (See Plate 1 a)
N	2.0 N	Bands obtained

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* Contribution from the Chemical Laboratory of Western Reserve University.

[1] Cadmium sulfide. Prost: Bull. Acad. roy. Belg. (3), 14, 312 (1887); Zinc sulfide. Winssinger: Bull. (2), 49, 452 (1888).

[2] J. Hausmann: Z. anorg. Chem., 40, 110 (1904).

TABLE II

One percent Agar-agar Gel

Conc. in gel Sodium sulfide	Conc. above the gel Cadmium sulfate	Results
0.1 N	0.5 N	No banding
.25 N	.75 N	Rings obtained
.3 N	.7 N	" "
.4 N	.8 N	Good bands
.5 N	N	Faint bands
.75 N	1.5 N	Rings formed
N	2.0 N	Best bands of this series

TABLE III

One percent Agar-agar Gel

Conc. in gel Sodium sulfide	Conc. above the gel Zinc chloride	Results
0.3 N	0.7 N	Broken bands
.4 N	.8 N	" "
.5 N	.8 N	Very good bands (Plate 2b
.75 N	1.5 N	Good bands
N	1.5 N	Best rings of this group (Plate 2 a)

(a) Silica. This gel was prepared as described by Holmes[1] and a series of experiments was carried out similar to those described below with gelatin. No banding was obtained in any case. The nearest approach was obtained with the metallic salt in the gel and a solution of ammonium sulfide above. Under these circumstances the metallic sulfide precipitated in a single band at the surface of the silica.

(b) Agar-agar. In these experiments solutions of ammonium or sodium sulfide were added to one percent agar-agar sol before it cooled, and after solidification solutions of cadmium or zinc salts were poured on top. Table I indicates the results obtained with various concentrations of sodium sulfide and cadmium chloride; in Table II are the data for sodium sulfide and cadmium sulfate; Table III shows the results obtained with sodium sulfide and zinc chloride. Reference to Table I shows that the most clearly defined rings were obtained in the tubes containing the normal sodium sulfide and 1.5 normal cadmium chloride. It is seen from Table II that concentrations of normal sodium sulfide and 2-normal cadmium sulfate give the best bands of this series. It was found that, in general, rhythmic banding resulted with the same concentrations of cadmium chloride and cadmium sulfate, but the bands obtained with the cadmium chloride were more sharply defined. Very good rings of zinc sulfide were obtained with all of the concentrations used, the best, as is shown in Table III, being obtained with normal sodium sulfide and 1.5 normal zinc chloride.

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[1] Holmes: J. Phys. Chem. 21, 709 (1917).

When ammonium sulfide was substituted for sodium sulfide in agar-agar, it was found that the gel withdrew from the sides of the tubes, and the sulfide precipitated there instead of inside the gel.

(c) Gelatin. Tables IV, V, and VI show the results obtained when gelatin was used as the medium for the precipitation of the cadmium and zinc sulfides. Here, as in the case with agar-agar, ammonium or sodium sulfides were added to the gel and the cadmium or zinc salt poured on top. As these tables show, the most clearly defined bands of cadmium sulfide were formed with ammonium sulfide 0.75 normal in concentration and 1.5 normal cadmium chloride. The best rings of zinc sulfide were obtained in the one case with 0.75 normal ammonium sulfide and 2 normal zinc chloride; in the other the rings were about equally as good with the various concentrations of sodium sulfide and zinc chloride. The table showing the results of the experiments in which cadmium sulfate was substituted for cadmium chloride is not included, for these results were similar to those obtained using cadmium chloride.

Plate 1

Plate 2

TABLE IV
Five percent Gelatin

Conc. in gel Ammonium sulfide	Conc. above the gel Cadmium chloride	Results
0.1 N	0.5 N	No bands obtained
.3 N	.7 N	Faint rings
.4 N	.8 N	Good bands
.5 N	N	Bands
.75 N	N	"
.75 N	1.5 N	Best rings of this series (Plate 1 b)

When sodium sulfide was used in gelatin, the gelatin did not set readily, and seemed to mold quickly. No rings of cadmium sulfide were formed in this case, for although there was a firm gel at the top of the tube, the gelatin was in the sol form lower down. Rings of zinc sulfide were obtained with the sodium sulfide and zinc chloride, but these were not as clear as those obtained with the ammonium sulfide, nor those obtained in agar-agar. Here also the gelatin was in the sol form in the lower half of the tube, so rings were formed only in the upper portion.

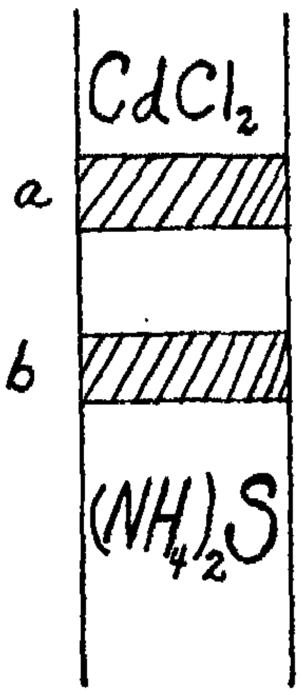

Fig. 1

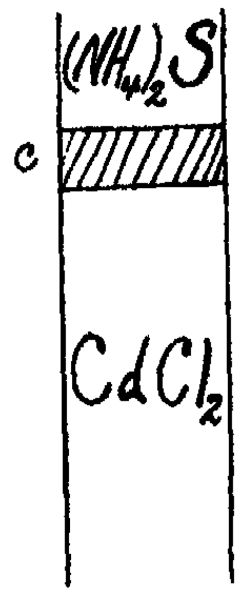

Fig. 2

Theoretical. The theory of Bradford[1] that rings of this sort are formed by the layer of precipitate adsorbing the ions of the adjacent electrolyte and thus giving zones practically free from them, seems to explain most adequately the results obtained. Rings were obtained when the cadmium ions were above the gel which contained the sulfide ions. One can account for this on the theory that the sulfide ions are strongly adsorbed by the first precipitated layer *a*, Fig. 1, leaving a space *a-b* so free from these ions that no further precipitation results until the cadmium ions encounter a sufficient concentration of sulfide ions somewhere below, as at *b*, where the process repeats itself. In case the sulfide ions are above the gel, a precipitate forms at the junction *c*, Fig. 2. This precipitate adsorbs sulfide ions strongly, and we have to assume, furthermore, that this adsorption is so strong that no sulfide ions pass through the precipitated layer and diffuse below to meet the cadmium ions. In other words, the assumption that cadmium ions are not so strongly adsorbed as sulfide ions, and can diffuse through the precipitated layer accounts for the facts observed.

This, of course, does not explain the non-formation of rings when silica gel was used; but this seemed to be directly related to the action of the strongly alkaline sodium and ammonium sulfide solutions on the acid gels.

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[1] Bradford: Science Progress, 10, 369 (1916); Biochem. J., 10, 169 (1916); 11, 14 (1917); 14, 29, 474 (1920). A summary of these articles is given in Kolloid-Z. 30, 364 (1922).

Table V

Five percent Gelatin

Conc. in gel Ammonium sulfide	Conc. above the gel Zinc chloride	Results
0.4 N	0.8 N	Good rings
.5 N	N	" "
.75 N	N	Best bands in this group
.75 N	2.0 N	Very good rings

Table VI

Five percent Gelatin

Conc. in gel Sodium sulfide	Conc. above the gel Zinc chloride	Results
0.4 N	0.8 N	These concentrations all give clearly defined rings, but not as good as in agar-agar. The gelatin did not set at the bottom of the tube.
.5 N	N	
.75 N	N	
.75 N	2.0 N	

II. Hydroxides

Colloidal cadmium hydroxide was prepared by a method formerly used in this laboratory for the preparation of colloidal nickel hydroxide.[1] A dilute solution of cadmium chloride was treated with an equivalent quantity of sodium hydroxide, and the resulting precipitate washed by decantation in a centrifuge. The procedure giving the best results is as follows: 50 cc. of half normal cadmium chloride were added to 500 cc. of water, and then 50 cc. of half normal sodium hydroxide were mixed rapidly with this solution (thus the concentrations were about 0.08 normal). A finely divided precipitate formed which settled slowly. If the solutions used were either too dilute or too concentrated a flocculent precipitate formed which settled rapidly.

Portions of 50 cc. each were centrifuged until the precipitate settled, the supernatant liquid poured off, distilled water added, and the process repeated several times. The precipitates were finally suspended in distilled water and allowed to stand over night. It was found on the average that after centrifuging five times the precipitated hydroxide tended to go into colloidal solution on standing. The colloidal solutions thus obtained were opalescent. The supernatant liquid from the seventh washing showed an absence of chloride ions, but the others which had been washed fewer times gave a test for chloride ions which would indicate that the sodium ion is probably adsorbed giving a stabilizing effect. There seems to be an optimum concentration of the electrolyte, for, if the cadmium hydroxide was not washed enough, a colloid was not obtained, as was also the case when too much of the sodium chloride was removed.

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[1] O. F. Tower: J. Phys. Chem., **28**, 176 (1924).

The amount of cadmium hydroxide in solution was determined electrolytically by the oxalate method of Classen.[1] It was found that, employing the concentrations of cadmium chloride and sodium hydroxide given above, the amount of colloid obtained at different trials was quite constantly 0.3466 grams of cadmium hydroxide per liter. This colloid is rather stable; after standing for about two weeks it slowly settles out.

A cataphoresis experiment showed that the cadmium hydroxide, like most other metallic hydroxides in colloidal solution, was positively charged.

Colloidal zinc hydroxide was prepared by the same method as the cadmium hydroxide. It was found in this case that a little more than the equivalent amount of sodium hydroxide gave the best results. A flocculent precipitate was at first obtained, but upon standing fifteen minutes or so, it was peptized, and a very finely divided precipitate obtained, which was hard to settle by the centrifuge. The time required to wash the zinc hydroxide was much longer than in the case of the cadmium hydroxide, because the precipitate settled so slowly. Approximately 0.08 normal solutions of zinc chlorides and sodium hydroxide were used in this case also, being mixed in the same way as above,—50 cc. of half normal zinc chloride in 500 cc. of water, and then about 55 cc. of the half normal sodium hydroxide added. No test for hydroxyl ion could be obtained after the second washing. 50 cc. portions were treated in the manner described for cadmium hydroxide. It was found here also that the portion which had been washed five times yielded the most stable colloid. 100 cc. of this colloidal solution were used to determine electrolytically the amount of zinc hydroxide, according to the method of Reinhart and Ihle.[2]

The colloidal zinc hydroxide was rather unstable, settling out after two days, and varying amounts were obtained in solution, the most being 0.1383 grams of zinc hydroxide per liter.

Hantzsch[3] in 1902 found that a solution of zinc hydroxide in alkalies is almost entirely in colloidal form. He did not dialyze these solutions, but he found a considerable excess of alkali necessary to hold the zinc hydroxide in solution. Zinc hydroxide, which was held in solution with a great excess of sodium hydroxide, was dialyzed until free from both hydroxyl ions and chloride ions. A precipitate of zinc hydroxide formed inside the parchment tube. If zinc hydroxide, which was prepared as described above, was dialyzed instead of being centrifuged, no colloid formed, a precipitate settling out as in the case just mentioned.

Gels of both cadmium hydroxide and zinc hydroxide were prepared by employing the method previously used in this laboratory for the preparation of nickel hydroxide gel.[4] For the cadmium hydroxide gels, a solution of cadmium acetate in glycerine, containing eight grams of cadmium acetate $[Cd(C_2H_3O_2)_2{:}3H_2O]$ to 100 cc. of glycerine, and a normal solution of potassium

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[1] Classen: "Quant. Analyse durch Elektrolyse," 4th Ed., p. 175.
[2] Reinhart and Ihle: J. prakt. Chem., (2), 24, 193 (1881).
[3] Hantzsch: Z. anorg. Chem., 30, 299 (1902).
[4] O. F. Tower and Martha C. Cooke: J. Phys. Chem., 26, 728 (1922).

hydroxide in alcohol, were used. The best gels were obtained when the following concentrations were employed; as is shown in Table VII: (1) 5 cc. of the cadmium acetate solution, 5 c.c. of glycerine, and 8 c.c. of the potassium hydroxide solution; (2) 5 c.c. of cadmium acetate solution, 5 c.c. of glycerine, and 10 c.c. of the alcoholic potassium hydroxide. When the cadmium acetate and alcoholic potassium hydroxide solutions were mixed without the further addition of glycerine, a gel did not form; the resulting solution was more viscous than the original, and was more opaque than the gel, but the cadmium hydroxide did not precipitate out. Too great a dilution with glycerine had the effect just mentioned, as did dilution with small amounts of alcohol and water. Some of these solutions formed gels several days later. If too much alcohol or water was employed for dilution, the cadmium hydroxide precipitated out upon standing. The gels, if shaken with water or alcohol, changed to the sol form, but the cadmium hydroxide remained in colloidal solution, as indicated by the viscosity and opalescence as well as the failure to form a precipitate.

The cadmium hydroxide gels when first formed were rather opaque, but upon standing became opalescent; the opaqueness seemed to be due to air bubbles, because these could be seen in the gel upon allowing it to stand. These gels were very stable, exhibiting only a small amount of syneresis upon standing four months.

The zinc hydroxide gels prepared by the same method were not as stable as the cadmium hydroxide gels, as the table indicates. A saturated solution

TABLE VII

Cadmium Hydroxide Gels

Concentration of cadmium acetate in glycerine—8%

Concentration of potassium hydroxide in alcohol—Normal

Cadmium acetate solution cc. used	Potassium hydroxide solution cc. used	Glycerine cc. used	Water cc. used	Alcohol cc. used	Results
3	6	7	0	0	No gel formed
3	8	7	0	0	Semi-gel, later forms gel
4	6	6	0	0	" " " "
4	8	8	0	0	Gel forms
5	8	5	0	0	Best gel in this group
5	8	0	5	0	No gel, later separates
5	8	0	0	5	" " " "
5	10	5	0	0	Very good gel
6	8	4	0	0	Good gel
6	8	0	6	0	No gel
6	8	0	0	6	" "
7	10	3	0	0	Semi-solid, gel later
8	5	0	0	5	Semi-gel, then ppt.
8	5	0	7	0	" " "
10	10	0	0	0	No gel formed

TABLE VIII
Zinc Hydroxide Gels

Concentration of zinc acetate in glycerine—5%
Concentration of potassium hydroxide in alcohol—Normal

Zinc acetate cc. used	Potassium hydroxide cc. used	Glycerine cc. used	Water cc. used	Alcohol cc. used	Results
5	8	5	0	0	Semi-solid
5	10	5	0	0	Opaque gel, syneresis in 5 min., ppt. next day.
6	9	5	0	0	" "
7	8	3	0	0	Good gel which shows syneresis next day, and ppt. in a few days.
10	10	0	0	0	" " " " (Best gel of this group)
10	6	0	0	5	No gel, ppt. soon
10	8	0	8	0	" "

(Other concentrations of alcohol and water give similar results.)

Note: The solutions formed when alcohol and water were added (Table VIII) appeared to be colloidal, but in a few hours a precipitate settled out.

of zinc acetate $[Zn(C_2H_3O_2)_2{:}3H_2O]$ in glycerine contains approximately five grams acetate per 100 cc. of glycerine. Equal amounts of this solution and normal potassium hydroxide solution (in alcohol) gave the best gels. Solutions which were diluted with small amounts of glycerine gave very unstable gels, those diluted with water or alcohol did not set, and a precipitate soon settled out. All of the zinc hydroxide gels were apaque. Those prepared with the favorable concentrations set immediately, as did the cadmium hydroxide gels. The ones which had been diluted with small amounts of glycerine underwent syneresis in about five minutes, and those which formed the best jellies exhibited syneresis the next morning. Upon standing a few days a white precipitate settled out. If these gels were shaken with water or alcohol, a solution which appeared colloidal was obtained, but a precipitate soon settled out.

Summary

1. The different conditions under which cadmium sulfide and zinc sulfide yield Liesegang rings have been investigated. It was found that rings could be obtained with either a gel of agar-agar or gelatin, and that the sulfide ion must be in the gel, and the metallic ion above the gel.

2. Bradford's theory of ring formation seems to account for the results obtained, with the addition that the sulfide ions are more strongly adsorbed by the precipitated sulfides than are the metallic ions.

3. Colloidal solutions of cadmium and zinc hydroxides have been prepared according to a method formerly used in this laboratory for obtaining colloidal nickel hydroxide.

4. Gels of cadmium and zinc hydroxides have been prepared in solutions containing glycerine.

SULPHURIC ACID AND HYDRIODIC ACID*

BY FLORENCE BUSH

Some years ago Professor Phelps of Marshall College called the attention of Professor Bancroft to a laboratory experiment which was done regularly by the students at Tufts College in the introductory course. To show a difference in stability between hydrochloric acid and hydriodic acid, potassium chloride crystals were added in one case, and potassium iodide crystals in another case, to concentrated sulphuric acid. With potassium chloride hydrochloric acid is given off, while sulphuric acid oxidizes hydriodic acid to iodine. This was what the experiment was intended to show, and did show. The interesting thing was that hydrogen sulphide is said to come off first, and sulphur dioxide later. The gas evolved by the reaction was tested immediately with lead acetate paper and a positive test for hydrogen sulphide was obtained. It seemed desirable to find out why the more strongly reduced compound was apparently produced first.

According to Mellor[1], Gay-Lussac found that concentrated sulphuric acid and hydriodic acid react according to the equation

$$H_2SO_4 + 2HI = SO_2 + 2H_2O + I_2,$$

while Soubeiran noted that this reaction reverses when the concentration of the sulphuric acid is sufficiently low. With concentrated sulphuric acid and an excess of hydriodic acid, the reaction product is hydrogen sulphide,

$$H_2SO_4 + 8HI = H_2S + 4H_2 + 4I_2$$

because hydriodic acid reduces sulphur dioxide to hydrogen sulphide. It should therefore be possible to get either hydrogen sulphide or sulphur dioxide from the reaction between sulphuric acid and hydriodic acid, depending on the relative amounts in the reacting zone.

The following experiments were made with the purposes of testing this qualitatively. A small beaker was used, fitted with a cover for stirring and testing gases. Concentrated sulphuric acid was treated with sodium bisulphite until the solution smelled strongly of sulphur dioxide. Potassium iodide crystals were added without stirring and a test for hydrogen sulphide was obtained at once. In this case the effective concentration of sulphurous acid was high enough so that it was reduced by the hydriodic acid to some extent. The formation of sulphur in considerable amounts shows that the hydrogen sulphide concentration was high enough to cause some of it to react with the excess of sulphurous acid (or sulphur dioxide) according to the equation

$$SO_2 + 2H_2S = 3S + 2H_2O.$$

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*This work was done as part of the senior thesis under Professor Bancroft in the autumn of 1926.

[1] "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 2, 204, 210 (1922).

The experiment was repeated, stirring vigorously the solution which contained an excess of sulphur dioxide. A test for hydrogen sulphide was obtained at once and sulphur was also formed, showing that stirring does not change the reaction qualitatively.

Concentrated sulphuric acid was next saturated with an excess of crushed iodine crystals and this mixture was stirred. Potassium iodide crystals were added in small amounts with constant stirring. A test for hydrogen sulphide was obtained immediately.

Powdered potassium iodide crystals were added in small amounts to a concentrated sulphuric acid solution which was kept stirred constantly. Sulphur dioxide alone was detected until a very large amount of iodine had formed. Further additions of powdered potassium iodide then gave a test for hydrogen sulphide. The addition of small crystals and the vigorous stirring kept the hydriodic acid concentration low and prevented the formation of hydrogen sulphide until a sufficiently high concentration of sulphurous acid had been built up.

That iodine itself affects the course of the reaction is shown by the following experiment. Concentrated sulphuric acid was saturated with an excess of crushed iodine crystals and was kept stirred vigorously. On addition of potassium iodide crystals in small amounts, a test for hydrogen sulphide was obtained at once. This may mean that the presence of iodine stabilizes hydriodic acid to some extent, so that the concentration of the latter builds up sufficiently to permit the hydrogen sulphide reaction to take place, or it may mean that iodine catalyzes the reaction between hydriodic acid and sulphurous acid. This result was quite unexpected and calls for further investigation.

The fact that hydrogen sulphide is obtained at once when potassium iodide crystals are added to concentrated sulphuric acid shows that there is something which causes a relatively high concentration of hydriodic acid. Initially we have a high concentration of sulphuric acid and neither sulphur dioxide nor iodine. The difference must occur at the surface of the potassium iodide crystals. With moderately large crystals we shall have at their surfaces a film of potassium bisulphate, hydriodic acid, sulphuric acid, and potassium iodide, in which the concentration of sulphuric acid may easily not be high enough to oxidize hydriodic acid rapidly, and which may not be high enough to oxidize it at all. In that case, oxidation will occur when the hydriodic acid in relatively high concentration diffuses out of the surface film.

If that is the case we ought to get no hydrogen sulphide if we stir vigorously or if we make the potassium iodide crystals small enough. It has already been stated that only sulphurous acid is formed when powdered potassium iodide crystals are added with vigorous stirring. We have also found the same result when we add coarser crystals of potassium iodide with vigorous stirring or very finely powdered crystals without stirring.

These experiments throw light on some work done by Faraday[1] in 1834 on the electrolysis of sulphuric acid. "On experimenting with sulphuric acid, I found no reason to believe that it was by itself a conductor of, or decomposable by, electricity, although I had previously been of that opinion. When very strong it is a much worse conductor than if diluted. If then subjected to the action of a powerful battery, oxygen appears at the anode, or positive electrode, although much is absorbed, and hydrogen and sulphur appear at the cathode, or negative electrode. Now the hydrogen has with me always been pure, not sulphuretted, and has been deficient in proportion to the sulphur present, so that it is evident that when decomposition occurred water must have been decomposed. I endeavoured to make the experiment with anhydrous sulphuric acid; and it appeared to me that, when fused, such acid was not a conductor, nor decomposed; but I had not enough of the dry acid in my possession to allow me to decide the point satisfactorily. My belief is, that when sulphur appears during the action of the pile on sulphuric acid, it is the result of a secondary action, and that the acid itself is not electrolyzable."

"Pure liquid sulphurous acid does not conduct nor suffer decomposition by the voltaic current,[2] but, when dissolved in water, the solution acquires conducting power, and is decomposed, yielding oxygen at the anode, and hydrogen and sulphur at the cathode.

"A solution containing sulphuric acid in addition to the sulphurous acid, was a better conductor. It gave very little gas at either electrode: that at the anode was oxygen, that at the cathode pure hydrogen. From the cathode also rose a white turbid stream, consisting of diffused sulphur, which soon rendered the whole solution milky. The volumes of gases were in no regular proportions to the quantities evolved from water in the voltameter. I conclude that the sulphurous acid was not at all affected by the electric current in any of these cases and that the water present was the only body electrochemically decomposed; that, at the anode, the oxygen from the water converted the sulphurous acid into sulphuric acid, and at the cathode, the hydrogen electrically evolved decomposed the sulphurous acid, combining with its oxygen, and setting its sulphur free. I conclude that the sulphur at the negative electrode was only a secondary result; and, in fact, no part of it was found combined with the small portion of hydrogen which escaped when weak solutions of sulphurous acid were used.

"I have already given my reasons for concluding that sulphuric acid is not electrolyzable, *i.e.* not decomposable directly by the electric current, but occasionally suffering by a secondary reaction at the cathode from the hydrogen evolved there. In the year 1800, Davy considered the sulphur from sulphuric acid as the result of the action of the nascent hydrogen.[3] In 1804,

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[1] "Experimental Researches in Electricity," **1**, 201, 223 (1839).

[2] See also De la Rive: Bibliothèque Universelle, **40**, 205; or Quarterly Journal of Science, **27**, 407.

[3] Nicholson's Quarterly Journal, **4**, 280, 281.

Hisinger and Berzelius stated that it was the direct result of the action of the voltaic pile,[1] an opinion which from that time Davy seems to have adopted, and which has since been commonly received by all. The change of my own opinion requires that I should correct what I have already said of the decomposition of sulphuric acid in a former series of these Researches (552): I do not now think that the appearance of the sulphur at the negative electrode is an immediate consequence of electrolytic action."

The opinion which Faraday had formerly held is to be found on p. 160 (1833). "The theory I have advanced accords in a most satisfactory manner with the fact of an element or substance finding its place of rest, or rather of evolution, sometimes at one pole and sometimes at the other. Sulphur illustrates this effect very well. When sulphuric acid is decomposed by the pile, sulphur is evolved at the negative pole; but when sulphuret of silver is decomposed in a similar way, then the sulphur appears at the positive pole; and if a hot platina pole be used so as to vaporize the sulphur evolved in the latter case, then the relation of that pole to the sulphur is exactly the same as the relation of the same pole to oxygen upon its immersion in water. In both cases the element evolved is liberated at the pole, but not retained by it: but by virtue of its elastic, uncombinable, and immiscible condition passes away into the surrounding medium. The sulphur is evidently determined in these opposite directions by its opposite chemical relations to oxygen and silver; and it is to such relations generally that I have referred all electro-chemical phenomena. Where they do not exist, no electro-chemical action can take place. Where they are strongest, it is most powerful; where they are reversed, the direction of transfer of the substance is reversed with them."

We know now that the shortage of oxygen at the anode, when sulphuric acid is electrolyzed, is due to the formation of persulphuric acid. It is easy to see that sulphuric acid can be reduced at the cathode to sulphurous acid and to hydrogen sulphide; but no direct reduction of sulphur to hydrogen sulphide is probable.

The answer is apparently that the electrolytic reduction is normal, giving sulphurous acid and hydrogen sulphide, which then react to form sulphur according to the equation,

$$SO_2 + 2H_2S = 3S + 2H_2O.$$

This is confirmed by the fact that a great deal of sulphur is formed, as Faraday himself says, when one electrolyzes a sulphurous acid solution to which some sulphuric acid is added. With a lead cathode in sulphuric acid, the amount of sulphur formed in a given time decreases markedly with rapid stirring, because then very little of the resulting sulphurous acid is reduced further. It is probable that with a platinum cathode and consequently a smaller over-voltage, the amount of sulphur formed for the same current density could be decreased still more; but this experiment was not tried.

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[1] Ann. Chimie, 51, 173 (1804).

While concentrated sulphuric acid oxidizes hydriodic acid to iodine, it is well known that in dilute solution[1] sulphur reduces iodine to hydriodic acid. "Sulphurous acid is oxidised quantitatively to sulphuric acid by N/10 iodine, without the separation of sulphur. The intermediate formation of the yellow compound, $SO_2.HI$, which occurs in solutions of moderate concentration, has no influence on the final result. The low results obtained when sulphurous acid is exposed to the air during the titration are due entirely to evaporation of sulphur dioxide, the amount of atmospheric oxidation being negligible.

"Sodium sulphite solution is more readily oxidised than sulphurous acid; consequently atmospheric oxidation is a more disturbing factor when sodium sulphite is titrated with iodine. Since the reaction between sulphurous acid and iodine is not reversed under the state of dilution obtaining in volumetric analysis, the addition of sodium hydrogen carbonate to neutralise hydriodic acid, as when solutions of arsenious compounds are being titrated, is unnecessary; and since a sulphite solution is oxidised so quickly, it is not necessary to allow a time interval for such oxidation to be completed."

Since concentrated sulphuric acid reacts with hydriodic acid to form iodine and sulphur dioxide, and since this reaction reverses when the sulphuric acid is more dilute, there must be a concentration of sulphuric acid at which the reaction reverses. As a first approximation fifty percent sulphuric acid is about the limit at which sulphur dioxide will still reduce iodine. It might be interesting to determine this point electrometrically.

From the experiments described in the first part of this paper it is evident that there is a range of concentrations over which hydriodic acid reduces sulphurous acid to hydrogen sulphide, which may then react with excess sulphur dioxide to give sulphur. That sulphurous acid or sulphur dioxide should be a stronger oxidizing agent in a more strongly acid solution is merely another instance of the almost universal fact that acid increases the oxidizing power of oxidizing agents and that alkali increases the reducing power of reducing agents, quite regardless whether the oxidizing or reducing agent is or is not an electrolyte in the ordinary sense of the term.

Wardlaw, Carter and Clews[2] are not satisfied with so simple a statement as the one just given. "The facts that sulphur dioxide reduces most readily in a dilute acid medium, and that it oxidises most readily in a strong acid medium,[3] may be correlated if oxidation and reduction are explained on an ionic basis, oxidation being represented by the surrender of positive charges and reduction by the transference of negative charges.

"Sulphur dioxide in aqueous solution is generally regarded as a moderately weak acid, ionising principally into $H^{\cdot}$, HSO_3', and SO_3'' ions. [It is not

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[1] Macaulay: J. Chem. Soc., 121, 552 (1922).

[2] J. Chem. Soc., 117, 1247 (1920).

[3] [They mean that sulphur dioxide reduces or oxidises something else—just the opposite of what they actually say.]

clear how this differs in principle from the ionization of sulphuric acid, which is usually classed as a strong acid.] It is in this condition that it reacts as a reducing agent. Thus:

$$2Fe^{\cdot\cdot\cdot} + SO_3 + H_2O = 2Fe^{\cdot\cdot} + SO_4'' + 2H^{\cdot}.$$

In strongly acid solution containing a large number of hydrions, the concentration of SO_3'' ions will be reduced, and, on the above assumption, its power of reducing should be diminished. This is in accordance with the experimental results.

"Now let it be assumed that sulphur dioxide is capable of ionizing to an extremely minute extent as a base, yielding a correspondingly minute amount of sulphur ions. It has been shown that the sulphoxides, the organic analogues of sulphur dioxide, have basic properties.[1] This tendency will be all the greater the larger the number of hydrions present in solution. Thus:

$$SO_2 \overset{H_2O}{\rightleftharpoons} OS(OH)_2 \rightleftharpoons SO^{\cdot\cdot} + 2\,(OH)',$$

$$SO^{\cdot\cdot} \overset{H_2O}{\rightleftharpoons} H_2OS^{\cdot\cdot\cdot\cdot} + 2(OH)'.$$

In view of the large number of hydrions present in the solution, the concentration of hydroxyl ions would be reduced to a very low value and the reaction toward the right favoured. Oxidation is now represented

$$S^{\cdot\cdot\cdot\cdot} + 4Fe^{\cdot\cdot} \longrightarrow 4\,Fe^{\cdot\cdot\cdot} + S.$$

If oxidation takes place due to the ion $SO^{\cdot\cdot}$,

$$2SO^{\cdot\cdot} + 4\,Fe^{\cdot\cdot} \longrightarrow 4Fe^{\cdot\cdot\cdot} + 2SO,$$

$$2SO + H_2O \longrightarrow H_2S_2O_3,$$

which represents an intermediate stage in the reduction of sulphur dioxide to sulphur. Thiosulphuric acid would break up into sulphur dioxide and sulphur. It may be observed that the latter hypothesis is in many respects a re-statement of the thionyl chloride hypothesis[2] applied ionically and more generally."

Wardlaw is apparently adopting a view similar to that advanced by Faraday in 1833 and discarded by him in 1834. He ignores the whole question of hydrogen sulphide. The reaction between hydrogen sulphide and sulphur dioxide has been studied recently by Matthews.[3]

"To bring about the decomposition of a mixture of sulphur dioxide and hydrogen sulphide in either the gaseous or the liquid state, the addition of a third substance is necessary, and it has been demonstrated that this third substance must be in the liquid phase. There is no rigid relationship between the values of the dielectric constants of substances and their chemical activity as measured by their ability to bring about the interaction of hydrogen sul-

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[1] Fromm and Raiziss: Ann., **374**, 90 (1910); Fromm: **396**, 75 (1913).

[2] Wardlaw and Clews: J. Chem. Soc., **117**, 1093 (1920).

[3] J. Chem. Soc., **1926**, 2270.

phide and sulphur dioxide. The assertion that hydrogen sulphide and sulphur dioxide when in a liquid state react vigorously, even when dry, has been disproved. It is suggested that the activity of a substance in causing decomposition is dependent on the solubility of the two gases in the substance when liquid, or on the solubility of the solid in the liquid mixture of the two gases."

Atmospheric oxygen oxidizes hydriodic acid more rapidly than it does sulphur dioxide. Consequently we may have the oxidation of sulphur dioxide by atmospheric oxygen taking place in two stages:

$$2SO_2 + 4H_2O + 2I_2 = 2H_2SO_4 + 4HI$$

and

$$4HI + O_2 = 2H_2O + 2I_2.$$

This is, therefore, an induced reaction[1] with oxygen as the actor, hydriodic acid as the inductor, and sulphur dioxide or sulphurous acid as the acceptor. Since the hydriodic acid is regenerated as long as there is an excess of sulphur dioxide and as long as the sulphuric acid concentration stays below about fifty percent, hydriodic acid catalyzes the reaction between sulphurous acid and oxygen, though not very rapidly.

The general results of this paper are:

1. Concentrated sulphuric acid oxidizes hydriodic acid to iodine. With a relatively low concentration of hydriodic acid the sulphuric acid is reduced to sulphurous acid; with a relatively high concentration of hydriodic acid the reduction goes to hydrogen sulphide. Sulphur is due to the reaction between hydrogen sulphide and sulphurous acid.

2. When potassium iodide crystals are dropped into concentrated sulphuric acid, the relative amounts of sulphurous acid, hydrogen sulphide: and sulphur can be varied within rather wide limits by changing the sizes of the potassium iodide crystals and the rate of stirring.

3. Iodine crystals seem to catalyze the reduction of sulphurous acid to hydrogen sulphide; but this has not been proved to be the case.

4. The formation of sulphur when concentrated sulphuric acid is electrolyzed is due to the reaction between hydrogen sulphide and sulphurous acid. There is no evidence for the existence of a sulphur or a sulphur-oxygen cation.

5. Since sulphurous acid reduces iodine to hydriodic acid in weakly, and oxidizes hydriodic acid to iodine in strongly, acid solutions, there must be a concentration of sulphuric acid above which sulphurous acid does not reduce iodine. This seems to come at about fifty percent sulphuric acid.

6. The change of sulphurous acid from a reducing agent to an oxidizing agent with increasing concentration of sulphuric acid seems to be another

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[1] Luther and Schilow: Z. physik. Chem., **46**, 777 (1903).

instance of the practically general case that a reducing agent is more powerful in an alkaline solution and that an oxidizing agent is more powerful in an acid solution.

7. Since atmospheric oxygen oxidizes hydriodic acid more rapidly than it does sulphurous acid, hydriodic acid acts as a catalyst in the oxidation of sulphurous acid by atmospheric oxygen so long as sulphurous acid is present in excess relatively to the hydriodic acid and so long as the sulphuric acid concentration is well below fifty percent.

8. If we consider the preceding reaction as an induced reaction, oxygen is the actor, hydriodic acid the inductor, and sulphurous acid the acceptor. This is a clean-cut case of catalysis in a homogeneous system with the intermediate formation of a definite chemical substance, iodine.

Cornell University.

STUDIES ON SILVER SOLS

BY SIMON KLOSKY

In view of the statements in the literature,[1,2,3,4] it was thought desirable to investigate thoroughly the effects of adding ethyl alcohol to a well-defined hydrophobic sol.

With the criticisms of Bancroft[5] in mind, silver sols were chosen as they are easy to prepare by the method of Kohlschütter[6] and according to the modification worked out in our laboratory, should be very pure as no extraneous chemicals are introduced.

The effect of adding alcohol to silver sols has been investigated formerly[11] but not under the controlled conditions wished for by the present writer.

Preparation of the Sols

It was found by Carmody[8] that if silver oxide, prepared by mixing equivalent solutions of analyzed silver nitrate and sodium hydroxide at 50°C. and washed by decantation until all sodium was absent, is suspended in water heated to 100°C. and rapidly filtered, an opalescent filtrate is obtained, which on reheating to 80°C. slowly produces a sol with all the characteristics of the familiar Kohlschütter[6] silver sol. This method differs from that of Garard and Duckers[10] who used gelatine as a protective agent.

Twenty liters of this sol were prepared and concentrated by evaporation on a water bath. Varying volumes of it were mixed with ethyl alcohol obtained from a well-known producer of this chemical, which has been fractionally distilled three times. No attempt was made to dry it, but the density was determined by pyknometer and the water content read from tables. In this way mixtures containing 0 to 90% alcohol by volume and differing by 5% were prepared. These sols were stable for over one year. This is known as series A.

Sol B was prepared in the same way but was not concentrated by evaporation. It was diluted with mixtures of alcohol and water, so that the amount of silver in each sol remained constant. The volumes of alcohol were 10, 20, 30, 40, and 50%. This is called series B. Similarly sol C was prepared, but it was used only for analysis.

Composition of the Sols

The sols were analyzed in the following ways: the total silver was determined by adding nitric acid and titrating with potassium sulphocyanate, or precipitating as silver chloride and weighing, or comparing in a nephelometer with a standard. Potassium nitrate was added to another sample of the same sol; this coagulated the colloidal silver and the supernatant liquid was analyzed by one of the methods mentioned, for soluble silver. The precipitated colloid was dissolved in nitric acid and analysed for colloidal silver.

In one case (sol C) an attempt was made to determine the unreduced silver in the micelle, by the method of Kohlschütter[6] which consists in reducing it with hydrogen in a platinum dish; but after four hours of this treatment no change having taken place the method was abandoned.

Sol B was titrated with mercuric chloride[11] and the unreduced silver in the micelle calculated.

The results are given in Table I, in which some of the analyses of Kohlschütter[6] are included for comparison.

TABLE I

Analysis of Silver Sols

Number of Sol	Total Silver	Soluble Silver	Colloidal Silver	Reduced Silver	Method	Observer
A	86 mg/l	72.4	13.6	—	Neph.	Kane[12]
B	50–55	23–15	27–30	19–20	KSCN	Harriman[13]
C	49.5	42.9	6.7	—	KSCN	Woo[9]
C	49.8	40.9	8.9	—	AgCl	Woo[9]
12	52.8	30.2	22.6	21.6	KSCN	Kohlschütter[6]
13	88.4	77.6	10.8	8.6	KSCN	Kohlschütter[6]
14	47.4	33.4	14.0	12.9	KSCN	Kohlschütter[6]

Physical Properties

The densities of series A were determined at 25°C. by pyknometer[15] and found substantially the same as that of the pure dispersion media. These data were used in the determination of the viscosities, by aid of an Ostwald pipette. The viscosities are slightly less than those of the dispersion media.[15] This is not in agreement with Woudstra[16] who found the viscosity of silver sols in water more than the viscosity of pure water. These results which were made preliminary to the determination of the migration velocities of the sols are given in Table II.

TABLE II

Physical Properties of Sol A at 25°C[15]

% Alcohol by weight	Relative Viscosity	Density	% Alcohol by weight	Relative Viscosity	Density
0.888	1.581	0.8197	0.422	2.374	0.9370
0.842	1.666	0.8357	0.374	2.186	0.9475
0.794	1.906	0.8508	0.327	2.185	0.9561
0.748	1.944	0.8606	0.281	1.978	0.9619
0.701	2.147	0.8720	0.234	1.844	0.9670
0.654	2.174	0.8844	0.187	1.667	0.9722
0.608	2.348	0.8940	0.140	1.461	0.9836
0.561	2.317	0.9082	0.094	1.263	0.9898
0.514	2.429	0.9146	0.047	1.116	0.9930
0.465	2.297	0.9233	0.000	1.003	0.9968

Cataphoresis Experiments

The results were obtained with a Burton[19] apparatus, modified in a way similar to that of others.[16,17] It was found difficult to fill the apparatus and keep the layers from breaking when the pure dispersion medium, of the same percentage of alcohol, was placed above the sol, due to the slight difference in density. But when 75% alcohol was used no trouble at all was experienced and for this reason it was employed throughout in the cataphoresis measurements of series B.

Measurements were made by taking readings on the height of each layer with a cathetometer and reversing the current at least three times. The sol was then run out and a new sample of the same composition run in and the process repeated.

The readings of each set were averaged and the mean of the two sets taken as final. A sample set is shown below:

TABLE III

Rate of right layer	Rate of left layer	Average Rate	Gradient volts/cm.	Mobility Cm/sec/volt/cm
0.00174	0.00130	0.00152	21.0/28	0.0000338
0.00200	0.00150	0.00175	24.0/28	0.0000341
0.00087	0.00174	0.00130	24.8/28	0.0000244
		Average		0.0000308

In this way the data of Table IV were obtained.

TABLE IV

Sol. No.	% Alcohol by weight	Mobility	D.E.K.*[20]	Viscosity[24]	Relative Boundary Potential
B–I	0.00	76×10^{-6}	79.5	0.894	1.000
B–II	7.65	42	75.6	1.220	0.795
B–III	15.61	29	73.7	1.600	0.739
B–IV	23.89	28	68.6	1.960	0.938
B–V	32.55	28	61.4	2.222	1.207
B–VI	41.56	30	58.3	2.382	1.436

From this data by use of the relative viscosity of the dispersion medium,[24] which Hipkins[15] has found to be practically equal to that of these sols, and the dielectric constants[20] the charge on the particles can be calculated.

In every case the velocity has been decreased by the alcohol. This is in agreement with similar measurements[12] made on series A, but these results were not so consistent as the voltage was only measured at the two terminal electrodes and the readings of the levels in the more dilute sols were uncertain.

When the potential of the double layer is calculated according to equation:[23]

$$\zeta = \frac{6\pi\eta u}{HD},$$

using the data already mentioned, it is seen to go through a minimum. These results seem to be at variance with the precipitation values which will now be considered.

Precipitation Experiments

The effect of ethyl alcohol on the precipitation values of potassium, calcium and aluminium ions were determined for both series A and B. These values were obtained by adding drops of each electrolyte to five c.c. of sol and observing the effect after 24 or 48 hours. These results are given in Tables V and VI.

The concentration of the precipitating ions is in every case decreased by the alcohol. This is in agreement with the data of Bikerman[7] who investigated the effect of adding propyl alcohol to arsenic sulfide sols.

The ratio of the equivalent concentrations of the different ions, necessary to cause precipitation is in agreement with the well-known Schultz-Hardy rule, in our case 1:63:1400 for series A, and 1:20:5650 for series B. In the case of the calcium-potassium ratio in series B which is 1:20, it remains practically thus independent of the percentage of alcohol.

From these results it is evident that the alcohol has sensitized the sols in every case.

TABLE V

Precipitation Values for Series A[12] (After 24 Hours)

% Alcohol by volume	Drops of N K to ppt. 5 c.c.	Drops of 0.02 N Ca to ppt. 5 c.c.	Drops of 0.001 Al to ppt. 5 c.c.
0	22	20	16
5	11	—	—
10	(7)	14	10
15	—	—	—
20	4	—	—
25	(3)	9	6
30	—	—	7
35	2	7	6
40	—	6	4
45	—	6	—
50	1	6	—
55	(1)	4	3
60	—	—	—
65	1	—	—
70	(1)	1	2
75	—	—	—
80	1	(1)	2
85	—	1	—
90	—	—	—
95	1	—	—

Table VI

Precipitation Values of Series B[14] (After 48 Hours)

% Alcohol by volume	Drops of N K to ppt. 5 c.c.	Drops of 0.02 N Ca to ppt. 5 c.c.	Drops of 0.001 N Al to reverse 5 c.c.
0	6	17	—
10	3–4	12	5
20	2–3	8	5
30	1–2	5	3
40	1	4	2
50	1	3	1

Discussion of Results

The sols prepared by our method are undoubtedly of the same nature as those of Kohlschütter, as the analyses show.

The precipitation values for the colloid are in every instance lowered by the alcohol; but the calculated value of the boundary potential (ζ) is seen to rise again after the addition of twenty-five per cent alcohol. This is a contradictory behavior, and no reason is known for it.

The boundary potential has been observed to deviate from expected behavior by other observers, who are mentioned by Kruyt[22] in his discussion of this matter.

The writer has a thought, which may explain the present behavior. It is well known that the solubility of nitrates which were the precipitating electrolytes used, is decreased in the presence of alcohol. It is also well known that the adsorbability of a substance by a given adsorbent increases as the solubility of the adsorbate decreases.[21] Consequently in this case, if the boundary potential rises in the sols of higher alcoholic content, more electrolyte will be necessary to neutralize the charge; but as the amount adsorbable at a given concentration has been very much increased by the alcohol, perhaps an actually smaller concentration of precipitating ion will be all that is necessary to cause coagulation.

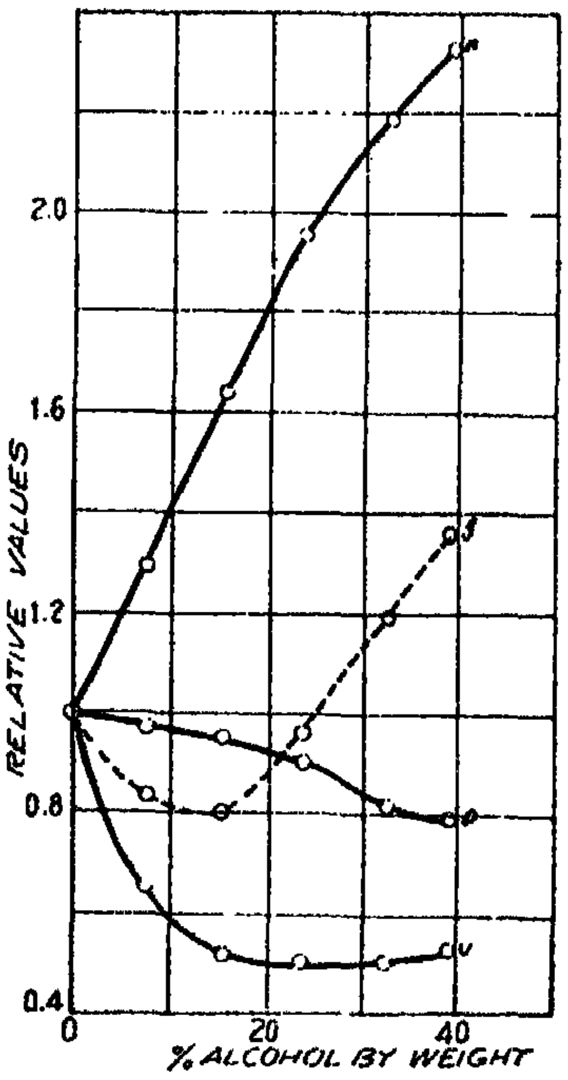

Fig. 1

For convenience in visualizing the variables involved, they are all plotted as relative values in Fig. I.

Summary

A simple method of preparing silver sols has been shown, and the approximate composition of the micelle has been determined.

The density and viscosity of these sols in the presence of varying amounts of ethyl alcohol have been measured.

The migration velocities have also been determined, and the boundary potential calculated.

The coagulation values of potassium, calcium and aluminium ions were included and the sensitizing effect of alcohol has been proven.

The writer wishes to thank his students and coworkers for their co-operation in this investigation, especially W. R. Carmody, E. A. Kane, C. C. Hipkins, L. P. L. Woo, A. J. Harriman, J. A. Mathews, and George D. Rock.

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The Martin Maloney Chemical Laboratory,
The Catholic University of America,
Washington, D. C.
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OSMOTIC AND ACTIVITY COEFFICIENTS

BY R. C. CANTELO

Debye and Hückel[1] in their brilliant paper on the theory of strong electrolytes, on the assumption that interionic forces exist between the ions obtain for the potential energy U_e, of the ions in the solution, the expression:

$$U_e = -\Sigma \frac{N_i z_i^2}{2} \cdot \frac{\epsilon^2 \kappa}{D} \cdot \frac{1}{1 + \kappa a_i} \tag{1}$$

where

$$\kappa^2 = \frac{4\pi\epsilon^2}{DkT} \Sigma\, n_i z_i^2 \tag{2}$$

and the other symbols have the following significance:

U_e = potential energy of the ions, or the electrical energy of the solution in ergs; N_i is the total number of ion-molecules of the ith kind of valence z_i in the solution; ϵ is the charge on a univalent positive ion viz: 4.774×10^{-10} e.s.u.; D is the dielectric constant of the medium at the absolute temperature T; k is the gas constant for 1 molecule viz: $k = R/N$, where N is Avogadro's number (6.061×10^{23}); and n_i is the number of ions of the ith kind per cubic centimeter of solution.

Now the Electrical Free Energy of the solution represents the potential free energy of the *solution*, due to the potential energy U_e of the ions. It may be defined by the equation:

$$\frac{F_e}{T} = \frac{A_e}{T} = -\int \frac{U_e}{T} \cdot dT \tag{3}$$

This gives for F_e,

$$F_e = -\frac{\epsilon^2\kappa}{3D} \Sigma N_i z_i^2 X_i \tag{4}$$

Where X_i is a function of the ionic diameter a_i. If now in place of a_i and X_i we introduce an average value of a and, therefore, of X, we obtain:

$$F_e = -\frac{\epsilon^2\kappa X}{3D} \Sigma N_i z_i^2 \tag{5}$$

Debye and Hückel introduce also a function σ defined by the equation:

$$\sigma = \frac{d(\kappa X)}{d\kappa} \tag{6}$$

This function is so related to X that

$$2X + \sigma = \frac{3}{1 + \kappa a} \tag{7}$$

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[1] Debye and Hückel: Physik. Z., 24, 185 (1923).

Now the simplest way of testing the validity of the theory is to derive expressions for the activity coefficient or activation, and osmotic coefficient of an electrolyte, and then to compare the values calculated from these expressions with the values obtained experimentally from freezing point or electromotive force measurements.

Debye and Hückel derived equations for f and ϕ, the activation and osmotic coefficient, and these equations have been tested experimentally by many investigators. In the present paper, the writer gives a simple alternative derivation of these equations.

Let us consider a symmetrical binary electrolyte forming a total of n ions. Then the electrical free energy of the solution is

$$F_e = -\frac{\epsilon^2 \kappa X}{3D} nz^2 \tag{5}$$

Then

$$\begin{aligned} \bar{F}_{1,e} = \frac{dF_e}{dn} &= -\frac{\epsilon^2 z^2}{3D} \frac{d(\kappa X)n}{dn} \\ &= -\frac{\epsilon^2 z^2}{3D}\left[\frac{\partial(\kappa X)}{\partial \kappa} \cdot \frac{\partial \kappa}{\partial n} \cdot n + \kappa X\right] \\ &= -\frac{\epsilon^2 z^2}{3D}\left[\sigma \frac{d\kappa}{dn} \cdot n + \kappa X\right] \\ &= -\frac{\epsilon^2 z^2}{3D}\left[\sigma \frac{\sigma\kappa}{2} + \kappa X\right] \\ &= -\frac{\epsilon^2 z^2}{6D}\left[\sigma + 2X\right] \end{aligned}$$

Hence,

$$\bar{F}_{1,e} = -\frac{\epsilon^2 z^2 \kappa}{6D} \cdot \frac{3}{1 + \kappa a} = -\frac{\epsilon^2 z^2 \kappa}{2D(1 + \kappa a)} \tag{8}$$

Activity Coefficients

If F_0 be the free energy of the ions when they are at the infinitely small concentration C_0, and F the corresponding free energy when the ions are at the finite concentration C_1, we have the relation,

$$F - F_0 = NRT \ln a_1/a_0 \tag{9}$$

where a_0 and a_1 are the activities and N is the number of ion-mols in the solution. Using n, the number of ion-molecules, we have

$$F = F_0 + n\,kT \ln c_1/c_0 + n\,kT \ln f_1/f_0 \tag{10}$$

where f_0, and f_1 are the activations. F is evidently the free energy of the ions in the solution. Since C_0 is infinitely small, the last term becomes n k T ln f. If the ions were uncharged we should have for F,

$$F = F_0 + n\,k\,T \ln c_1/c_0 \tag{11}$$

Hence the last term of (10) must represent the partial electrical free energy of the ions in the solution. Hence from (8), we can write

$$\mathrm{nkT} \ln f = -\frac{\epsilon^2 z^2 \kappa}{2D(1 + \kappa a)} \cdot n \qquad (12)$$

Then

$$\mathrm{kT} \ln f = -\frac{\epsilon^2 z^2 \kappa}{2D(1 + \kappa a)} \qquad (13)$$

or

$$-\ln f = +\frac{\epsilon^2 z^2 \kappa}{2DkT(1 + \kappa a)} \qquad (14)$$

where f is the activation of a single ion. Now Equation (2) can be transformed into:

$$\kappa^2 = \frac{8\pi\epsilon N\mu}{1000DkT} \qquad (15)$$

where μ is the ionic strength[1] of the electrolyte. When numerical values are substituted in (15) we obtain for 25°C,

$$\kappa = 0.3283 \times 10^8 \sqrt{\mu} \qquad (16)$$

Using this value of κ, substituting numerical values and changing to decadic logarithms transforms Equation (14) to

$$-\log f = +\frac{0.505\, z^2 \sqrt{\mu}}{1 + 0.328 \times 10^8 a \sqrt{\mu}} \qquad (17)$$

for the activity coefficient of a *single ion* at 25°C.

Now what we are interested in is the mean activation $f\pm$ of an electrolyte. The mean activation of an electrolyte of the type $A_{\nu_1} B_{\nu_2}$ is defined by:

$$f \pm = (f_1^{\nu_1} f_2^{\nu_2})^{1/\nu} \qquad (18)$$

where $\nu = \nu_1 + \nu_2$

Again for an electrolyte of the type $\overset{z_1}{A}_{\nu_1} \overset{z_2}{B}_{\nu_2}$, $\nu_1 z_1 = \nu_2 z_2$. Hence

$$\frac{\nu_1}{z_2} = \frac{\nu_2}{z_1} = \frac{\nu_1 + \nu_2}{z_2 + z_1} = \frac{\nu}{z_1 + z_2}$$

From (18)

$$\ln f \pm = \nu_1/\nu \ln f_1 + \nu_2/\nu \ln f_2$$

$$= \frac{z_2}{z_1 + z_2} \ln f_1 + \frac{z_1}{z_1 + z_2} \ln f_2$$

$$-\ln f \pm = \frac{z_2}{z_1 + z_2}\,\frac{\epsilon_2 z_1^2 \kappa}{2DkT(1 + \kappa a)} + \frac{z_1}{z_1 + z_2}\,\frac{\epsilon^2 z_2^2 \kappa}{2DkT(1 + \kappa a)}$$

$$= \frac{\epsilon^2 \kappa z_1 z_2}{2DkT(1 + \kappa a)} \left[\frac{z_1 + z_2}{z_1 + z_2}\right]$$

$$-\ln f \pm = \frac{\epsilon^2 \kappa z_1 . z_2}{2DkT(1 + \kappa a)} \qquad (19)$$

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[1] Lewis and Randall: J. Am. Chem. Soc., 43, 1141 (1921).

When numerical values are substituted, Equation (19) becomes:

$$-\log f \pm = \frac{0.505\ z_1 z_2 \sqrt{\mu}}{1 + 0.328 \times 10^8 a \sqrt{\mu}} \qquad (20)$$

If we expand the denominator, this gives

$$-\log f \pm = 0.505\ z_1 z_2 \sqrt{\mu}\left[1 - 0.33 \times 10^8 a\sqrt{\mu} + 0.1089 \times 10^{16} a^2\mu + \ldots\right] \qquad (21)$$

When the solution is dilute, the terms higher than the first become negligible since a is of the order of 10^{-8}cm. Hence for a dilute solution Equation (20) becomes equivalent to that of Debye and Hückel for the limiting case of c → 0, i.e.[1]

$$-\log f \pm = 0.505\ z_1 z_2 \sqrt{\mu} \qquad (22)$$

Osmotic Coefficient

The partial *molal* free energy of the solvent in a perfect solution or in an infinitely dilute solution is defined by the equation:—

$$\bar{F}_2 - F_2 = RT \ln (1 - x) \qquad (23)$$

where F_2 is the free energy of the pure solvent and x is the mol-fraction of the solute.

For an infinitely dilute solution, this reduces to

$$\bar{F}_2 - F_2 = -R\,T\,x \qquad (24)$$

Equation (24) defines the behavior of the solvent for the ideal state of an infinitely dilute solution. For an actual state other than an ideal one we shall correct for the deviation in the behavior of the component from its behavior in the state of zero concentration of solute, by means of an osmotic coefficient ϕ; and we shall define ϕ by

$$\phi = \frac{\Delta_{obs}}{\Delta_{ideal}} \qquad (25)$$

where Δ refers to the depression of the freezing-point of the solvent. Then for *any* solution, Equation (23) can be written:

$$\bar{F}_2 - F_2 = -R\,T\,x\,\phi \qquad (26)$$

and for several solutes,

$$F_2 - F_2 = -R\,T\,(x_1 + x_2 + x_3 + \ldots.)\phi \qquad (27)$$

We shall now define a quantity, $F_{2,e}$ by the equation,

$$\bar{F}_{2,e} = -R\,T\,\phi\,x - (-R\,T\,x)$$

$$\text{i.e. } \bar{F}_{2,e} = -R\,T\,x\,(\phi - 1) \qquad (28)$$

or for a single molecule

$$\bar{F}_{2,e} = -k\,T\,x\,(\phi - 1) \qquad (28a)$$

$$F_e = -\frac{\epsilon^2 \kappa X n z^2}{3D} \qquad (5)$$

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[1] See Brönsted and LaMer: J. Am. Chem. Soc., **46**, 561 (1924).

while the *partial* free electrical energy of the ions is n $\bar{F}_{1,e}$

$$\bar{F}_e = -\frac{\epsilon^2 \kappa z^2 n}{2D(1+\kappa a)} \tag{29}$$

$$X = 1 - \tfrac{3}{4}\kappa a + \tfrac{3}{5}\kappa a^2 + \ldots\ldots, \qquad \text{whence we get}$$

$$F_e = -\frac{\epsilon^2 \kappa z^2 n}{3D}\left(1 - \tfrac{3}{4}\kappa a + \tfrac{3}{5}(\kappa a)^2 - + \ldots\ldots,\right. \tag*{7(a)}$$

and

$$\bar{F}_e = -\frac{\epsilon^2 \kappa z^2 n}{2D}\left(1 - \kappa a + (\kappa a)^2 - + \ldots\ldots,\right. \tag{29a}$$

A comparison of Equations 7(a) and (29a) shows that a part of the free electrical energy of the solution must reside in the solvent. This electrical free energy of the medium is given, evidently, by Equation (28).

Now F_e, $\bar{F}_{1,e}$ and $\bar{F}_{2,e}$ are related according to the familar thermodynamic equation:

$$F_e = n\,\bar{F}_{1,e} + n_o\,\bar{F}_{2,e} \tag{30}$$

where n = number of ion-molecules, and n_o = number of solvent molecules.

Upon substituting the respective values from Equations (5), (29) and (28) we obtain,

$$-\frac{\epsilon^2 \kappa X n Z^2}{3D} = -\frac{\epsilon^2 \kappa z^2 n}{2D(1+\kappa a)} - kTxn_o\,(\phi - 1)$$

$$\frac{\epsilon^2 \kappa X n z^2}{3D} - \frac{\epsilon^2 \kappa z^2 n}{2D(1+\kappa a)} = kTxn_o\,(\phi - 1)$$

and for moderate concentrations we can write,

$$\frac{\epsilon^2 \kappa k n z^2}{D}\left[\frac{X}{3} - \frac{1}{2(1+\kappa a)}\right] = kT\,\frac{n}{n_o}\cdot n_o\,(\phi - 1)$$

$$\frac{\epsilon^2 \kappa n z^2}{D}\left[\frac{2X}{6} - \frac{3}{6(1+\kappa a)}\right] = kTn\,(\phi - 1)$$

$$\frac{\epsilon^2 \kappa z^2}{D}\left[\frac{2X}{6} - \frac{2X+\sigma}{6}\right] = kT\,(\phi - 1) \qquad \text{or}$$

$$-\frac{\epsilon^2 \kappa z^2 \sigma}{6D} = kT\,(\phi - 1) \qquad \text{whence we get}$$

$$1 - \phi = \frac{\epsilon^2 \kappa z^2 \sigma}{6DkT} \tag{31}$$

Equation (31) holds for a symmetrical binary electrolyte. From Equations (14) and (31) we obtain the relation

$$-\frac{\ln f \pm}{1-\phi} = \frac{3}{\sigma(1+\kappa a)} \tag{32}$$

Hence for any electrolyte, we have the relation

$$1 - \phi = - \frac{\sigma(1 + \kappa a)}{3} \ln f_{\pm}$$

Then from Equation (19) we obtain for the general equation for $1 - \phi$,

$$1 - \phi = \frac{\epsilon^2 \kappa z_1 z_2 \sigma}{6DkT} \tag{33}$$

Upon substituting numerical values we have finally, for 0° C.

$$1 - \phi = 0.373\ z_1 z_2 \sigma \sqrt{\mu}$$

and for the limiting case of extremely dilute solutions, for which $\sigma = 1$, we have

$$1 - \phi = 0.373\ z_1 z_2 \sqrt{\mu} \tag{35}$$

Department of Chemistry,
University of Cincinnati,
Cincinnati, Ohio.

NEW BOOKS

Colloid Symposium Monograph. *Edited by H. B. Weiser. Vol. VI. 23 × 16 cm; pp. 346. New York: Chemical Catalog Company, 1928. Price $6.50.* This volume contains papers by Sir William Hardy, the guest of honor; W. D. Harkins; D. R. Briggs; Kenrick and Griffin; McBain, Wynne-Jones and Pollard; Laing; McBain and Harrison; Bancroft and Barnett; Burton and Deacon; Stamm; Moloney and Taylor; Abramson; Mudd, Lucké, McCutcheon and Strumia; Hastings; Wasteneys and Borsook; Krantz and Gordon; Hauser, Miedel and Hünemörder; Trumbull; Whitby, McNally and Gallay; Fanselow; Olsen; Sheppard and Lambert; Holmes and Williams; Nichols; Neville and Jones; Weiser and Cunningham.

"The third great advance is in the recognition of ferments as the active agents in the machine. In my early days ferments were still classified as organized and unorganized. The former were living cells, such as yeast cells, the latter free ferments produced by living cells. I cannot recall anyone bold enough to suggest that inside the cell were ferments whose business it was to control chemical change.

"Buchner made the first great necessary step when he conducted alcoholic fermentation in the absence of living cells but by ferments extracted from living cells. Since then *endoferments* have been demonstrated in plenty. Meyerhof, for example, has prepared from muscle an extract practically free from protein which contains a catalyst, or catalysts, which reproduces *in vitro* the changes in carbohydrate characteristic of intact muscle.

"Let us look a little more closely at this question of catalysts, for it is not without its difficulties. Clearly their activities are controlled during life because at death they become a disorderly mob who pull the very fabric to pieces, protein and all becoming involved in the breakdown. They are during life restrained, subject to a coordinating timing device in the intact machine.

"It is a plausible suggestion, due to Jordan Lloyd, that the proteins exert the control. There are plenty of instances in the chemistry of living matter. Haemoglobin, the red pigment of blood, carried oxygen from the air in the lungs to the tissues, and the dissociation constants of the haemoglobin of different animals are such as fit it for the peculiar needs of that animal. Now haemoglobin is composed of an active molecule haematin which, though capable of oxidation and reduction, is totally unsuited to carry oxygen in the blood. It is only when combined with protein that it is fitted for its task. And there is more. Haematin seems to be the same in all animals in which it is found, but the protein ally is different. The inference is so obvious that it need not be stressed," p. 10.

"Milk, a solution of chlorophyll-like muscle juice, can be coagulated by freezing and thawing, but the molecular changes need time for their accomplishment and therefore, as is well known, they can be avoided if both cooling and thawing are sufficiently rapid. I do not recall a colloidal solution which does not give this evidence of a time lag in the process of coagulation,

"Now here are two facts which seem to me to have immense significance. By no procedure has it been found possible to freeze and thaw living muscle without causing instant death. Whatever the key structure may be, the presence of what means life, there is no evidence of a time lag in its destruction.

"The second fact is that it is not cold which destroys, but dehydration. The freezing point of frog's muscle is −0.42°, and muscle can be frozen and thawed without causing death unless a critical temperature is over-passed, namely −2.0°. The quantity of water withdrawn in the form of ice at −2° can be calculated. It is 77.5 per cent of the total water and Moran, to whom these facts are due, finds that 77.5 per cent of the water can be removed from living frog's muscle by simply drying over calcium chloride without killing it. The muscle when the water is restored is again irritable and has the alkaline reaction and other qualities of living muscle. Muscle is not killed by cold. It can be over-cooled to −4° for days without impairment of its properties," p. 12.

"Hardy states that benzene spreads on the surface of water, while Langmuir considers that it does not spread. The phenomena involved have been investigated by Harkins and Jordan. *They find that if enough pure benzene is dropped on the surface of pure water to give a layer about 1 mm. thick it spreads over the whole surface to give an apparently* uniform layer. This behavior agrees with the fact that the initial spreading coefficient has a value of 8.9. As the benzene evaporates, holes appear in the layer, and the optical effects indicate that the angle of contact is not zero. If the surface tension of the water in one of these "holes" is determined, it is found that here, where the film of benzene appears to be absent, it is actually present. That is, the water is covered with a monomolecular, or thicker, invisible film of benzene. The layer of benzene around the holes is sufficiently thick to be easily visible. The fact that this layer does not spread over the contaminated surface *of the water in the hole is in accord with the value of the final spreading coefficient*, which is found to be -1.49 ergs per sq. cm. and indicates the existence of a considerable angle of contact," p. 23.

"In aqueous solutions of low specific conductivity present in the interstices of a diaphragm material, *e.g.*, a pad of pure paper pulp, the electrical conductance through the interface phase is much greater than that through an equal volume of the liquid in bulk. This fact has been largely neglected in calculations of the ζ-potential at interfaces when electrokinetic technic was used," p. 51.

"It was found that some powders, glass for example, conducted with even small concentrations of water vapor and that the *conductivity increased as the partial pressure of* the water vapor approached the saturation value, while others, such as salicylic acid, remained practically non-conducting until the saturation point was nearly reached, when, as might be expected, all powders conducted well," p. 54. Apparently the powders which conduct with even small concentrations of water vapor do not produce bubbles when introduced into solutions supersaturated with oxygen, while the others do.

"Since it is now found that the partial pressure and activity of aqueous *p*-toluidine are proportional to the concentration, the two-fold conclusion of McBain and Davies is strengthened:—firstly, that the direct experimental observations show that in all these solutions of soluble substances, even when far from saturation, not only *is the surface covered with a* monomolecular film of the solute but that there is also a large excess in the neighborhood of the surface probably extending in the form of oriented molecules well into the solution. Secondly, that the thermodynamic treatment of Willard Gibbs which has been followed by all subsequent writers is insufficient, because it omits consideration of adsorption resulting from the admitted electrification of all such surfaces, as exhibited for instance in experiments on electrokinetics," p. 62.

"On the surface of an N/20 solution of sodium oleate there is adsorbed one oleate radicle for each 11 sq. Å. The cross-section of a hydrocarbon chain is known to be 20 sq. Å, hence the soap adsorbed in the surface of this dilute solution is more than can possibly be close-packed into a single monomolecular layer. The only other available quantitative data for soluble substances are those of McBain and Davies who obtained exactly the same result with, for example, aqueous solutions of amyl alcohol. It therefore appears probable that all these solutions even when removed from saturation are covered by a complete monomolecular film of solute, and that there is an additional adsorption comparable in amount in the solution underneath the monomolecular film. The most plausible picture is that of chains of oriented molecules of solute, extending from numerous points on the monomolecular film deep into the surface layers of solution, as pictured for example in the diagrams of McBain and Davies. Such chains would be regarded as evanescent but extremely numerous continually growing out from the oriented molecules of the monomolecular film until broken up through thermal vibration in the liquid," p. 70.

"Contrary to the predictions of the Gibbs theorem, both in its popular and in its exact form, sodium oleate is positively adsorbed in the air-water interface. The amount adsorbed is nearly twice as great as can be packed into a monomolecular film. This parallels the findings of McBain and Davies with aqueous solutions of such substances as para-toluidine, camphor, and amyl alcohol and supports their suggestion that the surface of a solution may be covered with a monomolecular film of adsorbed solute but may also exhibit a high concentration of solute in the neighborhood of the surface, probably in the form of chains of oriented molecules of solute extending from the monomolecular film deep into the surface. The adsorbed soap is in hydrolytic equilibrium with the solution but its hydrolysis is completely suppressed by a small excess of alkali," p. 72.

"For every concentration of dye the amount of adsorption by a powdered solid is a function of the apparent pH of the solution. It is not possible at present to use the maximum adsorption of a dye by crystals as a measure of the total surface. Paneth's method is therefore not reliable in its present form," p. 76.

The copper sol prepared by Burton coagulated after half an hour's heating at 187°, while it is necessary to heat for ninety minutes at 107°. At 80° the sol remained uncoagulated after four hours' heating at 81.° It consequently seems probable that "at room temperature such a colloidal solution might be expected to remain stable for an infinite time," p. 82.

"Though the wood sections studied are somewhat permeable to colloidal mercury and to India ink sols, they also act as partial ultrafilters. This fact should be expected, since the mercury particles, although about a tenth as large as the largest pit-membrane pores, are of the same order of size as the average pit-membrane pore diameters," p. 108.

"Three individuals who gave marked reactions to an intradermal injection of diluted commercial antitoxin—purified by the ammonium sulfate method—were tested intradermally with dilutions of the solutions used for the experiments on minimum solubility in alcoholic solution. All the solutions used including the commercial antitoxin were diluted *to contain 0.15 per cent protein.* With two of these individuals there was markedly less reaction to the four solutions of antitoxin which had been purified by the alcohol method than to the dilution of the commercial antitoxin. Of the four antitoxins purified by the use of alcohol, the one which had not been treated with acid or alkali gave as little reaction as the antitoxins which had been so treated. With the third individual the reactions to all five intradermal injections were the same," p. 114.

"Quartz particles of the most different forms suspended in water and in sugar solutions (whose higher density permitted larger particles to be definitely outlined) migrated with practically identical velocities. As the speed of the fluid within the cataphoresis cell varies appreciably at different levels, it is important that particles observed be studied at the same level, preferably in the center where the change is least. The migration of all the types of particles takes place under normal conditions without orientation. If, however, the drop in potential per cm. in the cataphoresis cell is increased, with increased water-flow, as well as increased velocity, orientation does take place. This absence of orientation is particularly strikingly observed in soft gelatin gels (to be described later) where large elongated particles maintain the same direction during hours of study. The particles of the sizes studied ($1\mu - 30\mu$) are not oriented by the electrical field. Any orientation occurring can be ascribed to secondary causes," p. 119.

"The leucocytes have been shown to migrate with the same speed as quartz with an adsorbed protein film. Shibley had shown the same phenomenon for sentitized bacteria and denatured globulin," p. 130.

"Sera which in these experiments have increased the phagocytosis of bacteria have concomitantly increased the cohesion, decreased the surface potential difference and altered the wetting properties of the bacteria. Conversely, but with certain exceptions, when sera have altered the surface properties of bacteria as indicated, they have caused the bacteria to be spread upon and engulfed by leucocytes. The exceptions have been with aged or heated sera or sera of another species than the leucocytes. These exceptions show the *requirements for spreading of the leucocytes to* be more delicate than the physical-chemical reactions we have been able to apply. These results are consistent with the conclusion that the various surface reactions including phagecocytosis are all dependent upon the deposition on the bacterial surface of serum components," p. 138.

"Emulsions formed with benzaldehyde, benzoic acid, benzene, toluene, and chloroform have a definite accelerating effect on the peptic synthesis of proteins. Emulsions formed with oleic acid or olive oil show no accelerating effect on synthesis. The presence of talc powder, kieselguhr, and barium sulphate accelerates peptic synthesis slightly. Under certain conditions, the presence of effective emulsions causes an augmentation of the equilibrium amount of protein synthesized; but under optimum conditions for synthesis no such augmentation of the amount synthesized is affected, although such an acceleration of the rate of synthesis always occurs. The effective emulsions are found to induce some synthesis even in the absence of enzyme. It is found that the proteins synthesized vary in their physical and chemical properties according to the means which have been employed to effect synthesis," p. 172.

"With mineral oil as with Harkins' observation with benzene magnesium, calcium, cobaltous, nickelous, manganous and aluminum oleates produce emulsions of the water-in-oil type. With valeric acid, as with Harkins' and Newman's observations with oleic acid, the univalent salts produce oil-in-water emulsions, whereas the salts of divalent metals produce water-in-oil emulsions. The salts of arabic acid produce oil-in-water emulsions irrespective of the valence of the metallic atom in combination. It is entirely possible that acacia always tends to produce an oil-in-water emulsion because of the buffered emulsion characteristic which has been demonstrated, or that it is the divalent salt of an acid in which there are several hydroxyl groups. According to the observations made with the divalent salts of *i*-galactonic and gluconic acids it is possible that the presence of hydroxyl groups in the molecule of arabic acid in addition to the fact that acacia contains some univalent salts of arabic acid, is partly responsible for its invariably producing emulsions of the oil-in-water type. As the gum tragacanth is essentially the calcium salt of bassoric acid and produces emulsions of the oil-in-water type, it is probable that this condition exists for reasons similar to those proposed for the salts of arabic acid," p. 203.

Microscopical methods have been developed whereby it is possible to show that the form in which sulphur reappears in vulcanized rubbers varies when one has rubber and sulphur, rubber, sulphur and zinc oxide or rubber, sulphur, zinc oxide, and an accelerator, p. 211.

"The problem of producing a rubber latex from crude rubber was assigned by Dr. W. C. Geer of the Goodrich Laboratories first to Dr. John B. Dickson and subsequently to the writer. Both men first approached the problem from the classical point of view, which is to disperse a rubber cement in an aqueous medium containing protective colloids. Although dispersions were obtained such as those which had been previously prepared by the workers in this field, it was obvious that these dispersions did not resemble latex for at least three reasons, firstly, the concentration of rubber was low, not over 5 to 10 per cent; secondly, solvent invariably remained in the rubber particles, hence the dispersed phase was a rubber cement rather than rubber; thirdly, the particles formed under any set of circumstances were larger and creamed much more rapidly than latex particles.

"It occurred to the author that if rubber could be frozen in order to embrittle it, the action of a high-speed abrasive wheel on its surface might be effective in producing a dispersion. A block of masticated rubber was first allowed to absorb about an equal volume of benzene and then frozen for several days at −39°C. Immediately upon removal from the refrigerator the solid block was held closely against a high-speed aloxite wheel which was porous enough to permit a lubricant of five per cent glue in water at 0°C. to flow through it from the axis to the periphery. This lubricant served as a protective colloid for the dispersion. Under the vigorous abrasive action rubber particles were sheared off from the face of the block, and some of them were small enough to remain suspended in water over night (less than 1% concentration).

"The bulk of the rubber was either not removed from the block or was rolled off to form pea-sized pellets. Heat, developed by friction, apparently softened the rubber at the contact point so that it could not be abraded as could a brittle solid. Nevertheless the fact remained that some rubber had been dispersed, and that by a mechanical method.

"An operable method of effecting rubber dispersion was arrived at as a result of the joint invention of Dr. J. B. Dickson and the author. This method required two smooth-roll rubber mills, one to masticate rubber and the other to serve as the dispersing machine.

In order to operate the latter a thick paste of equal parts of glue and water was placed upon the rolls of one mill, and rubber from the other mill was cut in thin strips and gradually worked into the glue paste preferably at a temperature of about 70°C," p. 214.

"In experiments on precipitation of benzene sols of meta-styrene by ethyl alcohol and in experiments on the precipitation of benzyl alcohol sols of cellulose acetate by tertiary butyl alcohol, it was found that, for sols of any given specimen, the higher the concentration of the sol, the smaller was the proportion of precipitant required. Mardles found similarly that the volume of light petroleum required to precipitate sols of cellulose nitrate and of cellulose nitracetate in acetone was smaller, the greater the concentration of the sol. Further, the authors found on comparing samples of meta-styrene representing different degrees of polymerization, that samples yielding more viscous sols at a given concentration required less precipitant than samples yielding less viscous sols. Hence it seems reasonable to conclude that, the smaller the proportion of bound solvent in a sol of a given organophilic colloid, the smaller is the proportion of the given precipitant required to produce separation," p. 226.

"In no case does the amount of a liquid which it is possible to determine by direct measurement as being imbibed by massive pieces of colloids such as rubber and meta-styrene approach the amount which Hatschek's equation for the viscosity of emulsoids, $\eta = \eta_0/(1 - \sqrt[3]{f})$ would indicate as being bound in the disperse phase. Thus, for example, over the range of concentrations where, using Hatschek's equation, the volume of solvent bound by 1 gram of the solute is constant, this volume is in the case of benzene sols of rubber and of meta-styrene about 160 and 135 respectively. Yet the volume found to be imbibed by these colloids by immersing pieces of them in benzene and noting the increase in weight is of the order of 30 and 6 volumes only, respectively. It is, however, doubtful whether direct measurements of swelling afford any reliable information as to the volume of solvent which a colloid is capable of binding when dispersed in a sol. When a piece of raw, unmilled rubber is placed in benzene or other solvent and left undisturbed, it imbibes the liquid and swells, in most cases quickly at first and then more gradually; but before imbibition has ceased and equilibrium has been attained, diffusion of the hydrocarbon from the swollen mass begins and the weight begins to fall. In the case of meta-styrene dispersion of the colloid from the surface of the swollen mass begins after swelling has proceeded to a much smaller extent than is necessary for the dispersion of rubber to begin. Probably, in the case of rubber, dispersion would similarly begin after a relatively small amount of swelling were it not for the protein network in which the hydrocarbon particles are enmeshed. It seems, then that the amount of solvent bound by such colloids when dispersed in a swelling agent may be much greater than the maximum amount which it is possible to determine as being imbibed by a massive piece, and may conceivably be of the order which Hatschek's equation would indicate," p. 231.

"The artificial elastic colloids, polyvinyl acetate and meta-styrene, are highly heterogeneous, being composed of mixtures of an unbroken series of polymers of different molecular magnitudes. Thus, a sample of polyvinyl acetate was separated into four fractions ranging in molecular weight from 566 to 6192. Now it has been supposed recently by several writers that the hydrocarbons of rubber consists of two sharply distinct phases, which have been designated "sol" and "gel" rubber, and correspond to the "soluble" and "pectous" forms of rubber of which Caspari wrote a considerable time ago. The present authors, however, believe that natural caoutchouc is heterogeneous in a way similar to that in which polyvinyl acetate and meta-styrene are heterogeneous, and in which synthetic rubber has been found to be. The so-called "sol" phase of rubber has been looked upon as that portion of the rubber which will diffuse out of the swollen mass when rubber is allowed to stand in ether, the "gel" phase being that portion which is left behind. Experiments by the authors show, however, that there are not two sharply distinct phases in rubber, since the proportion of "gel" rubber determined in a given sample of raw rubber depends on the swelling agent used, and, further, since the "gel" phase is itself heterogeneous. If benzene is used, a higher proportion of "gel" rubber is obtained than if ether is used; if petrolic ether is used, a lower proportion is usually obtained, while if a little piperidine, diethylamine or other strong organic base (which has the effect of increasing the swelling) is added to petrolic ether an increased proportion is secured. As showing the heterogeneous character of the "gel phase," it was found that as diffusion proceeds successive fractions yield sols which at the same concentration possess different viscosities," p. 234.

"In summary it may be stated that the variation in properties of gelatin systems at low temperatures as described in this and other similar studies has not been accounted for by the view that the gelatin combines stoichiometrically with electrolytes. Experimental evidence seems to the author to indicate that the influence of electrolytes upon the optical activity and relative resistance to shear of gelatin systems is the same as the influence of these substances upon the properties of lyophobic systems, but that the evidence of the influence is complicated somewhat by the amino acid nature of the micellae surfaces and is masked to a certain extent by the increased stability of these systems caused by the high affinity of the gelatin phase for the dispersion medium. However, these complications do not alter the view that the behavior of gelatin systems can better be explained by the laws obtained from the behavior of highly dispersed heterogeneous systems than by the classical laws of stoichiometry," p. 251.

"Since powder has been found to burn in layers parallel to the surface, it will be seen that the web is the critical dimension of the grain. Powder which is used in the famous war-time weapon, the French 75-mm. gun, is required to have a web of about 0.020 inch. Careful ballistic tests have indicated that a variation in web thickness of one-one-thousandth of an inch will cause the projectile to miss the target at maximum range by 75 yards. Numerous examinations of accepted lots of powder have shown that the normal maximum variation in the web dimension of individual grains from a given lot of powder is ten one-thousandths of an inch, so that if charges were made for the gun in which these maximum differences prevailed in each of the charges, a variation in range of 750 yards would result. The remedy which is generally applied consists in blending the grains of powder, and the known accuracy of the weapons is undoubtedly in part attributable to this practice of mixing heavy- and light-web grains. However, this remedy is only partially satisfactory to powder technologists, who are now spending much effort in eliminating, if possible, those factors which cause variations in the shrinkage of the gel," p. 254.

"In the first stage of digestion [of photographic emulsions] the process of Ostwald ripening is occurring, grains below a certain size are dissolving, and grains above a certain size growing by accretion from solution. This process proceeds to exhaustion of the grains whose solubility is appreciably different from that of the largest. . . . This would lead to practical cessation of grain growth. . . . We find, however, that actually the grain growth goes on but at a new and decreased rate. This we assume to be due to recrystallization within the aggregates produced by collisions and coalescence," p. 273.

"We decided to secure uniformity of solid deposit in a porous support by first immersing the porous solid in a solution of the salt desired, drying, admitting a suitable water-soluble gas and finally immersing the porous solid containing the dry salt in water," p. 283.

"The development of the ultra centifuge has been traced from its inception to its present form capable of exerting an effect 100000 times that of gravity on a solution," p. 308. "If the swelling of gelatin in pure water may be assumed to be a strictly colloidal process consisting in the adsorption of water to form a hydrated material of gel structure but no definite hydrates, the setting of plaster of Paris and the setting of Portland cement may be considered as quite analogous phenomena," p. 316.

"It appears that the physical character of precipitated sulfur thrown down in the presence of alkali cations varies from gelatinous to plastic as we go down in the series from lithium to caesium. Likewise, the precipitate thrown down by alkaline earth cations changes in the same way as we go down in the series from magnesium to barium. In other words, precipitates formed in the presence of those ions which are generally recognized as the most highly hydrated, are the most gelatinous, and the precipitation is reversed by washing; while the precipitates thrown down in the presence of the less hydrated ions are dense and plastic, and the precipitation is not reversed by washing.

"The order of hydration of the alkali cations is believed to be: Li ⟩ Na ⟩ K ⟩ Rb ⟩ Cs; and of the alkaline earth cations: Mg ⟩ Ca ⟩ Sr ⟩ Ba. Unfortunately, no one has yet succeeded in measuring quantitatively the ion hydration, much less its dependence on concentration, temperature, and the presence of foreign substances in the solution. Nevertheless ion hydration numbers are frequently given," p. 336.

"Ultramicroscopic observation of the change taking place when a highly hydrated cation is removed from a gelatinous sulfur clump, by displacing with a less hydrated, more strongly adsorbed cation, shows a very marked shrinkage as the result of the loss of adsorbed water and the coalescence of the particles. Ultramicroscopic convection currents in the surrounding liquid, due to the outflow of the adsorbed water, are visible during the change. Motion pictures have been made of this change in the physical character of the clumps under the influence of various ions, and selected views from the motion pictures are included in this paper," p. 341.

The paper by Weiser and Cunningham on the change in the properties of sulphur with the precipitating agent is a brilliant piece of work. This and the paper by Wasteneys and Borsook on the peptic synthesis of protein are the high spots in what is a good volume.

Wilder D. Bancroft

Lehrbuch der physikalischen Chemie. *Vol. II, Parts II and III. By Karl Jellinek, pp. 273-660; 661-923 Stuttgart: Ferdinand Enke, 1928.* These two numbers complete the second volume. Up to p. 606 deals with crystalline solids: specific heat; entropy; heat conduction; vaporization; melting and freezing; surface energy of crystals; formation and growth of crystals; the relation of the crystalline state to the liquid and gaseous ones. The rest of the volume is devoted to dilute solutions. Forty pages are given up to mixtures of gases, one hundred and thirty-five pages to liquid solutions, and about twenty pages to solid solutions.

The theory of Debye for specific heats is given in considerable detail, p. 277, though one is rather left to struggle over the significance of Θ. There is a very interesting cut, p. 281, showing the applicability of the formula. Simon and Lange are said, p. 311, to have found the molecular heat of amorphous glycerol to be eighty percent higher than that of the crystals at 9° abs. It is not clear whose data are given in Fig. 249. Five pages, p. 478, are devoted to the equation of state for solids put forward by Richards and by van Laar.

There is a good agreement between the observed and calculated heats of sublimation of the metals, p. 486. The author does not seem especially enthusiastic, p. 499, over Nernst's heat theorem. There is a good presentation, p. 565, of the work of Volmer and Estermann on the precipitation of crystals from vapors. The pages on adsorption by growing crystals, p. 567, were written before Saylor's work appeared and are therefore inadequate. The author considers that superheated crystals have only been obtained with some of the silicates, p. 589. That is to some extent a matter of definition; but the reviewer would have included under this head all cases of crystals with variable melting-points, such as acetaldoxime, for instance. It is rather satisfactory to have tabulated data, p. 600, on the change of the melting-point with the pressure.

The author has a bad time, p. 606, differentiating solutions from mixtures because he does not make use of the phase rule. He has to accept the definition that a solution is optically homogeneous. Owing to the fact that the author is really interested only in the kinetic presentation of a subject his treatment of osmotic pressure, pp. 651-736, is hopelessly confused. After he has deduced in several ways that the volume term refers to the solution, the author mentions casually, p. 730, the possibility of the volume of the solvent being the important thing. One must admit, however, that the author does not make the mistake, so common in America, of identifying Henry's law with the so-called Raoult equation, p. 781. He gives some good tables for Henry's law, pp. 772-774, for the distribution law, p. 777, and for the molecular lowering of the freezing-point, pp. 828-835.

Wilder D. Bancroft.

The Viscosity of Liquids. *By Emil Hatschek. pp. vii + 239. London: G. Bell and Sons, Ltd., 1928. Price: 15 shillings.* In the investigation of colloids, especially of emulsoids, the measurement of viscosity seems to have become a standard practice, and many and varied are the conclusions drawn from the results in spite of the fact that the subject of viscosity is full of difficulties from the theoretical standpoint, even when pure liquids are concerned. From his own experience as a teacher the author has found it difficult to recommend a book on the subject to his students, and he has found, as is so often the case, that the only way out of the difficulty was to write a book himself. Since, by his own theoretical and experimental investigations he has contributed largely to our knowledge of viscosity questions, it is fortunate that the author has not hesitated to help not only his own, but other students, and the result is a volume of moderate size which gives a reasonably complete account of the subject. The mass of data available is enormous, and the selection from it must have been a task of great difficulty, but the author has been successful in his choice of material and has been able to include some investigations of importance, such as those of Bridgman on the influence of pressure on viscosity, which have not so far found their way into any other text books. The treatment given is such that the reader should be able to get a grasp if the fundamental principles and acquire a general view of the subject; an excessive knowledge of mathematics is not assumed.

After an historical introduction, the theory of the principal methods of determining the co-efficient of viscosity is given, followed by a description of the design and use of various types of viscometers. The variation of viscosity with temperature and pressure, its relation to constitution and connection with conductivity, the viscosities of solutions, liquid mixtures and pitch-like substances are all dealt with in a critical manner. Finally the viscosity of colloidal solutions is discussed in some 40 pages.

The value of the book lies not simply in the account of the subject given by Mr. Hatschek, but also in the criticisms he makes of the various methods and theories. It may be recommended to all who are interested in the subject.

T. Slater Price.

Atomstruktur und Atombindung. *By J. Stark. 22 × 15 cm. Berlin: A. Seydel, 1928. 9 marks.* The author, well known for his experimental researches in molecular physics, develops in this book his own views on the atomic theory and its application to the chemical behaviour of the elements. His attitude towards the Bohr theory is a critical one. He regards it as 'dogmatic,' while his own theories are claimed to be based solely upon experiment. In spite of this, his conclusions do not differ so much as might appear at first sight from the results of the new quantum mechanics. Many of Stark's views are involved in the quantum theory; for instance his idea of the 'Axialität" of the electron and its importance for the theory of valency. In place of the "stationary states" and the "Eigenfunktionen" Stark uses the conception of the existence of equilibrium positions of the electrons in the atoms, with certain symmetry properties.

The book is divided into three sections. In the first the author develops his own views on the atomic theory, often referring to his earlier book entitled "Die Axialität der Lichtemission und Atomstruktur." The second deals with the arrangement of the electrons and the magnetic axes in the atom, derived from optical and chemical facts. A shorter part of this section deals with the structure of the nucleus and the space which Stark calls "Atomzwischenraum." This section seems in great measure obscure and hypothetical. There is no mention of Pauli's principle as a key to the Periodic Table. The last section deals with chemical compounds and forces between atoms and molecules, on the basis of the previous sections. The same problems have, of course, been previously explored by the quantum theory.

E. Hückel.

A STUDY OF THE EFFECT OF CERTAIN CATIONS ON THE FLOTATION OF GALENA*

BY NELSON W. TAYLOR AND HENRY B. BULL**

Introduction

Our purpose in this research has been to determine the effect of certain cations on the flotation of galena (PbS), and if possible to determine the reasons for the quite characteristic effects of these cations.

We have endeavored in our work to reduce the number of variables to a minimum. Even with the simplest system that we could devise, there still remained a relatively large number of factors which had to be controlled in order to obtain reproducible results. Much time was spent in the study of these factors before we obtained satisfactory results.

Historical

Much empirical knowledge concerning flotation of minerals is available but only within the last few years have there been serious attempts at a theoretical treatment.

A study of the theories of flotation is disappointing. There has been much time spent in discussion where more should have been spent in experimenting with simple systems involving only one variable factor at a time.

Most of the theories of flotation center around two fundamental concepts. One involves the free surface energy changes at the various interfaces, and the other primarily involves electrostatic changes on the ore particle and the bubble surface.

The method of attack on the theory involving the free surface energy changes at the various interfaces has been principally a study of the contact angle.[1] By contact angle we mean that angle which the surface of a drop of a liquid makes with the mineral surface.

Briefly we have the following:[2]

Let

σ_{sg} be the surface tension of the gas-solid interface.

σ_{sl} be the surface tension of the solid-liquid interface.

σ_{lg} be the surface tension of the liquid-gas interface.

For a drop of liquid to remain at equilibrium on a solid surface we have the following:

$$\sigma_{lg} \cos \alpha + \sigma_{sl} = \sigma_{sg}$$

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* From the School of Chemistry, University of Minnesota, Minneapolis.

** Submitted in partial fulfillment of the requirements for the degree of Master of Science. University of Minnesota, June 1928.

[1] Sulman: Trans. Inst. Min. Met., 29, 159; "The Concentration of Minerals by Flotation," by Edwin Edser: Fourth Report on Colloid Chemistry, Brit. Ass. Adv. Sci.

[2] Rideal: "Surface Chemistry, 63 (1926).

where α is the contact angle. Of course, if σ_{sl} or σ_{lg} is increased α would tend to decrease, and if σ_{sg} is increased σ would tend to increase. The tendency for a liquid to wet a solid would depend on the values of these factors. Sulman states that the angle of contact between water and the mineral must approach, and preferably exceed, 90° in order to get pronounced flotation of the mineral. Sulman[1] and Langmuir[2] have attempted to measure the contact angles between various minerals and water but the measurement of the contact angle is rather unsatisfactory. To quote directly from Adams[3] concerning contact angles:

"Even with the utmost precautions against contamination physicists are unable to arrive at close agreement, and it is evident that the most minute alterations in the conditions obtaining at the surfaces of the three phases may affect the angle considerably."

Freundlich[4] expresses considerable doubt as to the reliability of contact angle measurements and states that minute traces of foreign substances change the contact angle materially. So it seems from these considerations that the value of contact angle measurements in the interpretation of flotation is questionable, although the theory of the hysteresis of contact angles has been investigated by Edser[5] and Sulman.[6]

The development of the electrostatics of flotation has been meager and unsatisfactory. Bains[7] in two papers proposes a theory based on electrostatic changes, but his treatment is inadequate and unconvincing.

Fahrenwald[8] points out the possibility of such an explanation. Ralston[9] suggested an electrical theory based on the electrostatic attraction between the air bubble and the ore particle. Many have condemned the electrostatic explanation and maintain that it is altogether inadequate to explain the observed facts.

In order to get a picture of flotation we present the following discussion. We have made it as general as possible in order to reduce the number of assumptions to a minimum.

In actual practice there are two reagents added to the flotation circuit: a *frother*, usually an oil, which will lower the surface tension of water and so permit the formation of bubbles upon agitation; and a *collector*, the purpose of which is to coat the mineral particles with a surface which is not wetted by water. When the circuit is agitated a froth is produced consisting of many small bubbles. Particles coated with the collecting agent are thrown into contact with the air bubble. If the decrease in free surface energy resulting

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[1] Trans. Inst. Min. Met., 29, 159.

[2] Trans. Faraday Soc., 15, 71.

[3] J. Chem. Met. Min. Soc. of S. Africa, Oct. 1920.

[4] "Colloid and Capillary Chemistry."

[5] Trans. Inst. Min. Met. 29, 159.

[6] Fourth Report on Colloid Chemistry, Brit. Ass. Adv. Sci.

[7] Min. Sci. Press, 111, 824, 883.

[8] "Surface Reactions in Flotation," Trans. Am. Inst. Min. Met. Eng. Jan. 1924.

[9] "Why do Minerals float?" Min. and Sci. Press, 111, 623.

from the coalescence of the filmed ore particle and air bubble exceeds the potential energy increase due to movement against the gravitational field the particle will be floated.

Some excellent work has been done by Gaudin and his associates on the "toxic" or unfavorable effect of electrolytes on the flotation of minerals.[1] Gaudin seems to feel that the major factor controlling cation toxicity in flotation is the formation of an insoluble soap between the oil and the cation, thus reducing the oil available for frothing. His experimental results on calcite flotation with various fatty acids seem to justify such conclusions. Other factors which he considers to be important in governing the toxicity of a cation are (1) the formation of an insoluble polar compound between the cation and one of the ions of the mineral to be floated, and (2) the electrostatic effect between the cation, air bubble, and ore particle.

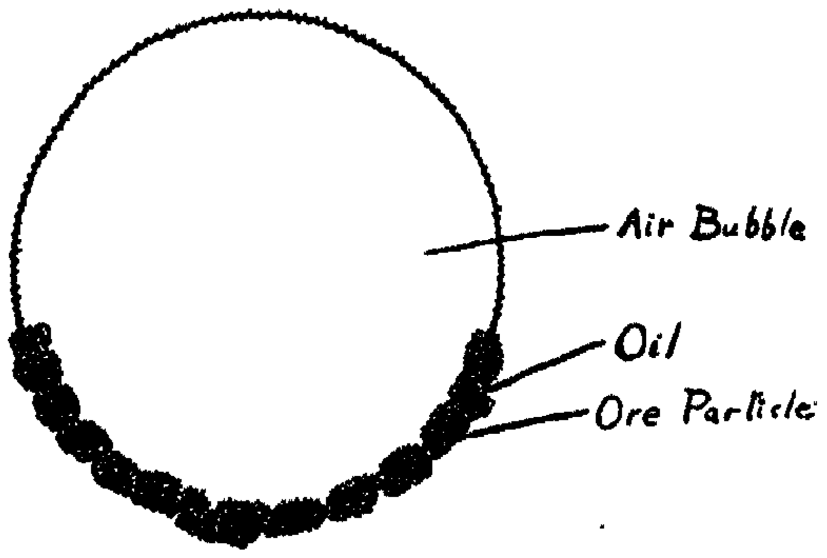

Fig. 1
"Armor Plated" Bubble

Experimental

The experimental work can be conveniently divided into two sections. The first deals with the determination of the actual quantitative relationship between the concentration of the toxic salt added and the loss in galena produced by the addition of the toxic agent. The second is the experimental work done to determine the causes for the effects produced by the added cation on the flotation of galena.

In order to determine the quantitative relationship between the concentration of the toxic salt added and the loss in galena produced by the addition of the toxic agent we constructed of thick plate glass a flotation cell as shown in Fig. 2. The reason for constructing it of glass was to eliminate any possibility of a reaction between the walls of the cell and the toxic agent added, and also to allow us to observe the progress of the flotation experiments. The volume capacity of the cell was 396 cc. when the stirring device was in place. The sides of the cell were cemented together with a glass cement and all joints shellaced. The motor which supplied the power to the agitator was

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[1] A. M. Gaudin: "Flotation Fundamentals," Am. Inst. Min. Met. Eng. Tech. Pub., No. 4 (1927).

A. C. 1/6 H.P., with a speed of 1140 R. P. M. The strength of the motor was sufficient, we feel certain, to have maintained a constant speed of agitation. The agitating paddles were of steel and the shaft, which was also of steel, was firmly set in a brass bearing, which was rigidly maintained in exactly the same position at all times by means of a rather heavy clamp projecting from a ring stand which was in turn securely attached to the laboratory table. The source of water used to replenish that lost by frothing during a flotation experiment was obtained from an inverted flask and conveyed to the cell through a rubber tube, and finally through a glass tube to the bottom of the cell. We found by experience that if the water is introduced at the top of the cell it materially reduces the flotation for a short time. The amount of water added was accurately controlled by means of a pinch clamp on the rubber tube. A constant water level was at all times maintained in the cell. Distilled water was used in all experiments.

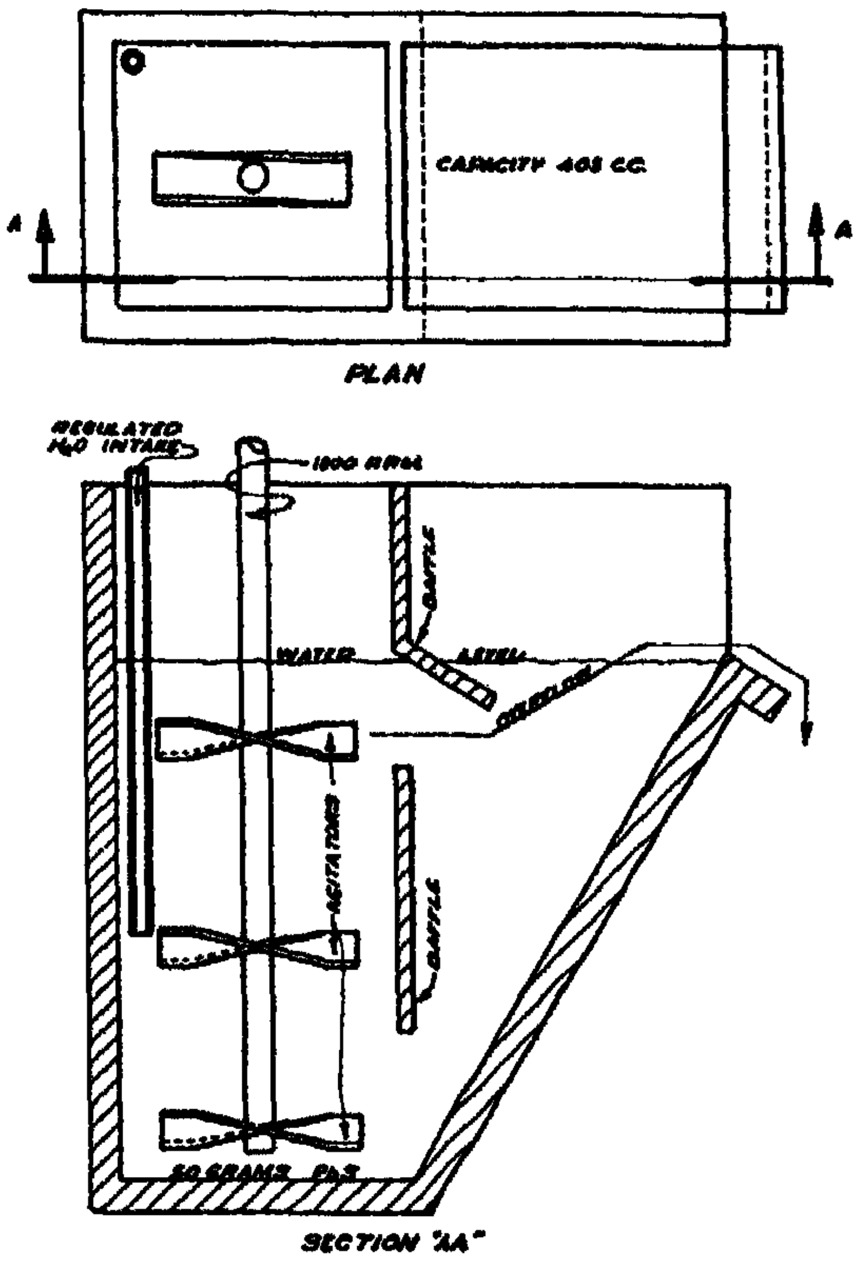


Fig. 2

In keeping with our intention to use as simple a system as possible and reduce the number of possible variables to a minimum, eucalyptus oil was used as both a frother and as a collector. No xanthate or other collector was used. The oil was added to the flotation cell by means of a capillary tube and a definite number of drops used. The constancy of the amount of oil used was checked at various times and this method was found to give accurately reproducible results.

The galena used was of the purest variety of crystallized material that could be obtained and after having been ground to the desired degree of fineness by means of a Braun pulverizer, was stored under carbon dioxide in a flask to prevent oxidation. Two lots of galena were used. One approximately 3000 grams and the other 5000 grams. After grinding each lot was thoroughly mixed so as to be uniform throughout.

Tenth molal solutions of $Th(NO_3)_4$, $Cu(NO_3)_2$, $Al(NO_3)_3$, $Cd(NO_3)_2$, $Pb(NO_3)_2$, $Ni(NO_3)_2$, $Co(NO_3)_2$, $Ba(NO_3)_2$, $Mg(NO_3)_2$, and $AgNO_3$ were made up as accurately as possible using only pure chemicals. These solutions were measured and added to the flotation circuit by means of pipettes.

The time of pre-agitation and length of the flotation experiment was controlled by a stop watch. The froth bearing the galena was skimmed from the surface of the cell in a uniform manner every 20 seconds.

The froth bearing the galena was collected in a weighed beaker and evaporated to dryness over a small flame. The yield was determined by simply weighing the beaker and the dried galena. In all the experiments exactly fifty grams of galena was used in the original charge.

The procedure followed in all the experimental work was as follows:

1. 50 grams of galena were put into the cell.
2. 100 c.c. distilled water were added.
3. The mixture was agitated for 30 seconds.
4. The solution of the "toxic ion" was added.
5. The mixture was agitated for 30 seconds.
6. Six drops of eucalyptus oil (wt. 0.0451 gr.) were added.
7. The mixture was agitated for 30 seconds.
8. The cell was filled with distilled water.
9. The mixture agitated for 7 min., skimming every 20 seconds.
10. The froth bearing the galena was evaporated.
11. The dried galena was weighed and the yield determined.

Data

We have two sets of data dealing with the effects of varying concentrations of the toxic agent on the recovery of the galena. One set was obtained on galena which had been ground to pass a 300 mesh sieve and the other set on galena which had been ground to pass a 200 mesh sieve. With the exception of a few determinations which were obviously incorrect we have included the data on all the flotation experiments. The results have been plotted in 2 ways: 1, with concentration in cc. of the toxic agent added as abscissa and the loss in grams of the galena as ordinate, and 2, the logarithm of the concentration as the abscissa plotted against the logarithm of the loss as the ordinate.

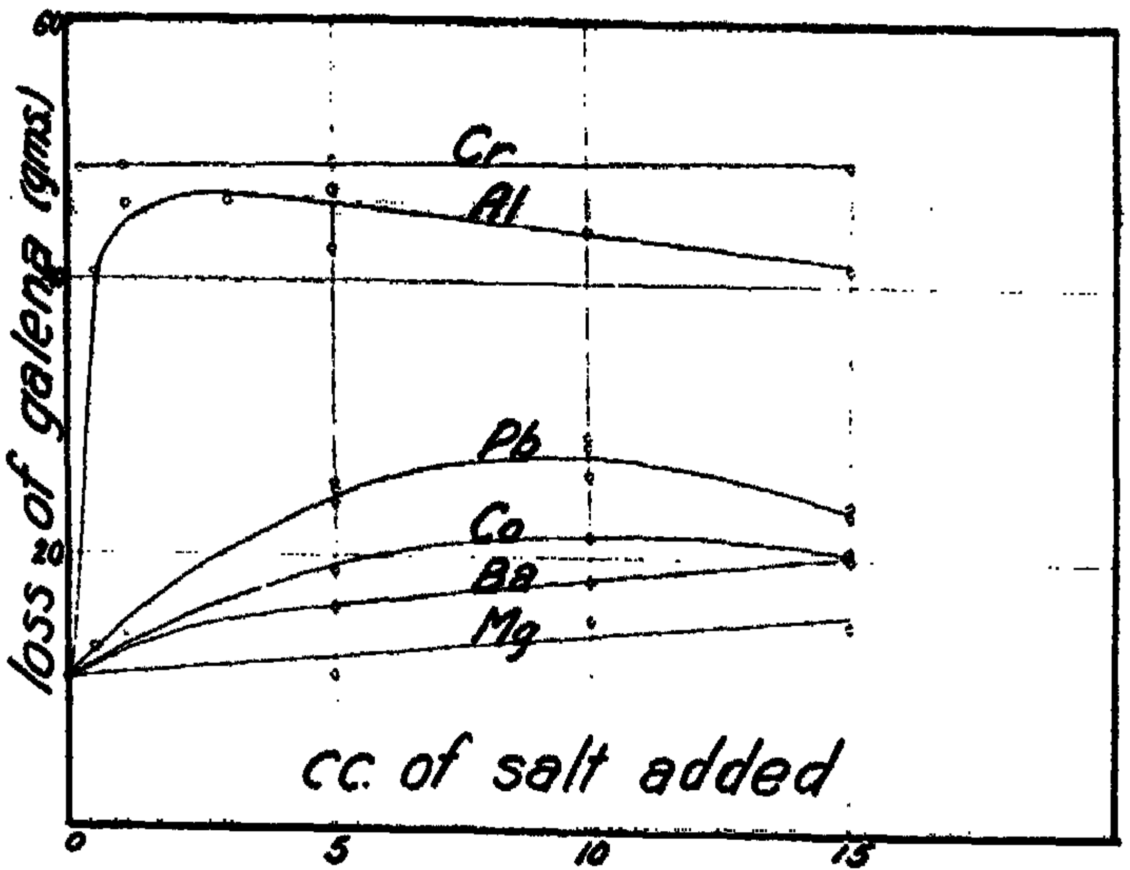
The data will now be presented.

TABLE I

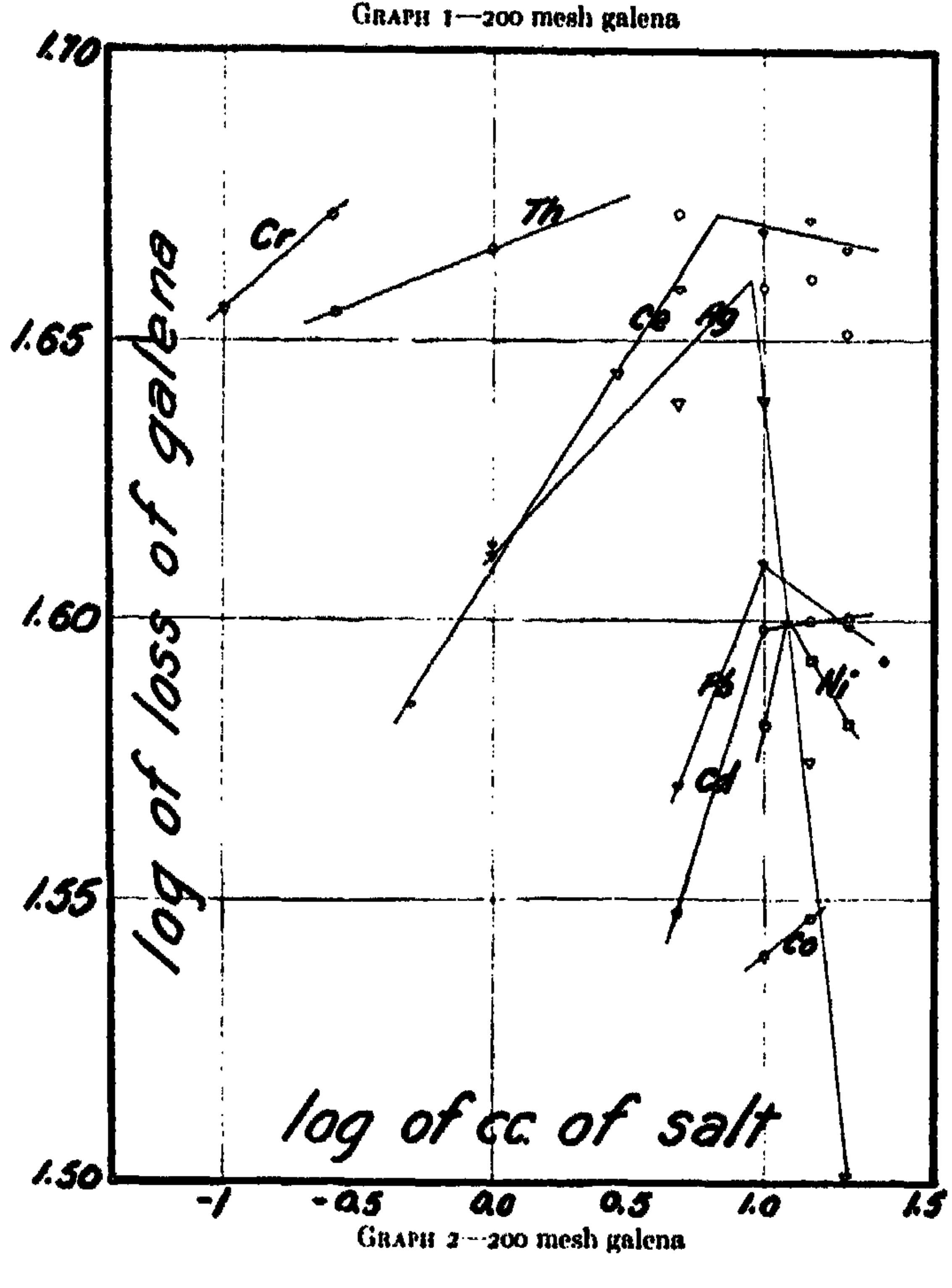
Toxic Action of Cations

(300 Mesh Galena)

NO_3 added	Amt. salt added (cc.)	Conc. of salt in cell $\frac{(mols)}{(cc.)}$	Total loss of galena (grams)	Loss of galena (grams) due to salt	Log of loss due to salt
Co	5.0	1.26×10^{-6}	19.01	7.91	.8982
Co	10.	2.52	21.71	10.61	1.057
Co	15.	3.78	20.75	9.65	.984
Pb	.5	.126	13.02	1.92	.283
Pb	1.	.252	14.15	3.05	.484
Pb	3.	.756	16.87	5.77	.7612
Pb	5.	1.26	24.06	12.96	1.1126
Pb	5.	1.26	24.92	13.82	1.1405
Pb	5.	1.26	25.95	14.85	1.1717
Pb	10.	2.52	26.29	15.19	1.1816
Pb	10.	2.52	28.19	17.09	1.2327
Pb	10.	2.52	28.86	17.76	1.2497
Pb	15.	3.78	23.81	12.71	1.104
Pb	15.	3.78	24.03	12.93	1.1116
Ba	5.	1.26	16.64	5.54	.7435
Ba	10.	2.52	18.58	7.48	.874
Ba	15.	3.78	20.03	8.93	.950
Mg	5.	1.26	11.54	.44	− .356
Mg	5.	1.26	11.40	.30	− .523
Mg	10.	2.52	15.68	4.58	.661
Mg	15.	3.78	15.56	4.26	.629
Al	.5	.126	40.65	29.55	1.4706
Al	1.	.252	45.25	34.11	1.533
Al	3.	.756	46.03	34.93	1.5432
Al	5.	1.26	42.6	31.50	1.498
Al	5.	1.26	47.18	36.08	1.5573
Al	10.	2.52	44.14	33.04	1.519
Al	15.	3.78	41.21	30.11	1.4787
Cr	.25	.063	48.21	37.11	1.569
Cr	1.	.252	48.33	37.23	1.5709
Cr	5.	1.26	48.96	37.86	1.578
Cr	15.	3.78	49.26	38.16	1.5816
		Controls			
None	.0	.0	10.53		
			11.87		
			10.91		



GRAPH 1—200 mesh galena



GRAPH 2—200 mesh galena

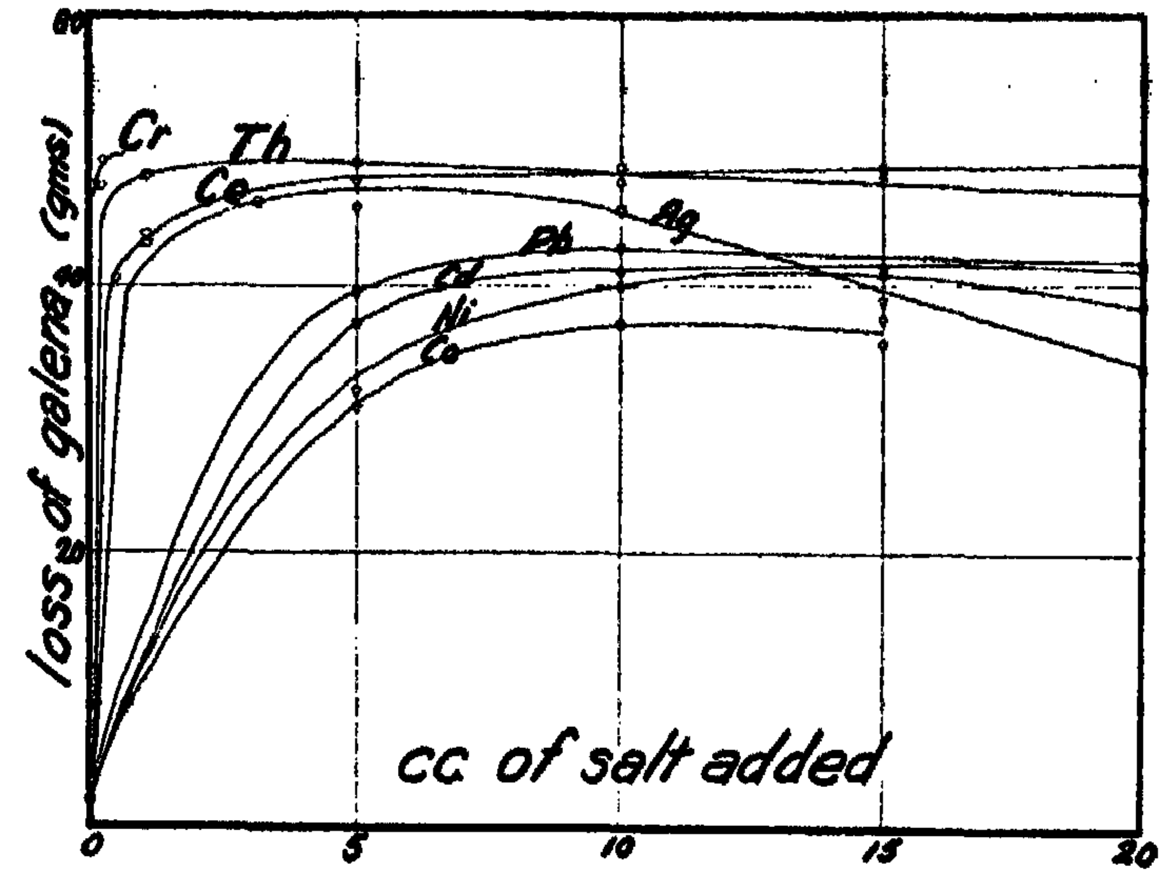
TABLE II

Toxic Action of Cations

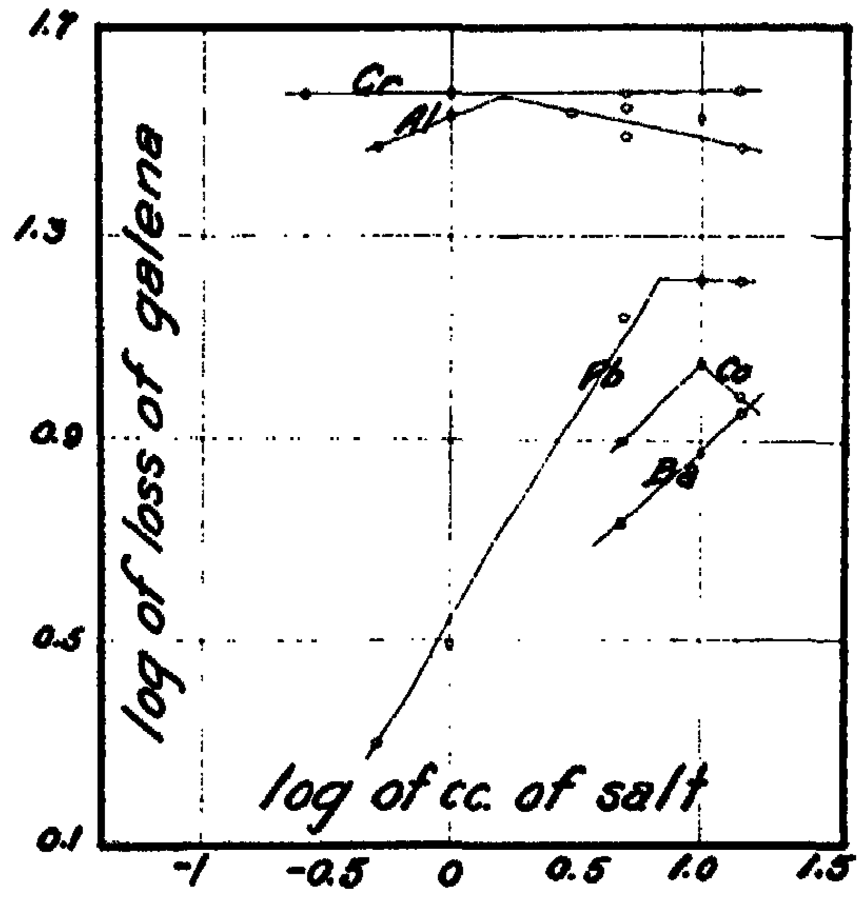
NO_3 added	Amt. salt added (cc.)	Conc. of salt in cell $\frac{(\text{mols})}{(\text{cc.})}$	Total loss of galena (grams)	Loss of galena due to salt (grams)	Log of loss due to salt
Ni	5.	1.26 × 10^{-6}	31.73	29.87	1.475
Ni	10.	2.52 ”	39.93	38.07	1.580
Ni	15.	3.78 ”	41.93	39.17	1.593
Co	5.	1.26 ”	30.63	28.77	1.459
Co	10.	2.52 ”	36.58	34.72	1.5406
Co	15.	3.78 ”	37.10	35.24	1.547
Co	15.	3.78 ”	35.25	33.39	1.523
Cd	5.	1.26 ”	37.10	35.24	1.547
Cd	10.	2.52 ”	40.93	39.07	1.5918
Cd	15.	3.78 ”	41.76	39.90	1.6009
Cd	20.	5.04 ”	41.75	39.89	1.6008
Pb	5.	1.26 ”	39.03	37.17	1.5702
Pb	10.	2.52 ”	42.66	40.80	1.6106
Pb	20.	5.04 ”	41.58	39.72	1.599
Ag	1.	.252 ”	42.80	40.94	1.612
Ag	3.	.756 ”	46.63	44.17	1.645
Ag	5.	1.26 ”	45.41	43.55	1.639
Ag	10.	2.52 ”	45.47	43.61	1.6396
Ag	15.	3.78 ”	38.63	36.77	1.5655
Ag	15.	3.78 ”	39.40	37.54	1.5745
Ag	20.	5.04 ”	33.70	31.84	1.503
Th	.25	.063 ”	47.08	45.22	1.655
Th	1.	.252 ”	48.01	46.15	1.664
Th	5.	1.26 ”	48.90	47.04	1.6724
Th	10.	2.52 ”	47.55	45.69	1.6598
Th	15.	3.78 ”	47.91	46.05	1.6632
Th	20.	5.04 ”	46.53	44.67	1.6500
Ce	.50	.126 ”	40.31	38.45	1.585
Ce	1.	.252 ”	43.19	41.33	1.6163
Ce	5.	1.26 ”	47.48	45.62	1.6592
Ce	10.	2.52 ”	48.50	46.74	1.6697
Ce	15.	3.78 ”	48.76	46.90	1.6712
Ce	20.	5.04 ”	48.18	46.32	1.666
Cr	.1	.0252 ”	47.09	45.23	1.6555
Cr	.25	.063 ”	48.93	47.07	1.6727

Controls

None	0.	0.	1.73
None	0.	0.	2.00



GRAPH 3
300 mesh galena



GRAPH 4
300 mesh galena

Experimental (II)

In an endeavor to determine the underlying cause of these effects the following series of experiments was carried out.

(a) *Surface Tension Measurements.*

In these experiments a DuNouy tensiometer was used. The instrument was standardized against pure benzene and checked against distilled water. We experienced considerable difficulty due to the evaporation of the eucalyptus oil during the measurement, but this disturbing factor was largely overcome by shaking the oil and water in a stoppered flask and making the measurements of surface tension as quickly as possible. In Fahrenwald's[1] work on the determination of surface tension of oil in water he has shown that the surface tension changes with time. In our case we were probably measuring an intermediate value between the static and the dynamic surface tension. But we feel that, inasmuch as in all our measurements we used exactly the same technique, we have results capable of comparison with one another.

We determined the relation existing between the surface tension and the concentration of eucalyptus oil. Varying amounts of oil were added to 405 cc. of water and shaken, a small amount of the liquid poured out and its surface tension determined. These results are as follows:

No. of drops	0	½	1	2	3	4	5	6
γ in dynes/cm.	72	53.5	51.3	49.3	48	45.4	45.5	45.6

TABLE III

Surface Tension of Certain Solutions

Salt added	Conc. of salt	No. drops oil	Surface tension in dynes per cm.
$Pb(NO_3)_2$	3 cc.	6	47
"	5 "	6	45.5
"	10 "	6	47.5
"	15 "	6	47.5
"	20 "	6	49.2
$Co(NO_3)_2$	5 "	6	44.8
"	10 "	6	46.2
"	15 "	6	45.3
"	20 "	6	46.5
$Pb(NO_3)_2$	10 "	2	50.8
"	15 "	2	50.5
$Co(NO_3)_2$	10 "	2	48.6
$Cr(NO_3)_3$	1 "	2	49.2
None	0.0 "	6	45.6
"	0.0 "	2	49.9
"	0.0 "	1	51.3
$AgNO_3$	1 "	1	52.4

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[1] Surface Reactions in Flotation. A. W. Fahrenwald: Min. and Met., Jan. 1924.

In order to find what effect the toxic agent might have upon the surface tension of the oil-water mixture, we mixed 6 drops of oil with 400 cc. of distilled water and added M/10 $Pb(NO_3)_2$ in amounts varying from 3 cc. to 30 cc. These experiments were repeated using M/10 $Co(NO_3)_2$ in place of $Pb(NO_3)_2$. We also tried the effect of 1 cc. M/10 $Cr(NO_3)_3$ on 2 drops of oil in 405 cc. water and then 5 cc. M/10 $AgNO_3$ on one drop of oil in 400 cc. water. The data on these determinations are given in Table III.

We then tried to determine the effect of the addition of galena on the oil-water mixture and also what effect the addition of the toxic agent would have upon the surface tension of this system. For this purpose we carrried out the experiments summarized in Table IV.

TABLE IV

Surface Tension of Certain Solutions after Contact with Galena

Galena	Water	Electrolyte		Oil	Surface tension in dynes per cm.
8.33[1]	66				66.5
8.33	66			1 drop	60.0
8.33	66	M/10 $Pb(NO_3)_2$	1.66cc.	1 "	60.4
8.33	66	"	1.66cc.		61.0
10.00	66	"	1.66cc.	1 "	61.0
10.00	66	M/10 $Cr(NO_3)_3$	1.66cc.	1 "	52.5
	66	M/10 $Mg(NO_3)_2$	1.66cc.	1 "	61.0
	66	M/10 $AgNO_3$	1.66cc.	1 "	59.7

Adsorption of Cations by Galena

Fifty-gram lots of the galena passing a 200-mesh sieve were thoroughly washed and 400 cc. of distilled water added. Then 10 cc. of the tenth molal solution of toxic agent were added and the mixture well shaken. After sixteen hours standing the solution was filtered from the galena and the amount of toxic cation in the filtrate determined by standard gravimetric procedure. The difference between the amount of cation found in the filtrate and the amount in 10 cc. of a tenth molal solution gave us the amount adsorbed on the surface of the galena. The following results were obtained:

1. Number of equivalents $AgNO_3$ adsorbed by 1 gr. galena 3.6×10^{-6}
2. Number of equivalents $Ba(NO_3)_2$ adsorbed by 1 gr. galena 2.66×10^{-6}

Discussion

From an examination of graphs 2 and 4 where the log of the concentration of the toxic salt added has been plotted against the log of the amount of galena that failed to be floated we conclude that up to a certain concentration of the toxic salt we can use an equation of the type

$$\log L = \log a + b \log c$$

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[1] This concentration of material corresponds to those used in the flotation experiments, using 10 cc. of M/10 electrolyte.

where c = cc. of the toxic salt added, a = a constant, b = a constant, and L = the amount of galena that failed to float. The above equation can be thrown into the form

$$L = ac^b.$$

The constants a and b can easily be determined.

We have the following values for the two sets of data:

TABLE V

Constants for Curves in Graphs 2 and 4

Salt added	200-mesh galena a	200-mesh galena b	300-mesh galena a	300-mesh galena b
Mg			.50	.579
Ba			1.30	.760
Co	7.54	.622	2.30	.665
Ni	9.54	.602		
Cd	11.14	.543		
Pb	13.34	.485	3.05	.755
Ag	40.94	.069		
Al			34.11	.0212
Ce	41.33	.061		
Th	46.15	.0114		
Cr			37.23	.0101

The above expression, which shows the relation between the concentration of the salt added and the loss in grams suggest Freundlich's adsorption isotherm, which is commonly written,

$$x/m = ay^{1/n}$$

and would indicate an adsorption of the toxic agent by the galena. We find also from an examination of the curves that at a certain point there is a break. The new line having very nearly the same absolute value as the old but of opposite sign. The equation for this part of the curve thus assumes the form

$$L = a'c^{-b}$$

It appears from these considerations that we are dealing with two adsorption curves. Such a state of affairs is not uncommon. We obtain just such a curve when we add $AlCl_3$ to a negatively charged gum mastic sol.[1]

All cations investigated, except chromium, produced this characteristic change in the shape of the curve, indicating that there may be different factors entering into the cause of the toxicity of chromium ion.

From an examination of Table III it is evident that there is no reaction between eucalyptus oil and the toxic salts examined for if there had been we would have gotten an increase in the surface tension due to reduction of the amount of oil available. Hence we cannot in our case resort to Gaudin's

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[1] Kruyt-van Klooster: "Colloids."

explanation of the toxic effect of the salts by formation of insoluble soaps between the oil and the cations.

The series of experiments in Table III indicates that there is no reaction between the salt added and the oil. Nor is the oil displaced from the surface of the galena by the addition of a toxic agent except in the case of chromium. In all cases except that of chromium we cannot postulate the formation of a surface which is more wetted by water than by oil.

At this point we wish to consider the evidence for a theory which attempts to explain the effects of electrolytes on the flotation of galena by means of the electrostatic changes produced on the galena particle by the cations and anions of the electrolyte.

It has been shown that the amount of a cation adsorbed by an As_2S_3 sol[1] bears a marked relation to the solubilities of the sulfides of the cations. We may make a similar test with galena. The following table gives the relative toxicity of the cation on the flotation of galena compared with the solubility of the corresponding sulfides in pure water.

TABLE VII

Solubility of Sulfide and Toxic Action of Cations

Gaudin (using xanthate)	Bull & Taylor (using eucalyptus oil)	Mols per liter[2] solubility of sulfide
Ag most toxic	Ag most toxic	Ag_2S 0.52×10^{-6}
Pb	Pb	PbS 1.21×10^{-6}
Cd	Cd	CdS 9.00×10^{-6}
Co	Ni	NiS 39.62×10^{-6}
Ni least toxic	Co least toxic	CoS 41.62×10^{-6}

One would expect this adsorption of cations to result in a positive charge on the galena particle. There would thus be an actual repulsion between the galena particles, with a corresponding decrease in flotation.

In the case of those cations which do not form an insoluble sulfide we may suggest that the different toxicities observed are the result of different adsorption of the cations on the surface of the galena or to varying effects on the charge on the the air bubble. Of course the differences in valence of the cation must also be taken into consideration since for equal molal amounts adsorbed the toxicities of the cations could be expected to stand in direct ratio to their valence because a divalent ion carries twice the electrostatic charge of a monovalent ion and so on. In fact a general grouping of the cations according to their valences may be observed.

The quite characteristic decrease in the loss of galena after a certain concentration of the toxic salt is reached is due, probably to an adsorption of the negative NO_3 ion. A similar case is the adsorption of the Cl ion after a certain concentration of $AlCl_3$ solution has been added to a negatively charged

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[1] Z. physik. Chem., 100, 1425.

[2] Boeke-Eitel: "Grundlagen der physikalisch-chemischen Petrographie," 2d Ed., p. 385

gum mastic sol;[1] and also in the reversal of the zeta potential of cellulose with increasing concentration of electrolytes, as observed by Briggs.[2]

Finely ground galena when suspended in water floculates in a very short time and the supernatant liquid is entirely clear. If an electrolyte be added and thoroughly mixed the galena is peptized and the supernatant liquid becomes cloudy and filled with a suspension of fine particles of galena. This condition remains for several days. Upon the addition of sodium sulfate the galena is flocculated completely and the supernatant liquid clears up. This behavior is entirely analogous to that of a colloid and the only satisfactory explanation of such a behavior is based upon the assumption of electrostatic charges on the mineral particles.

In addition to this highly suggestive evidence of the important role played by electrostatic charges in the toxic effects of salts in flotation we have data[3] which shows that the initial positive charge carried by galena is greatly increased by the addition of $AgNO_3$, $Pb(NO_3)_2$, $Co(NO_3)_2$ in concentrations comparable with those used in our flotation circuit. $AgNO_3$ increased the potential on the galena the most, then $Pb(NO_3)_2$, and finally $Co(NO_3)_2$. It will be observed that this is also the order of the toxicity of these salts, $AgNO_3$ being the most toxic. Apparently as far as these salts are concerned their toxic effect is simply due to the increasing of the positive charge or galena particle which tends to peptize the galena and so prevent it from coalescing on the surface of the air bubble.

We are at a loss to account for the extreme toxicity of $Cr(NO_3)_2$ and $Th(NO_4)$, since both of the salts decreased the positive potential on the galena.

Perhaps the following considerations will help somewhat to clarify the part played by chromium. Its behavior is distinctly different from any of the ions investigated. The shape of the curve connecting the loss of galena with the concentration of the salt added is different from any of the other curves. It shows no maximum even at high concentrations, which was shown quite clearly by every cation tried except chromium. The surface tension of 10 grams of galena, 66 cc. water, one drop of oil, and 1.66 cc. of M/10 $Cr(NO_3)_3$ was 52.5 dynes per centimeter while the surface tension of 10 grams of galena, 66 cc. water, and one drop of oil was 61.0 dynes per centimeter, indicating clearly that oil is not adsorbed as readily by a galena surface which has been treated with a $Cr(NO_3)_3$ solution and suggest that the surface is now more easily wetted by water than before the treatment with $Cr(NO_3)_3$. This might explain the extreme toxicity of the chromium ion on the flotation of galena.

Summary

In this research a large number of measurements have been made on the flotation recovery of galena by means of eucalyptus oil when various nitrates are present. The cations of these salts have toxic or unfavorable effects on

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[1] Kruyt: "Colloids."

[2] Briggs: J. Phys. Chem., 32, 641 (1928).

[3] Bull: The Electrostatics of Flotation, J. Phys. Chem., 32, 000 (1929).

flotation, reducing the yield. The form of the curve of loss versus concentration of electrolyte strongly suggests an adsorption isotherm and leads to the belief that the cation is adsorbed on the galena surface. It is very probable that the normal mechanism of flotation of galena by eucalyptus oil in absence of any electrolyte consists: (1) in the formation of air bubbles in which the oil is the frothing agent, (2) in the filming of the galena particles by the oil, and (3) in the adherence of the filmed particles to the external surface of the bubble so as to form an "armor-plated bubble" which does not break down readily and thus floats the galena. On the other hand the toxic action appears to be due to the electrostatic repulsion of similarly charged mineral particles which reduces the adherence to air bubbles necessary for flotation. The applicability of the Schultze-Hardy valence rule to the toxic process and the regular increase in toxicity of bivalent cations of increasing adsorbability on the galena surface give very strong support to this hypothesis. Studies which have been made by various investigators of the effect of ions on the charge or zeta potential of suspended particles demonstrate a rather complex behavior. It is probable that the complete story of flotation toxicity cannot be told until such measurements have been made on pure minerals.

Minneapolis
Minnesota,
July, 1928.

THE ELECTROSTATICS OF FLOTATION

BY H. B. BULL

The purpose of this research was to investigate the electrostatic charge carried by finely ground galena particles in distilled water and in solutions of different concentrations of salts in hopes of being able to give a more logical and certain interpretation to the observed "toxic" effects of these salts on the flotation of galena.

As is well known, there is quite a definite relationship between the concentration of a salt added to a flotation circuit and its toxic effect. This is clearly shown by the work of Gaudin and his associates[1] and also by Taylor and Bull.[2] The following graph shows the typical effects of a number of cations on the flotation of galena.

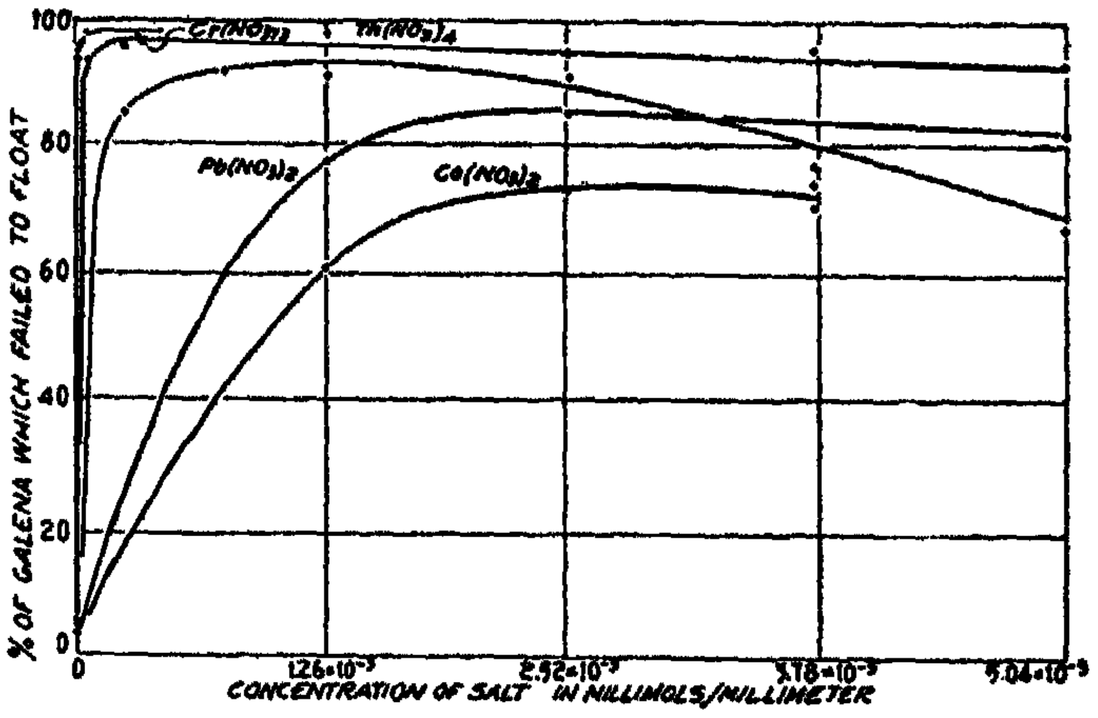

FIG. 1

Showing "toxic" effect of electrolytes on the flotation of galena

An attempt was made to determine the electrostatic charge on finely ground galena by the streaming potential method in an apparatus developed by Briggs.[3] But the resistance of the galena was so low that no difference of potential could be observed.

The method finally adopted was based on a phenomenon discovered by Dorn[4] in 1878 and bearing his name. He found that when a body falls through a liquid there is a difference of electrical potential established between the top and bottom of the liquid. Freundlich and Mäkelt[5] attributed the existence

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[1] "Flotation Fundamentals" by A. M. Gaudin, Harvey Glover, and C. W. Orr Hansen.

[2] J. Phys. Chem., 32, 641-656 (1929).

[3] J. Phys. Chem., 32, 641 (1928).

[4] Dorn: Ann. Physik., (4) 3, 20 (1878); 9, 513; 10, 46 (1880).

[5] Freundlich and Mäkelt: Z. Elecktrochemie, 15, 161 (1912).

of this difference of potential to what is termed the zeta potential, that is the electrical potential existing across the immovable absorbed layer of ions and the boundary layer of movable molecules.

The actual experimental technique was to allow ten grams of the purest crystallized galena, which had been ground to pass a 100 mesh sieve and retained on a 325 mesh sieve, to fall through a glass tube 65 cm. long and 3 cm. in diameter, which contained the liquid in question. Platinum wires fused into the walls of glass tube 2 cm. from each end were used as electrodes. A quadrant electrometer was used to register the difference of potential between the top and bottom of the tube. The observed deflection of the quadrant electrometer, which was produced by the falling of the galena, was reproduced by an electromotive force whose strength could be accurately determined and thus the difference of potential produced by the falling galena was obtained.

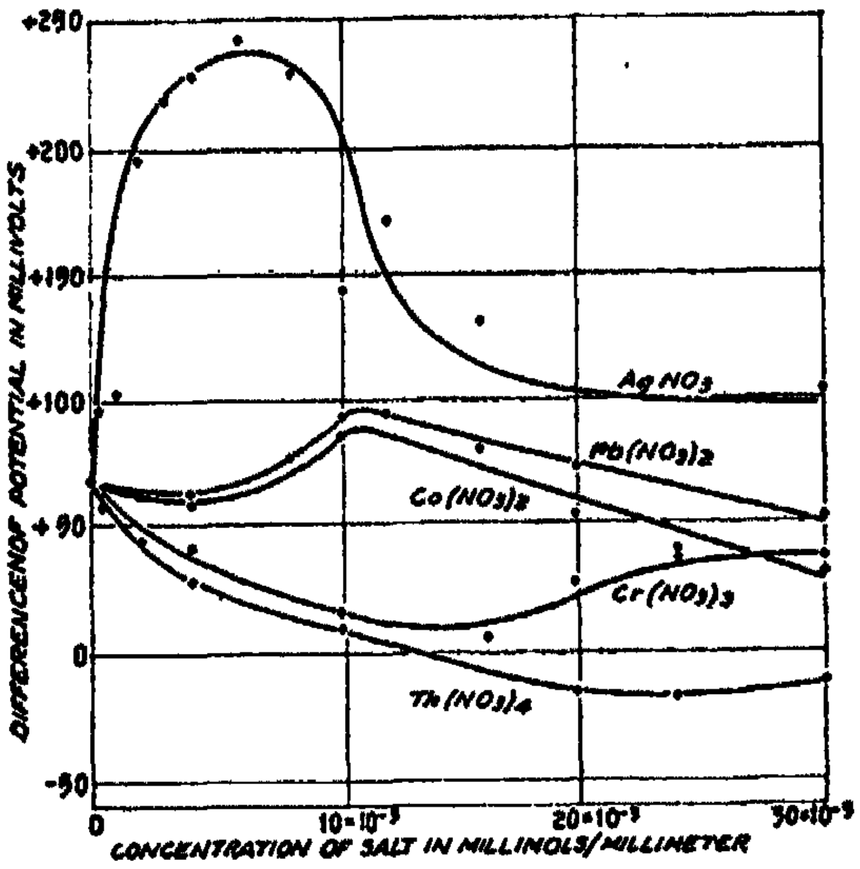

Fig. 2

The galena was allowed to fall through varying concentrations of the nitrates of Th, Cr, Ag, Pb and Co.

Results

In Fig. 2 the observed difference of potential is plotted as the ordinate against the concentration of salt added in millimols per milliliter as the abscissa. The sign of electrostatic charge on the galena is indicated.

Discussion

It is quite clear that in this series of determinations the zeta potential has not been actually determined but we have reason to believe[1] that while

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[1] Freundlich and Mäkelt: Z. Elektrochemie, 15, 161 (1912).

the difference of potential between the top and bottom of the liquid is not equal to the zeta potential it is, within certain limits, proportional to it.

A comparison between the toxic effect of Ag, Pb, and Co and the effects that these ions produced on the electrostatic charge of the galena is highly suggestive. It indicates, perhaps, that a large part of the toxic effect of these ions is due to the raising of the electrical charge on the particles of galena and so preventing them from collecting on the air bubble thereby reducing the yield in flotation. This explanation becomes more convincing in light of E. F. Burton and J. E. Currie's[1] work who found that when small lead shot were dropped through solutions of salts of different concentrations that there was a marked repulsion between the shot at certain salt concentration as evidenced by scattering of the shot as they fell and that these concentrations correspond to salt concentrations where there was a maximum difference of potential between the top and bottom of the liquid.

The reason for the large effect of the silver ion as compared with the lead and cobalt ion is probably due to the fact that the silver ion is absorbed to a much greater degree than the lead and cobalt ion, this greater absorbability being due to the fact that silver sulfide is three times more insoluble than lead sulfide and eighty times more insoluble than cobalt sulfide.

In as much as neither thorium nor chromium form stable sulfides and since the galena carries an initial positive charge, the nitrate ion in these cases plays a predominating role. There is apparently no connection between the extreme toxic effect of these ions on flotation and the electrostatic charge carried by the galena while in a solution of these salts.

It is also highly suggestive that finely ground quartz was found to carry a relatively large negative charge while it is well known that air bubbles in water are also negatively charged.[2]

Summary

1. There is an apparent connection between the toxicity of Ag, Pb, and Co on the flotation of galena and the electrostatic charge carried by finely ground galena in solutions of the nitrates of these cations.

2. There is apparently no connection between the toxicity of Th and Cr on the flotation of galena and the electrostatic charge carried by finely ground galena in solutions of the nitrates of these cations.

University of Minnesota,
Minneapolis.

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[1] N. A. McTaggart: Phil. Mag. (6), 27, 297 (1914).

[2] E. F. Burton and J. E Currie: Phil. Mag., (6) 49, 194 (1925).

ULTRA-VIOLET SPECTROSCOPY OF THE FLAMES OF MOTOR FUELS

IV.[1] The Practical Utilization of a Small Quartz-Prism Spectrograph for the Quantitative Determination of Lead Tetraethyl in Gasoline.

BY G. L. CLARK AND H. A. SMITH[2]

Introduction

Many of the chemical engineering problems of today, and most certainly those of tomorrow, are intimately concerned with the detection and determination of very small amounts of foreign material acting as catalysts and with the study of obscure reaction mechanisms. It is too little realized that the optical spectrograph is one of the most powerful instruments known for attacking such problems as these. There are many examples of the use of spectroscopy in qualitative and quantitative analysis, particularly with line emission spectra.[3] In the preceding papers of this series the method has been applied, with interesting and valuable results, to the analysis of the flames of motor fuels, particularly as they occur in internal combustion engines. Detonation was distinguished by a radiation running far into the ultraviolet, while much of this is not emitted or is absorbed by suppressors such as lead tetraethyl, aniline, or iodine. Definitely banded spectra were observed to characterize specific conditions. The radiation in the four quarters of an engine stroke has been studied, and various gasolines have been rated from their ultraviolet flame spectra. The presence of lead tetraethyl was found to be sensitively indicated by the presence of characteristic lead lines.

The purposes of the present investigation were as follows:

(1) to test the method systematically as a means of qualitative and quantitative analysis for lead tetraethyl in motor fuels;

(2) to establish the limits of sensitiveness and accuracy of a small and inexpensive quartz prism spectrograph and to show its applicability to chemical and industrial problems in general;

(3) to ascertain, if possible, any further facts concerning the mechanism of the action of lead tetraethyl as a detonation suppressor.

The Spectrograph

A Gaertner quartz spectrograph of the type L250, holding a plate of 8.25 cm. × 1.08 cm., was used in this investigation (see Fig. 7). A stainless steel slit with micrometer screw was designed to replace the usual type of slit and it was satisfactory in every way. An optical quartz window was

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[1] For the first three papers of the series, see Ind. Eng. Chem., **18**, 528-531 (1926); J. Soc. Automotive Engineers, **20**, 264-269 (1927); **23**, 166-173 (1928).

[2] Holder of the Standard Oil Company of Indiana Research Fellowship, which made possible this and other related investigations.

[3] An outstanding contribution is the series of papers by Negresco: J. Chim. phys. **25**, 142, 216, 308, 343, 363 (1928).

framed and fitted over the slit, however, so that it was necessary to clean the slit only once a month even in the presence of oil or very humid conditions. But it was established as good practice, before a plate was exposed, to reset the slit and examine the spectrum on the fluorescent screen.

The spectrograph is small, light, easily portable and can be operated in any position so that it may be adapted to a variety of sources which it may be desirable to examine. A spectrum 4.45 cm. long, covering wave lengths from 2225 A.U. to 5461 A.U. can be obtained with the photographic plates used, and any spectral line can be identified from the wave length measurements, if a standard line spectrum is chosen in which the lines are relatively close together.

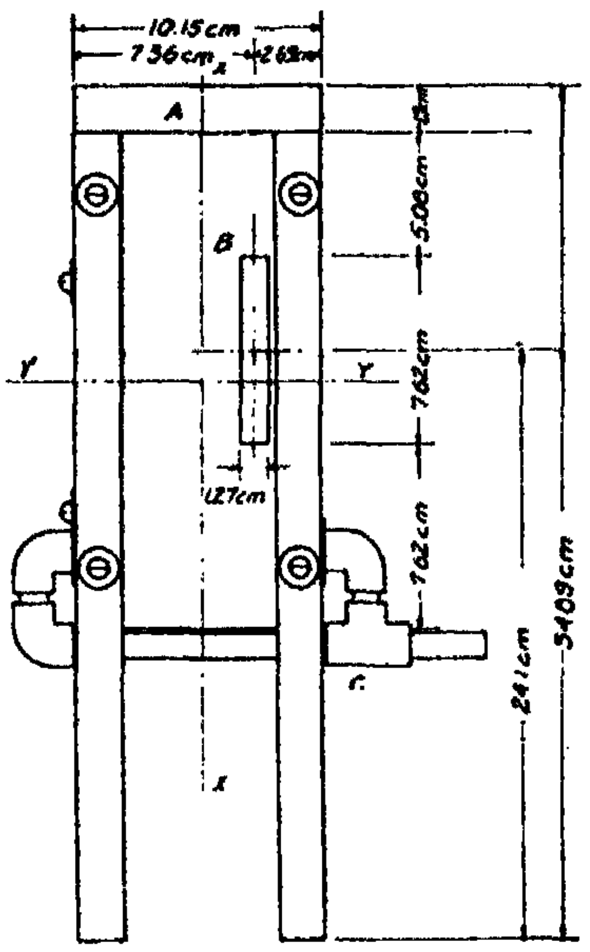

Fig. 1
The Mercury Arc Housing Front Elevation

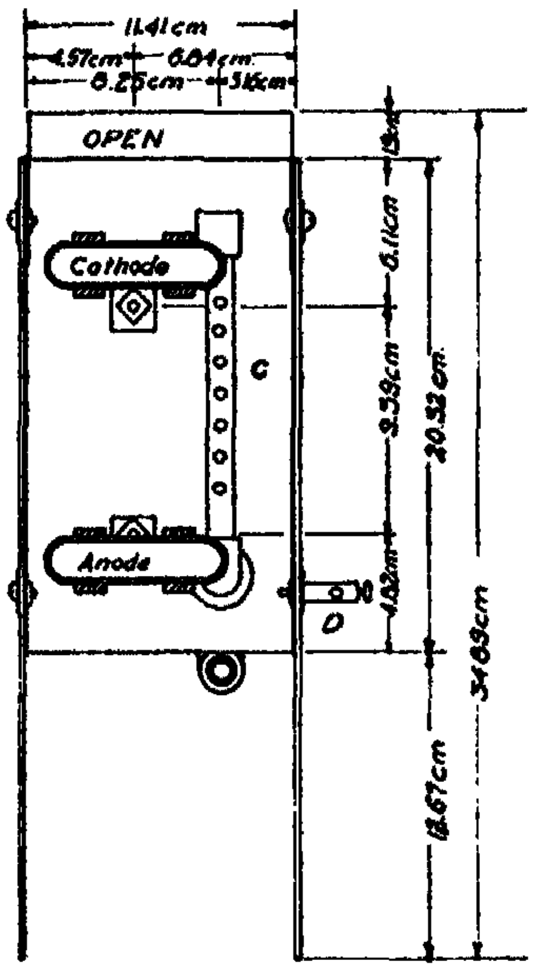

Fig. 2
The Mercury Arc Housing Section X—X Fig. 1.

The Standard Line Spectrum

For the standard spectrum, by means of which the flame spectrum was measured, the mercury arc in vacuo in a quartz tube was chosen because the arc gives a good number of well-defined lines in the ultra-violet as well as in the visible region.

The details of construction of the mercury arc and its housing appear in Figs. 1, 2, and 3. Since a standard apparatus was not available, the arc and its housing were designed for the purpose of economy, simplicity and portability, and were built in the laboratory. This home-made lamp was found eminently satisfactory for the purpose used.

Eastman 36 plates were used for photographing the ultraviolet and visible regions. Mineral oil, such as Nujol, has commonly been used for sensitizing plates to the ultra-violet, due to its property of being fluorescent when it is excited by high frequencies. The results of a test on these plates, however, indicate that such an oil did not sensitize the plate beyond the limit reached without the oil, but appreciable fogging did occur.

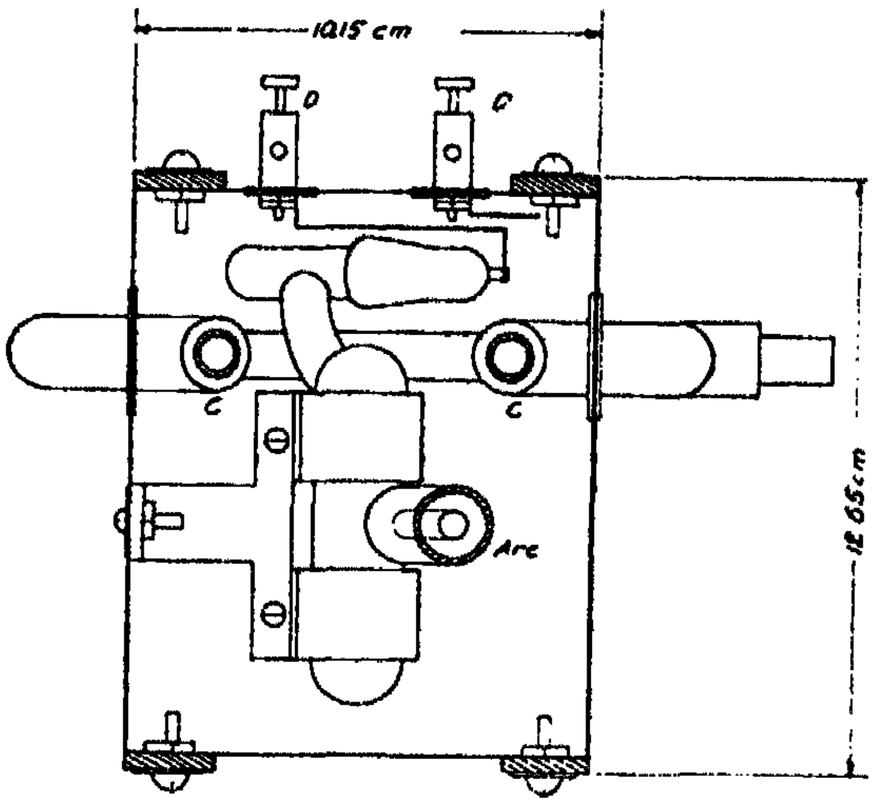

Fig 3
The Mercury Arc Housing Section Y—Y Fig. 1.

Type of Burner Employed and Procedure for burning Fuel

The first type of burner employed as a source of radiation was a small gasoline blow-torch. It was soon found, however, that on burning a solution of gasoline and the commercial lead tetraethyl liquid the torch was badly choked by black carbonaceous material and possibly some lead. It was evident that super-heating and decomposition were going on and that a quantitative determination was doubtful. Two things were done to correct this. First, the commercial liquid was distilled from the red dye, *under reduced pressure*, since the dye is not volatile and would decompose and cumulatively clog any apparatus depending on the principles of distillation. Second, a new type of still and burner were developed in which the temperature of distillation could be controlled and indicated.

The details of the still appear in Figs. 4, 5, and 6. Fig. 4 is a front elevation showng the exterior arrangement. Fig. 5 is the cross section Z-Z of Fig. 4 while Fig. 6 is the cross section o—o of Fig. 5. The electrical heating system consists of two terminals insulated from the galvanized sheet iron housing of the still by two blocks of transite board (see Fig. 5). The heating element itself is a coil of chromel wire which is wound around a Pyrex tube L, Figs. 5 and 6, held in place by a thin layer of alundum cement worked in between the wires on the Pyrex tube. The temperature of the still is indicated by a 360° Centigrade thermometer which is placed in the annular space midway between C and L, Figs. 5 and 6. The still will heat up to operating temperature, 225°, in 15 minutes if the power input is regulated properly. All exterior piping is lagged with a winding of asbestos yarn covered with friction tape. The still coil and heating coil A and L, Figs. 5 and 6, are insulated by a magnesia filling between a 7.62 cm. pipe N, Figs. 5 and 6, concentric with the coil and the galvanized sheet iron housing.

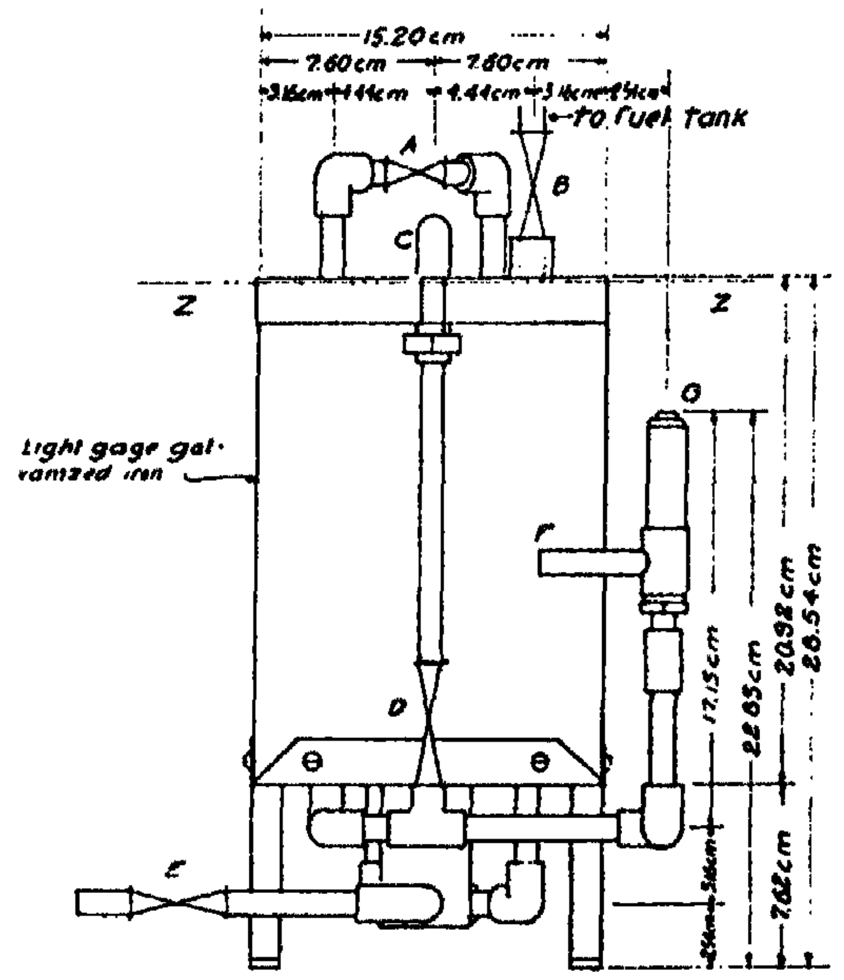

Fig. 4
Still, Front Elevation

When the still has reached 225° and the 3.2 mm. needle valves E and A and gate valve B, Fig. 4 are closed, an hour's supply of fuel, 150 cc., is put into the tank indicated at the top of Fig. 4, and a pressure of 2.64 kg. per sq. cm. applied by compressed air. The 3.2 mm. gate valve B and the needle valve A, Fig. 4, are then opened a small amount, determined by experiment, and the gasoline-lead tetraethyl mixture flows slowly down the 3.2 mm. iron pipe B, Fig. 5. When the lower part of the pipe carrying the liquid phase, including the blow-off valve E and its connections, is filled with the liquid mixture it rises into the 3.2 mm. copper spiral still M, Figs. 5 and 6, which is at 225°. The solution here contains constituents boiling from 60-200° but the lower boiling portions soon flash into vapor leaving some of the higher boiling portions which are forced up into the spiral still by the oncoming liquid until sufficient time has elapsed for the vaporization of all the liquid. A balance between the pressure applied to the lead tetraethyl solution and the opening of valves B and A must be determined and maintained within limits to damp the oscillations in pressure and hence in flow, tending to occur in a still of this small capacity.

The gaseous mixture, having the same composition as the liquid mixture in the tank and being under a pressure of 2.64 kg. per sq. cm., is reduced through valve A to atmospheric pressure. The gas then flows down the 3.2 mm. iron pipe A, Fig. 5, and mixes with the preheated primary air at C″, Fig. 5. The primary air is introduced at C, Fig. 5, at a pressure of 2.64 kg. per sq. cm. and is led upward through the 3.2 mm. iron pipe C′, concentric with and within the heating element L. The air is heated to 225° in its passage through the pipe C′ and is then brought down through the exterior pipe C, Fig. 4, and is reduced to atmospheric pressure through the 3.2 mm. needle valve D, Fig. 4, where it mixes with the gases from the still at the same temperature. The air-gas mixture is then led to the burner G, Figs. 4 and 5, which is a 3.2 mm. iron pipe of the required length from the top of which the flame burns. Valves D and B are set at the best operating conditions by trial and are left at these settings throughout the tests, all regulation of the flame being accomplished through needle valve A.

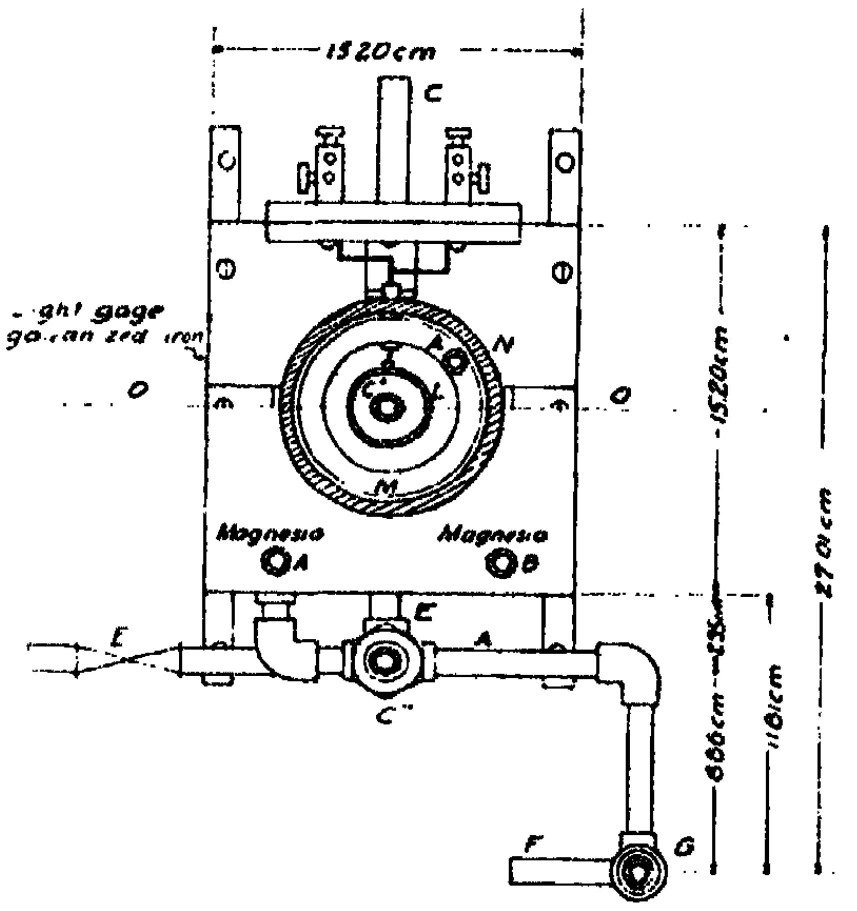

FIG. 5
Still, Cross-Section Z-Z of Fig. 4

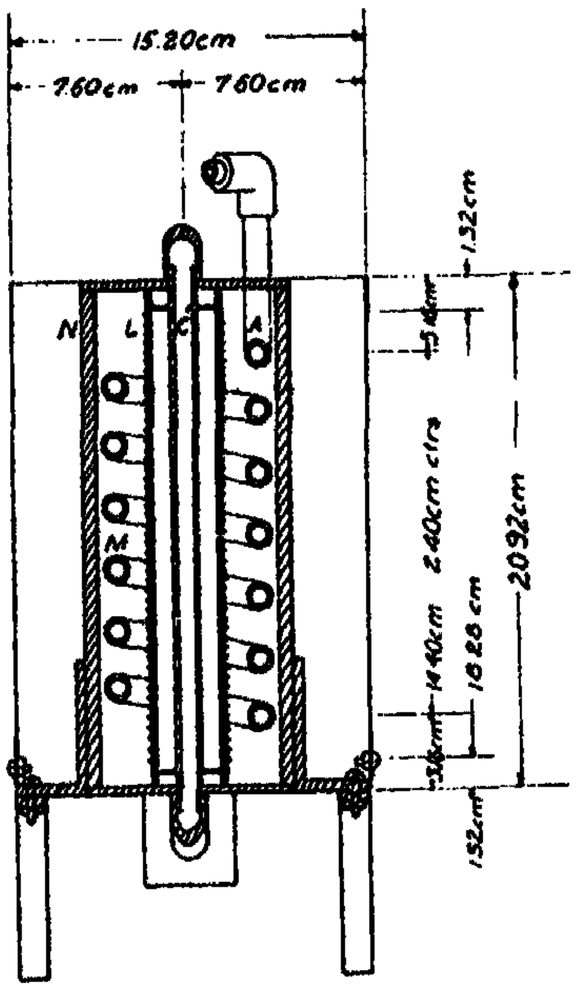

FIG. 6
Still, Cross-Section O-O of Fig. 5.

The still was fairly smooth in operation but it was impossible, with the small capacity of the still, to obtain an absolutely steady flame, the result being that the product "time × intensity" is not the same for a given time. This product should be practically constant or otherwise the spectra will not be comparable. Since no readily available method was at hand to measure this product it remained to fix the intensity of the flame just above the port. Now, the intensity of the flame varies with the air-gas ratio; the larger the ratio, in general, the greater the intensity. It was inconvenient to regulate the primary air so that it was kept constant and the flame was surrounded at the port with an atmosphere of oxygen supplied through F, Figs. 4 and 5, to a 10 mm. pipe concentric with and surrounding the burner pipe G.

For the purpose of improving combustion and limiting the radiation from the incandescent carbon in the flame, appearing when the air-gas ratio is low, a 3.8 cm. pipe 20.32 cm. long, drilled with holes (for observation) every 2.54 cms. for 12.70 cms. from the lower end, was clamped 1 cm. above the port of the burner. A pilot flame of gas was kept burning in this pipe at all times. A shutter or galvanized iron blind, fitted to a slide and clamped to a stand, was kept down in front of the slit except when making an exposure. After an exposure is made using a solution of lead tetraethyl and gasoline the still is washed with 75 cc. of pure gasoline at 225°. Then, of course, the blow-off is opened to drain the system completely. The next spectrum taken is always one of pure gasoline. Then in making an exposure to the mercury arc the sliding screen is moved over to the desired position and the standard spectra made without moving the plate holder.

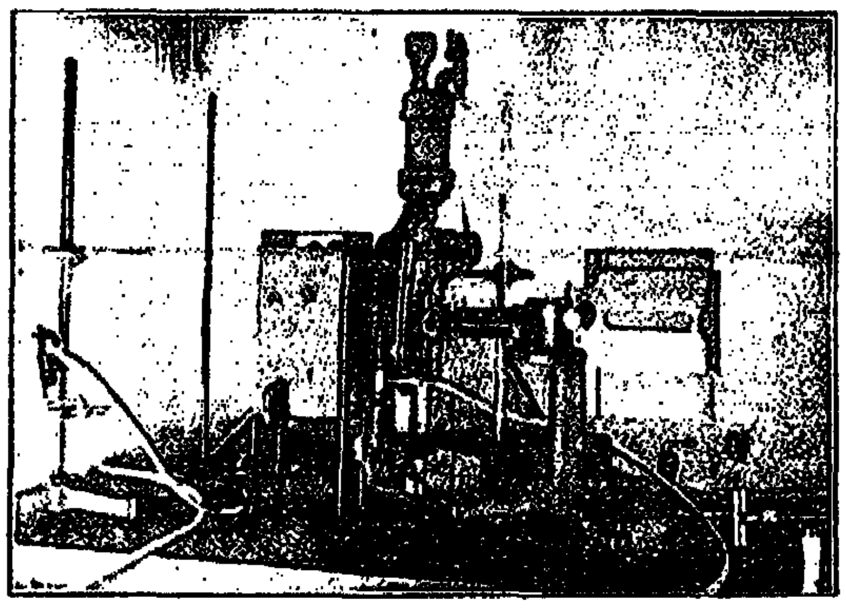

Fig. 7
The Apparatus set for an Exposure to the Mercury Arc

The general disposition of the apparatus is photographed in Figs. 7 and 8, the former showing an exposure to the mercury arc and the latter an exposure to the fuel flame.

The burner was designed especially so that the vaporized fuel should maintain a constant composition throughout a given experimental run; in other words to assure that the concentration of the lead tetraethyl in the liquid should not increase in the residual liquid. The following experimental facts prove the validity of the design and of the method of quantitative analysis:

(1) The end point of the gasoline used was 208°, the arithmetic mean of the end-points of two other standard grades of gasoline. The boiling point of lead tetraethyl, 202° at atmospheric pressure, comes within 4° of the end point of the gasoline used.

(2) The residue of decomposition obtained in the blowtorch by superheating was analyzed for lead with negative results.

(3) There was at all times a positive flow of fuel, the still being under a positive pressure of 2.64 kg. per sq. cm. and 25 cc. of fuel above the required amount for an exposure being used so that no air passed through the still during an exposure.

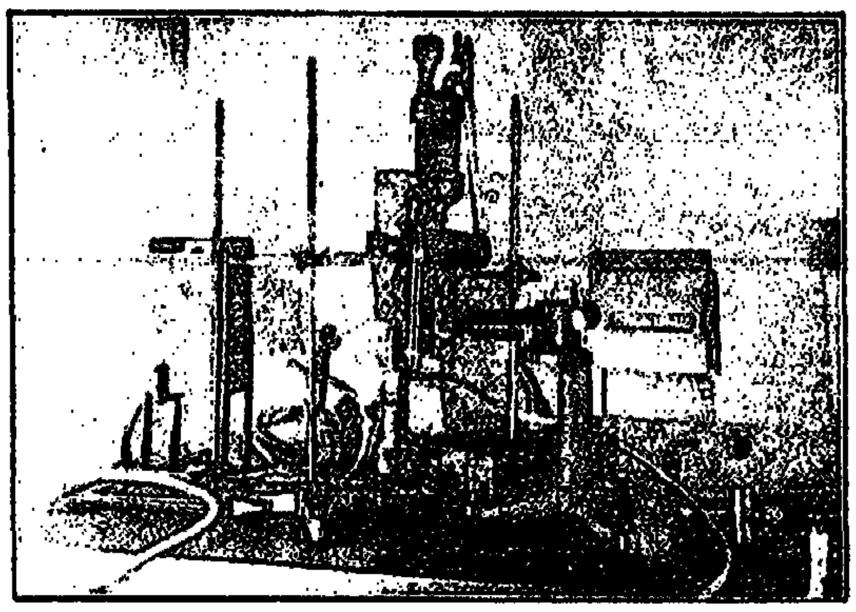

Fig. 8
The Apparatus set for an Exposure to the Fuel Flame

(4) Vaporization was practically instantaneous as the fuel within 3 cm. was brought from atmospheric temperature to 225° in a 3.2 mm. pipe in which the flow was upward.

(5) Spectra were taken of one solution at 10° intervals from 200° to 240°, no difference in the intensity of the lead lines appearing at any of the temperatures indicated.

(6) Within the error of a chemical analysis no increasing concentration of lead tetraethyl occurred.

Procedure in Analytical Experiments

After the distillation of the commercial lead tetraethyl liquid from its red dye, it was necessary to analyze the yellow distillate which consisted of ethylene bromide, lead tetraethyl, monochloronaphthalene and evidently some hydrocarbon. A method of analysis was worked out using the Parr sodium peroxide bomb as a means of decomposing the liquid. The bromine was determined as silver bromide and the lead as lead chromate, checks being obtained within 0.2%. After distillation, the liquid contained 43.7% tetraethyl. The specific gravity of the liquid was 1.831.

The gasoline used throughout this investigation was the standard gasoline marketed by a well known company, having an average specific gravity and end point of 0.738 and 208° C. respectively. All the gasoline was thus tested before it was used. Fig. 9 shows a typical set of distillation curves for the gasoline used.

All solutions were made up volumetrically from calibrated pipettes at a temperature of 20°. Two series of solutions were used:

(1) 1.0 cc. lead tetraethyl/1000cc. of gasoline to 0.1 cc. lead tetraethyl/1000 cc. of gasoline varying in steps of 0.1 cc. of lead tetraethyl.

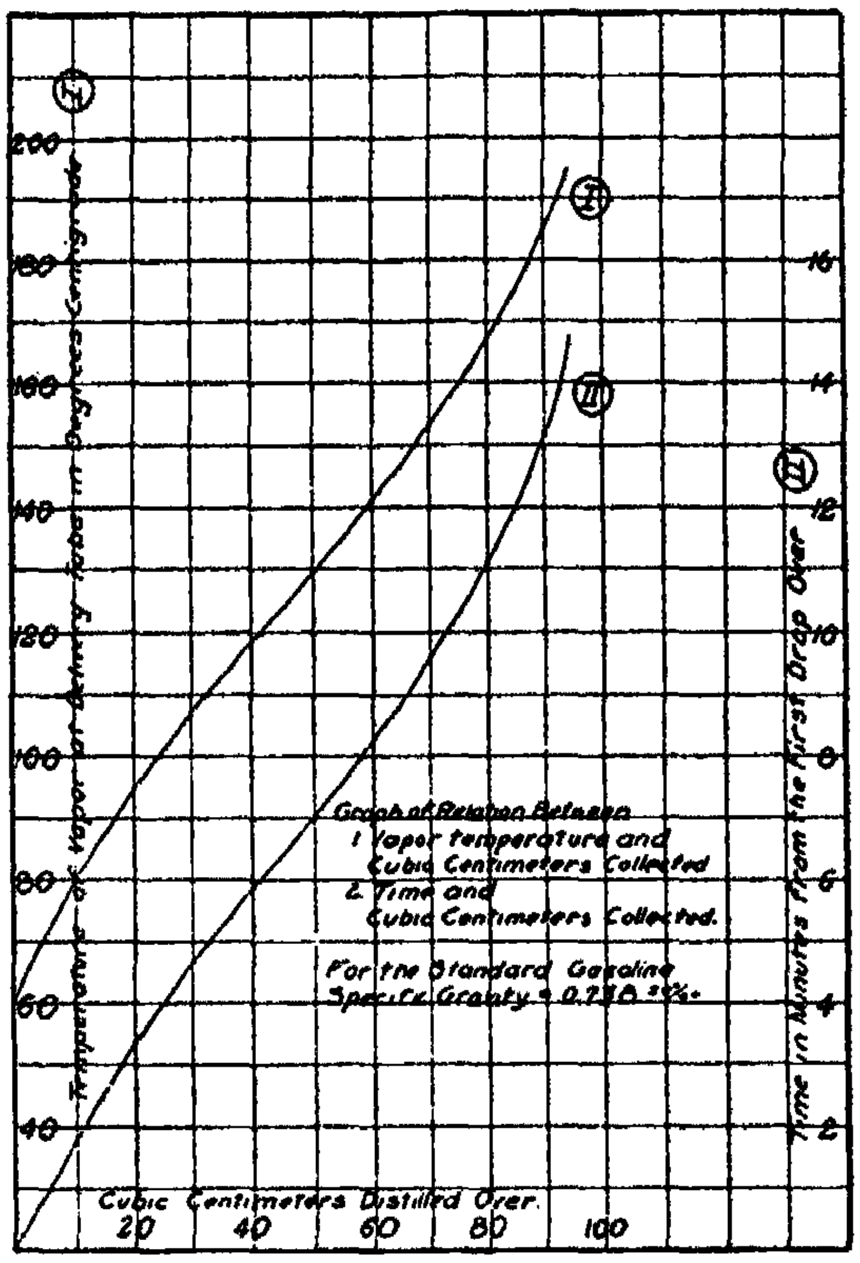

FIG. 9

(2) 0.1 cc. lead tetraethyl/1000 cc. of gasoline to 0.01 cc. lead tetraethyl/1000 cc. of gasoline varying in steps of 0.01 cc. of lead tetraethyl.

Several spectra of the 1.0/1000 cc. solution were photographed at various still temperatures varying from 200° to 240° in steps of 10° in order to determine any difference that might show up in the flames as a function of temperature. No difference was found in the spectra but the smoothest operation occurred between 220° and 225° so that this range of temperature was used throughout the tests. Exposures to the photographic plate in the spectrograph were one hour for solutions containing from 1.0 to 0.1 cc. lead tetraethyl per liter of gasoline and two hours for solutions containing from 0.1 to 0.01 cc. per liter. Longer exposures are not practical because the flame spectrum becomes so intense that the lead lines are obliterated. Between each spectrum of the lead tetraethyl solutions a pure gasoline spectrum was interposed for the purpose of comparison and for a check on any irregularities that might develop. Comparative spectra were also run on solutions of ethylene bromide and aniline, as well as on other fuels, benzene, ethyl alcohol, acetone, ether and carburetted water gas (Table III and Fig. 11).

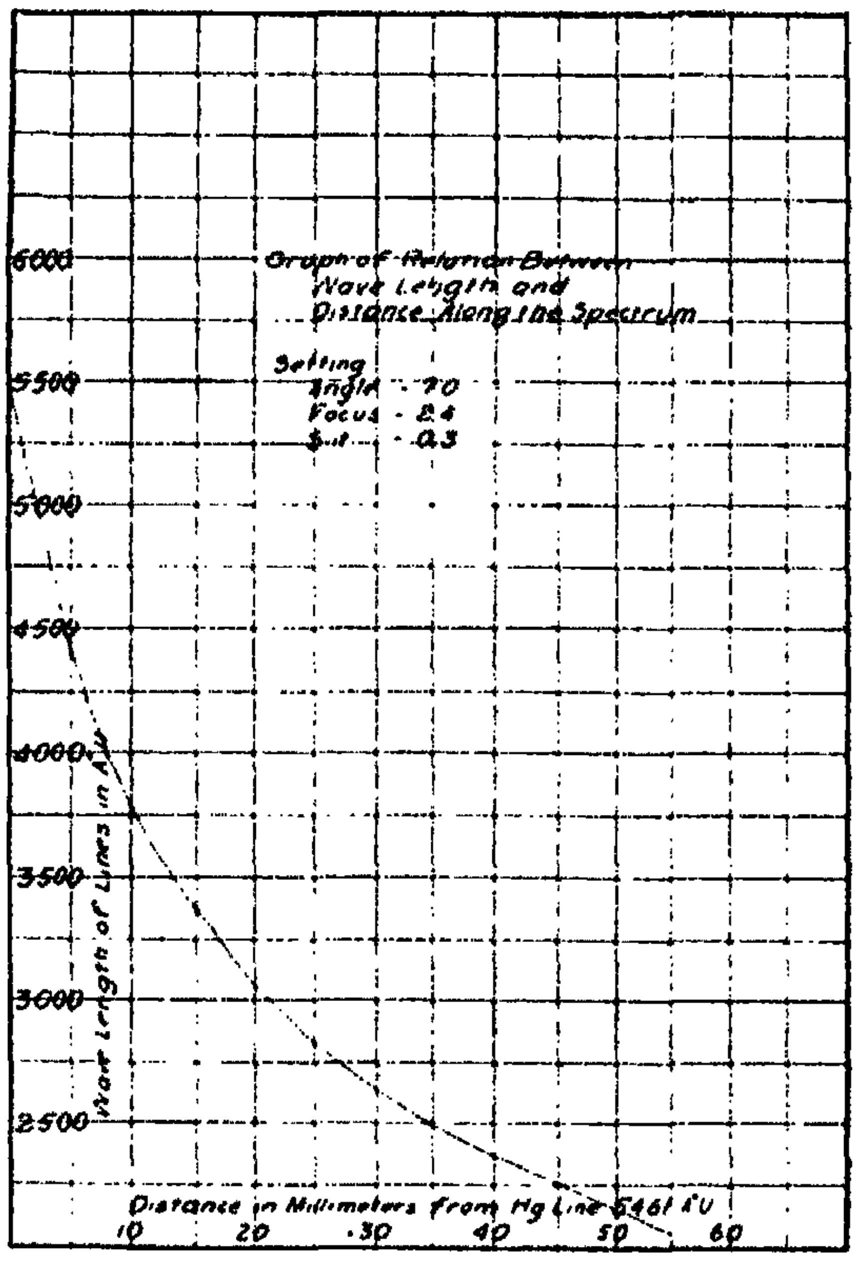

FIG. 10

Measuring the Spectra

The plates were measured by transmitted light on a Hilger measuring micrometer which could be read to thousandths of a millimeter. Readings were carried only to the hundredths, however, as the error introduced is negligible on a spectrograph of this resolution and dispersion. Each spectrum was measured twice to catch any error that may have been made the first time. After several standard spectra were measured it was very helpful to make a graph of wave length vs. millimeters measured, for a given resolution, using the average values of several readings. Thus a quick check on any line could be made from a single measurement. Fig. 10 is an example of such a graph, the data for this graph being taken from a set of five graphs covering the same range. The larger scale was chosen so that as nearly as possible the curve had on each sheet a slope of 1:1. These two precautions insure a greater accuracy in reading.

Results

Table I is a list of the lines of lead produced by the flame of lead tetraethyl in gasoline supplied with preheated primary air and burning in an atmosphere of oxygen. This list, it will be noticed, contains *17 lines* of which the line at λ/2167 has not been identified heretofore with the flame spectrum of lead. The wave lengths given in column 5 are the average of actual measurements upon the spectrum plates. For purposes of comparison and coordination values of the wave lengths of the lines in the line spectrum of lead as produced by the spark, arc and flame as determined by various authorities are included. No attempt was made to rate the intensities of the lines in the flame spectra, but the intensities of the lines in the spark and arc spectrum of lead are given, which, it is believed, are relatively representative of those of the corresponding lines in the flame spectrum. The intensities were taken as those values given for the spark spectrum except where lines occur in the arc that do not occur in the spark spectrum; in such cases the intensity of the arc line is used. All wave lengths are given in Angström units.

TABLE I

Lead Lines appearing in the Flame Spectrum of Lead

(1.0 cc. lead tetraethyl/1000 cc. gasoline; exposure, 3 hours; angle, 7.0; focus, 2.4; slit, 0.3)

(1)	(2)	(3)	(4)	(5)	(6)
4168.20	4168.21	4168.21	——	——	10
4062.30	4062.30	4062.30	——	——	10
4058.00	4057.97	4057.97	4057	4059	300R
4050.0	——	——	——	——	1
4041.5	——	——	——	——	1
4019.76	4019.77	4019.77	——	——	10
4004.45	——	——	——	——	1
3952.20	——	——	——	——	2
3927.8	——	——	——	——	1
3854.11	——	——	——	——	15
3842.2	——	——	3842	——	2
3833.15	——	——	——	——	3
3828.0	——	——	——	——	1
3786.5	——	——	——	——	4
3740.28	3740.10	3740.10	——	3741	30
3736.4	——	——	——	——	2
3715	——	——	——	——	2

TABLE I (continued)

Lead Lines appearing in the Flame Spectrum of Lead

(1.0 cc lead tetraethyl/1000 cc. gasoline; exposure, 3 hours; angle, 7.0; focus, 2.4; slit, 0.3)

(1)	(2)	(3)	(4)	(5)	(6)
3689.4	——	——	——	——	2
3683.64	3683.60	3683.60	3683	3685	50R
3671.72	3671.65	3671.65	——	——	10
3655.8	——	——	——	——	1
3639.72	3639.71	3639.71	3639	3644	20R
3593.1	——	——	——	——	1
3573.03	3572.88	3572.88	3572	3572	20
3455	——	——	——	——	1
3279.35	——	——	——	——	1
3276.6	——	——	——	——	1
——	3262.47	——	——	——	4
3243.00	——	——	——	——	1
——	3240.31	——	——	——	4
3220.7	3220.68	——	——	——	1
3176.62	——	——	3176	——	10
——	3150.9	——	——	——	3
3137.91	——	——	3138	——	10
——	3119.09	——	——	——	2
3089.21	——	——	——	——	2
3087.15	——	——	——	——	1
3044.00	——	——	3044	——	10
3031.8	——	——	——	——	1
3017.7	——	——	——	——	1
——	2980.29	——	——	——	2
2949.5	——	——	2949	——	2
——	2926.84	——	——	——	2
2873.42	2873.40	2873.40	2873	2873	10R
2864.5	——	——	——	——	1 R
2833.13	2833.17	2833.17	2833	2833	15R
2823.24	2823.28	2823.28	2823	——	10R
2802.10	2802.09	2802.09	2802	2805	30R
2717.2	——	——	——	——	1
——	2712.62	——	——	——	2
2697.6	2697.72	——	——	——	1
2663.22	2663.26	2663.26	2663	2663	10R
2657.17	2657.16	——	——	——	1
2650.4	2650.77	——	——	——	2
2628.47	2628.36	2628.36	——	——	2
2614.29	2614.26	2614.26	2613	2616	10R
2613.79	2613.74	——	——	——	3 R
2577.40	2577.35	2577.35	——	2580	5 R

TABLE I (continued)

Lead Lines appearing in the Flame Spectrum of Lead

(1.0 cc lead tetraethyl/1000 cc. gasoline; exposure, 3 hours; angle 7.0; focus, 2.4; slit, 0.3)

(1)	(2)	(3)	(4)	(5)	(6)
2568.54	——	——	——	——	1
2563.39	——	——	——	——	5
2476.49	2476.48	2476.48	——	2477	6 R
2446.46	2446.28	2446.28	——	2445	4
2444.10	2443.92	2443.92	——	——	4
2428.82	——	——	——	——	2
2411.85	2411.80	2411.80	——	2413	2
2402.18	2402.04	2402.04	——	2403	3
2399.70	2399.69	——	——	——	1
2393.90	2393.89	2393.89	——	——	4 R
2389.00	2388.89	——	——	——	1
2332.63	2332.54	——	——	——	1
——	2257.53	——	——	——	1
——	2254.02	——	——	——	3 R
2247.00	2247.00	2247.00	——	2243	2 R
2237.7	2237.52	——	——	——	1
2203.68	2203.57	——	——	——	4 R
——	2187.99	——	——	——	2
——	2175.88	——	——	——	4 R
2170.11	2170.07	——	——	2167	2 R
——	2115.1	——	——	——	5 R
——	2112.0	——	——	——	4
——	2088.5	——	——	——	5 R

(1) Wave length of lines in the spark spectrum of lead as given by F. Exner and E. Haschek: "Wellenlängen-Tabellen zu spektralanalytischen Untersuchungen auf Grund der ultravioletten Funkenspectren der Elemente" (1902).

(2) Wave lengths in the arc spectrum of lead as given by H. Kayser and C. Runge: "Über die Spectra von Zinn, Blei, Arsen, Antimon, Wismuth." Wied. Ann., **52**, 93-113 (1894).

[3] Wave lengths of lines in the coal gas flame of lead using a solution of an inorganic lead salt as given by Ch. de Watteville: "Spectres de flamme." Phil. Trans. **204A**, 139-168 (1904).

(4) Wave lengths of lines in the coal gas-hydrogen flame of lead using a solution of an inorganic lead salt as given by H. Auerbach: "Spectroscopic Untersuchungen über das Verhalten der Metallsalze in Flammen von verschiedenen Temperaturn." Z. wiss. Phot. **7**, 30-39, 41-66 (1909).

(5) Wave lengths of lines in the gasoline-lead tetraethyl-oxygen flame of lead as measured by the authors.

(6) *Intensities of the lines in the spark and arc spectrum of lead as given respectively by the authorities quoted for columns* (1) and (2).

Table II lists the lead lines found at various concentrations of lead tetraethyl in the gasoline. A concentration of 1.0 cc/1000 cc means 1.0 cc of the distilled lead tetraethyl fluid, specific gravity 1.831, in 1000 cc. of gasoline. A concentration of 513 p.p.m. means 513 grams of lead in a million cubic centimeters of the gasoline, measured at 20°. A + in the list of wave lengths refers to the presence of a line, a – to the extinction of a line; F means "faint" and VF means "very faint." The two ultimate lines, λλ3683.6 A.U. and 2614.2 A.U., correspond with the ultimate lines given for lead by Twyman. It should be further understood that a line gradually disappears and that it

TABLE II

The Wave Length of the Lead Lines, in A.U., appearing at Given Concentrations

Concentrations	1.0 cc/1000 513 p.p.m.	0.9 cc/1000 462 p.p.m.	0.8 cc/1000 410 p.p.m.	0.7 cc/1000 359 p.p.m.	0.6 cc/1000 308 p.p.m.	0.5 cc/1000 256 p.p.m.	0.4 cc/1000 205 p.p.m.	0.3 cc/1000 154 p.p.m.	0.2 cc/1000 102.5 p.p.m.	0.1 cc/1000 51.3 p.p.m.
Wave Lengths	4059	+	+	+	+	+	+	+	+	+ F
	3741	+	+	+ F	+ F	+ F	+ F	+ VF	–	–
	3685	+	+	+	+	+	+	+	+	+ F
	3644	+	+	+	+	+	+	+	+	+ F
	3572	+	+	+ F	+ VF	+ VF	+ VF	–	–	–
	2873 VF	+ VF	+ VF	–	–	–	–	–	–	–
	2833	+	+	+	+	+	+	+	+	+ F
	2805	+	+	+	+	+	+	+	+	+ F
	2663	+	+	+	+	+	+	+	+ F	+ VF
	2616	+	+	+	+	+	+	+	+	+
	2580 VF	+ VF	+ VF	+ VF	+ VF	+ VF	+ VF	+ VF	–	–
	2477	+	+ F	+ F	+ F	+ F	+ F	+ F	–	–
	2455 VF	+ VF	+ VF	+ VF	+ VF	+ VF	+ VF	+ VF	–	–
	2413 VF	+ VF	+ VF	+ VF	+ VF	+ VF	+ VF	–	–	–
	2403 VF	+ VF	+ VF	+ VF	+ VF	+ VF	+ VF	–	–	–
	2243 VF*	–	–	–	–	–	–	–	–	–
	2167 VF*	–	–	–	–	–	–	–	–	–

* These lines appear only on a 3 hour exposure.

Table II (continued)

0.09 cc/1000 462. p.p.m.	0.08 cc/1000 41.0 p.p.m.	0.07 cc/1000 35.9 p.p.m.	0.06 cc/1000 30.8 p.p.m.	0.05 cc/1000 25.6 p.p.m.
+ F	+ VF	+ VF	+ VF	+ VF
–	–	–	–	–
+ F	+ VF	+ VF	+ VF	+ VF
+ F	+ VF	+ VF	+ VF	+ VF
–	–	–	–	–
–	–	–	–	–
+ VF	+ VF	–	–	–
+ F	+ F	+ VF	–	–
+ VF	+ VF	+ VF	–	–
+	+	+	+ F	+ F
–	–	–	–	–
–	–	–	–	–
–	–	–	–	–
–	–	–	–	–
–	–	–	–	–
–	–	–	–	–
–	–	–	–	–

0.04 cc/1000 20.5 p.p.m.	0.03 cc/1000 15.4 p.p.m.	0.02 cc/1000 10.25 p.p.m.	0.01 cc/1000 5.13 p.p.m.
–	–	–	–
–	–	–	–
+ VF	+ VF	–	–
–	–	–	–
–	–	–	–
–	–	–	–
–	–	–	–
–	–	–	–
–	–	–	–
+ F	+ VF	+ VF	–
–	–	–	–
–	–	–	–
–	–	–	–
–	–	–	–
–	–	–	–
–	–	–	–
–	–	–	–

requires very careful observations in all cases to judge whether or not the line has disappeared. Perhaps a more standard method of carrying out such a determination, introducing less of the personal factor, would be to subject all the spectra to a microphotometer. This is now being done with a new densitometer. It is clear that with these small spectra the line λ2414.20 persists to a lead concentration between 5 and 10 p.p.m. and that larger amounts may be determined with considerable quantitative accuracy from the number and intensity of lines. Therefore the spectroscopic method has a decided advantage over chemical methods of analysis for lead in gasoline when traces only are present. Obviously still smaller concentrations could be detected with a larger spectrograph.

Details of Spectra

Table III is in explanation of Fig. 11 in which typical spectra are reproduced. These are all distinguished by banded structures. The water or steam bands have been identified as those bands caused by the burning of hydrogen and oxygen to form water. These bands appear in all of the spectra at λλ2811, 3064, 3428 and 3471. The other bands at λλ3877, 3897, 4320, 4366, 4781 and 5218 are of C-H and C-O origin and appear in all of the spectra which have been taken through the cone of primary combustion. The background of all of the spectra is continuous. Spectrum 4 is an example of the numerous exposures made with gasoline containing lead tetraethyl. In no case was any evidence of bands due to lead compounds found, again confirming the almost instantaneous decomposition of the tetraethyl molecule. Spectra 14, 17 and 18 are a series of spectra taken through the flame of city gas burning with oxygen. Spectrum 14 was taken through the flame at the base and therefore contains the primary and a little of the secondary cone of combustion, the color of the primary cone of combustion being a bright blue green. Spectrum 17 was taken through the secondary cone of combustion, the color of this cone being a bright lavender. Spectrum 18 was taken through the third cone of combustion which is much weaker in intensity than the other two cones. This cone is a pale straw yellow. In the first cone, reactions occur about which there is much argument, but in the second cone, the combustion reactions probably consist of the reaction of oxygen with hydrogen and carbon monoxide. For this cone, Spectrum 17, there are only the water bands and the continuous background characteristic of the flame of carbon monoxide. In the third cone, Spectrum 18, the only band appearing is one of steam. This cone consists, then, of the incipient combustion of the cooled and diluted hydrogen. These explanations are, in general, in agreement with the most recent hydroxylation theory of the combustion of hydrocarbons.[1]

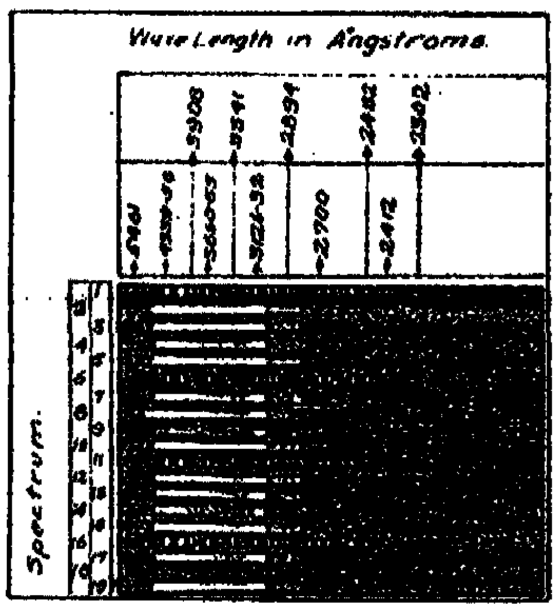

FIG. 11
The Ultra-Violet Quartz Prism Spectrogram of Fuel Flames referred to the Standard Spectra of a Mercury Arc

The spectra of all the fuels taken through the primary cone are similar in structure but it will be seen that they vary considerably in intensity. All

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[1] Haslam and Russell: "Fuels and Their Combustion," 170-192 (1926).

of these spectra were carefully measured and there is no shift of any bands in the spectra of the different fuels within the error of measurement. Without exception, however, the fuels that tend to show detonating properties are the most intense, namely gasoline, ether and acetone as compared with benzene, alcohol, gasoline and lead tetraethyl, gasoline and aniline and carburetted water gas. Much of the remarkable detail of the original spectrum negatives is lost in the reproductions.

The Status of Theories of Detonation Suppression

The line spectra of lead obtained in these and former experiments clearly indicate that the suppression of detonation in gasoline engines obtained when lead tetraethyl is used in the gasoline is accompanied by the complete decomposition of the lead tetraethyl molecule into metallic lead at first. In spectral photographs of the flames of motor fuels in an actual internal combustion engine, considered in previous papers of this series, only three of the lead lines have been particularly noted. The identification of as many as 17

TABLE III

In Explanation of Fig. 11

Spectrum	Source of Spectrum	Time of Exposure in Minutes
1	Mercury Arc	0.15
2	The Standard gasoline	60.0
3	1 cc ethylene bromide/1000 cc of the standard gasoline	60.0
4	1 cc lead tetraethyl/1000 cc of the standard gasoline	60.0
5	The standard gasoline	60.0
6	Mercury Arc	0.15
7	1 cc aniline/1000 cc of the standard gasoline	60.0
8	Benzene	
9	Ethyl alcohol	60.0
10	The standard gasoline	60.0
11	Mercury Arc	0.15
12	Acetone (dimethyl ketone)	60.0
13	Diethyl ether	60.0
14	Carburetted water gas, cone of primary combustion	60.0
15	The standard gasoline	60.0
16	Mercury Arc	0.15
17	Carburetted water gas, cone of secondary combustion	60.0
18	Carburetted water gas, cone of tertiary combustion	120.0
19	The standard gasoline	60.0

lines is to be ascribed partly to greatly improved spectrographic technique and to the efficiency of the special burner which scarcely reproduces the conditions of explosion in an engine. However, the act of molecular disintegration in the vapor phase seems to play a primary role in the suppressor action. The following experiments suggested by these studies are in progress: photography of the *absorption* spectra of liquid and gaseous lead tetraethyl alone and in solution in gasoline at a series of increasing temperatures; comprehensive experiments with colloidal lead in the effort to settle greatly discrepant data reported in the literature; and complete spectroscopic studies with a quartz-walled engine. The exact mechanism of the action of lead tetraethyl is not yet definitely established, largely because the mechanism of detonation is still mainly enigmatical.[8]

Summary

1. The flexibility, accuracy and simplicity of a small quartz prism spectrograph has been demonstrated, as applied to chemical and industrial problems, particularly the estimation of lead tetraethyl in gasoline and of its effect upon a detonation flame.

2. A simple and inexpensive mercury arc and housing adapted for spectroscopic use, and a successful combined still and burner for liquid fuels are described, serving as permanent equipment for analyses of this type.

3. In the system of analysis developed from the small spectra, 5 grams of lead per 1,000,000 cc of gasoline have been detected. From the standard spectra, made from solutions of known concentration, it is possible to estimate larger quantities with a high degree of accuracy.

4. Seventeen lines in the flame spectrum of lead have been identified and measured; one additional emission line has been discovered in the flame spectrum of lead for the first time ($\lambda 2167$).

5. The band positions, structures, and intensities have been compared for flames, under exactly the same conditions, of gasoline, gasoline plus ethylene bromide, gasoline plus lead tetraethyl, gasoline plus aniline, benzene, alcohol, acetone, ether and carburetted water gas in the cones of primary, secondary, and tertiary combustion.

6. Further evidence is obtained that the detonation suppressor action of lead tetraethyl is not due to this compound as such but to the process of its decomposition and to the disintegration products.

Department of Chemistry,
University of Illinois

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[8] For a critical analysis of mechanism theories, see the third paper of this series, ref. 1.

ADSORPTION FROM AQUEOUS SOLUTIONS BY SILICA

BY F. E. BARTELL AND YING FU*

Although a great amount of work has been done with both carbon and silica as adsorbents, the results reported by different investigators have been conflicting and satisfactory generalizations have been lacking. Bartell and E. J. Miller,[1] working on the assumption that many of the anomalies reported in the literature are due to the impurities in the adsorbents used, undertook the preparation of an ash-free active carbon. Exact methods of experimentation were observed and the results obtained with pure carbon appear to be free from anomalies. In view of the success of this work, it was thought desirable to make a similar study of adsorption with silica.[2]

It is well known that carbon exhibits a higher degree of adsorption from aqueous solutions than from solutions or organic liquids. Patrick and co-workers[3] have shown that silica adsorbs best from organic liquids. Work which has been carried out in this laboratory,[4] on adhesion tension of liquids against solids, has shown definitely that carbon has a high adhesion tension against organic liquids and a comparatively low adhesion tension against water. The order of adhesion tension of silica against these liquids is the opposite. In general, it can be stated that a liquid which exhibits a high adhesion tension against carbon will show a low adhesion tension against silica and vice versa. Other factors being equal, adsorption should be greatest from those solvents which have the lowest adhesion tension against the solid. It should, accordingly, follow that adsorption effects obtained with silica as an adsorbent should be very different, in fact, practically opposite to those obtained with carbon as adsorbent.

An extensive investigation on the adsorptive properties of hydrated silica has been carried out by Patrick and his co-workers.[5] They have studied the adsorption of gases, of vapors, of NaOH from solutions, and adsorption

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* The material presented in this paper is from a dissertation submitted by Ying Fu to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Science, 1928.

[1] J. Am. Chem. Soc., **44**, 1866 (1922); **45**, 1106 (1923).

[2] No attempt has been made to present a complete bibliography covering investigations on adsorption with silica and silica gel. Such a bibliography would include the classical researches of van Bemmelen and also the researches of many others. The work of this paper is most closely related to that indicated by the references cited herein.

[3] Patrick and Jones: J. Phys. Chem., **29**, I (1925).

[4] Bartell and Osterhof: Ind. Eng. Chem., **19**, 1277 (1927); Z. physik. Chem. Cohen-Festband, **130**, 715 (1927); "Colloid Symposium Monograph," **5** (1927); Bartell and F. L. Miller: Ind. Eng. Chem., **20**, 738 (1928).

[5] Patrick: Diss. Göttingen (1914); McGavack and Patrick: J. Am. Chem. Soc., **42**, 946 (1920); Patrick and Jones: J. Phys. Chem., **29**, 1 (1925); Patrick and Grimm: J. Am. Chem. Soc., **43**, 2144 (1921); Patrick and Barclay: J. Phys. Chem., **29**, 1400; Patrick and Eberman: 220; Patrick and Greider: 1031; Patrick and Long: 336; Patrick and Opdyke: 601; Patrick, Preston and Owens: 421 (1925); Patrick and Neugansen: J. Am. Chem. Soc., **43**, 1844 (1921).

from organic liquids. They have also studied heat of wetting and heat of adsorption with silica, as well as the displacement of water from the hydrogel by other liquids. The latter was also studied by Firth and Purse[1] who concluded that water can be completely displaced from the gel by alcohol. This was not in agreement with Patrick's results. The most active gel recorded was that of Holmes and Anderson[2] and Holmes, Sullivan and Metcalf[3] who precipitated the silica gel from water glass solution by adding an excess of dilute solution of nickel or iron salts. The salts were removed with hydrochloric acid after the gel had been dried slowly at a low temperature. Adsorption with quartz and with silica which had been ignited for a long time were studied by Jones[4] and Joseph and Hancock.[5] Silica gel containing about 85% water has been used in adsorption studies by Mukherjee and his coworkers.[6]

Method of Preparation of Silica

In nearly all previous investigations hydrated silica gel has been used in preference to the dehydrated gel or silica because of its greater activity. The method of preparing the gel has been essentially that used by MacGavack and Patrick.[7] Silicic acid is precipitated from water glass by the addition of hydrochloric acid and then is washed to remove the electrolytes. In the present investigation silica gel was at first prepared by this method and was partially dehydrated by heating. This treatment gave a very active gel, but the method was unsatisfactory, in that acid was left which was very difficult to remove without affecting the activity of the gel. It was found also that this gel was usually contaminated with a trace of sodium salt which, while not affecting the activity of the gel for the adsorption of gases, was undesirable for work on hydrolytic adsorption of salts. After trial of many methods, the method of Ebler and Felner[8] was finally adopted. Pure silicon tetrachloride was distilled into conductivity water surrounded by cracked ice until the resulting solution showed a slight blue tinge. The solution usually set to a gel within one hour. The gel was heated at a low temperature, about 60° C, to remove the major portion of the acid and the water. It was then transferred to quartz crucibles and heated in an electric oven at 260° C for two hours. Without being cooled down to room temperature the gel was taken out of the oven and immediately poured into warm conductivity water. After three or four washings by decantation, the gel was again placed in the oven at 260° C. Practically all the acid on the gel was removed by the first treatment, but the process was repeated at least six times to insure complete removal of impurities. Analysis showed that this silica contained no chloride and when

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[1] J. Phys. Chem., 30, 617 (1926).

[2] Ind. Eng. Chem., 17, 280 (1925).

[3] Holmes, Sullivan and Metcalf: Ind. Eng. Chem., 18, 386 (1926).

[4] J. Phys. Chem., 29, 326, 369 (1925).

[5] J. Chem. Soc., 123, 2022 (1923).

[6] Mukherjee, Krishnamurti, Ghosh, Nutza and Roy: J. Chem. Soc., 128, 3023 (1926).

[7] MacGavack and Patrick: J. Am. Chem. Soc., 42, 946 (1920).

[8] Ber., 44, 1915 (1911).

treated with hydrofluoric acid left no residue. The silica gel thus prepared was slowly dehydrated until the water content was reduced to about four per cent, after which it was further dehydrated by heating with a blast lamp. With experience it became possible to reduce the silica to a condition of constant weight at the same time avoiding prolonged heating which would tend to decrease its adsorbing capacity. A quantity of such gel was prepared so that uniform samples might be used throughout the work.

Method of conducting Experiments

The amount of adsorption was determined as follows. A definite quantity of solution, 40 cc., was placed in a glass-stoppered flask previously filled with CO_2 free air, and an accurately weighed amount of silica, 0.6 to 0.8 gram, was added. After four hours of shaking the change in concentration of solution was determined by titration, care being taken to eliminate carbon dioxide in every titration. The amounts of adsorption, represented by x/m, (expressed in miligram-equivalents per gram of silica) in the tables are admittedly not strictly accurate in as much as no attempt was made to correct for the adsorption of solvent nor for the volume change due to adsorption of the solute. An error was undoubtedly introduced, but it must be very small as the volume change was small, and the solutions were so dilute that the adsorption of the solvent would not alter the bulk liquid concentration materially.

Results of Experiments

Adsorption of Bases. The lithium hydroxide solution was prepared from lithium sulphate and barium hydroxide according to Harned's method.[1] The other bases were of C.P. quality. After treatment with silica as above described a portion of the liquid was pipetted off and titrated with bromthymol blue as indicator. All experiments were run in duplicate. The data given in Table I are averages of at least four independent determinations.

TABLE I

Adsorption of Inorganic Bases by Silica

Base	Equil. Conc.	x/m	Base	Equil. Conc.	x/m
LiOH	0.0502 N	1.93	KOH	0.0631 N	1.55
	0.0245 N	1.58		0.0345 N	1.32
	0.0100 N	1.24		0.0159 N	1.06
	0.0040 N	0.97		0.0090 N	0.91
	0.0025 N	0.85		0.0049 N	0.75
NaOH	0.0630 N	1.70	NH_4OH	0.0760 N	1.23
	0.0338 N	1.38		0.0298 N	0.85
	0.0199 N	1.12		0.0191 N	0.71
	0.0100 N	0.90		0.0112 N	0.60
	0.0040 N	0.66		0.0045 N	0.39

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[1] J. Am. Chem. Soc., 48, 127 (1926).

The data plotted with x/m and equilibrium concentration values as coordinates are given in the curves in Fig. 1. It will be noted that typical adsorption isotherms are obtained. This indicates that adsorption or surface reactions must predominate. It seems probable that in these systems "chemical reactions" may and probably do occur, but they are limited to the surface only. In effect then these reactions are adsorptions of the "heteropolar" type which have been discussed by Freundlich and others. With the fairly dilute solutions used there appears to be no reason to consider the process to be other than one of adsorption.

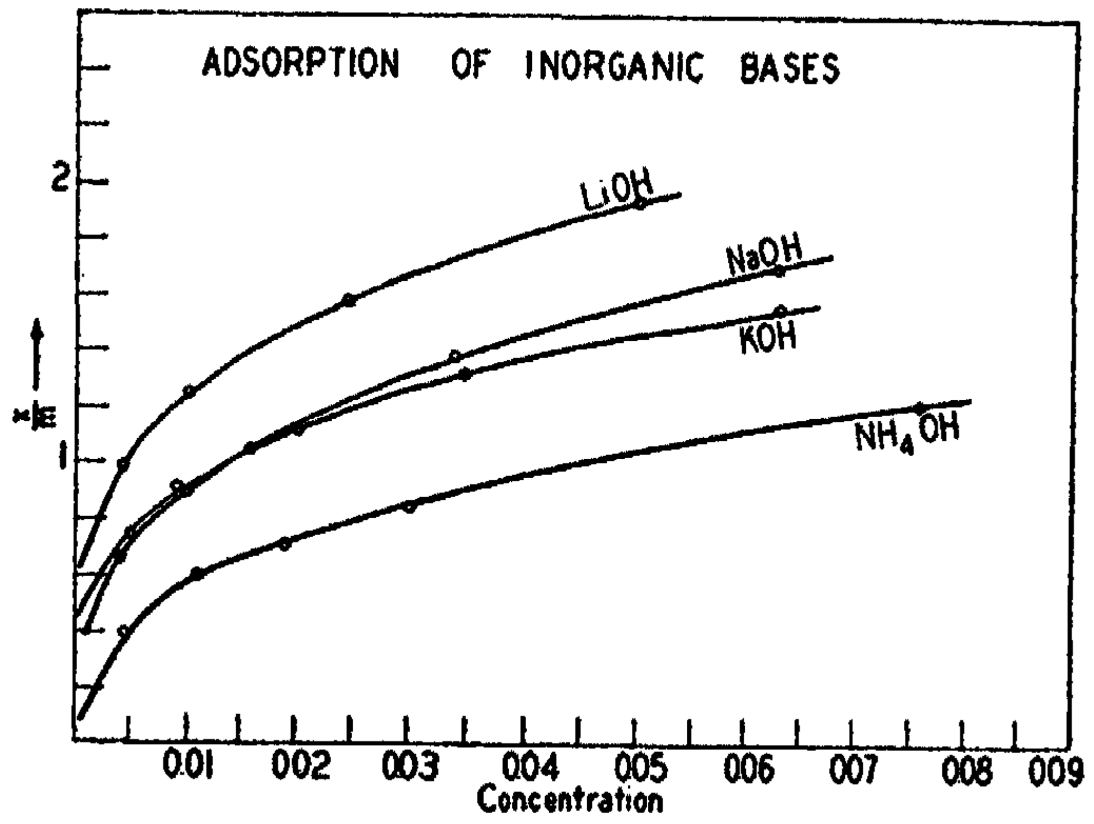

Fig. 1

Adsorption of Acids

Inorganic acids. The hydrochloric acid used was constant boiling acid diluted with conductivity water. Nitric acid, sulphuric acid and perchloric acid were of C.P. quality. The results obtained with these acids are given in Table II.

Table II

Adsorption of Inorganic Acids by Silica

Acid	Equil. Conc.	x/m	Acid	Equil. Conc.	x/m
Hydrochloric	0.0103 N	0.000	Sulfuric	0.0101 N	0.000
Hydrochloric	0.1052 N	0.000	Sulfuric	0.1000 N	0.002
Nitric	0.0096 N	0.000	Perchloric	0.0084 N	0.000
Nitric	0.0987 N	0.000	Perchloric	0.0913 N	0.000

The results show that none of these inorganic acids (i.e. within the range of the limits of experimental error) are adsorbed. This is contrary to the results of Mukherjee and co-workers who used a gel containing about 85% water. The difference in results may be due to the water content of their gel.

ORGANIC ACIDS

All the organic acids used were purified by standard methods. Subsequent treatment was as above described. The results obtained with these acids are given in Table III.

TABLE III

Adsorption of Organic Acids by Silica

Acid	Equil. Conc.	x/m	Acid	Equil. Conc.	x/m
Formic	0.0100 N	0.009	Succinic	0.0100 N	0.007
Formic	0.0994 N	0.010	Succinic	0.0316 N	0.008
Acetic	0.0099 N	0.006	Tartaric	0.0125 N	0.002
Acetic	0.0410 N	0.006	Tartaric	0.0892 N	0.004
Propionic	0.0104 N	0.007	Lactic	0 1038 N	0.004
Propionic	0.0548 N	0.006	Oxalic	0.0101 N	0.000
Butyric	0.0099 N	0.005	Oxalic	0.1064 N	0.000
Butyric	0.0503 N	0.006	Benzoic	0.0103 N	0.053
			Benzoic	0.0216 N	0.053
			Salicylic	0.0088 N	0.053
			Salicylic	0.0165 N	0.06

TABLE IIIa

Adsorption of Fatty Acids by Silica from Carbontetrachloride

Equil. Conc.	x/m in milimole per gram SiO_2	Equil. Conc.	x/m in milimole per gram SiO_2
Formic Acid		Propionic Acid	
0.0158 N	1.35	0.0135	1.07
0.0339	1.55	0.0309	1.22
0.0911	1.90	0.0500	1.30
0.2187	2.29	0.0890	1.41
0.5248	2.72	0.2779	1.70
		0.5010	1.82
Acetic Acid		Butyric Acid	
0.0204	1.24	0.0144	1.03
0.0347	1.36	0.0393	1.16
0.100	1.66	0.0740	1.26
0.2771	2.00	0.162	1.38
0.5502	2.24	0.251	1.43
		0.4025	1.53

It will be noted that all the organic acids with the exception of oxalic, appear to be slightly adsorbed by the silica. The greatest adsorption was obtained with salicylic and benzoic acids. These latter effects are not surprising since these acids are but slightly soluble in water.[1]

The fact that acids are so slightly adsorbed by silica from aqueous solutions does not imply that acids are not adsorbed by silica. The slight adsorption is due to the effect of the solvent used. If, instead of water, some organic liquid is used as solvent, quite different results will be obtained. Insamuch as a fuller account of work of this type will be given in another paper, only one series, the adsorption of fatty acids from carbontetrachloride, is presented here.

With carbon as adsorbent the adsorption of the fatty acids from aqueous solutions increases regularly as we ascend the homologus series. From the above data it is noted that the order of adsorption of fatty acids by silica is just opposite to that by carbon, i.e. the adsorption of these acids decreases as we ascend the homologus series. The order of surface tension lowering of the aqueous solutions of these acids is in the order of increasing molecular weights. This is the same as the order of interfacial tension lowering of these solutions against carbon but opposite to the interfacial tension lowering against silica. Apparently there is no relation between the adsorbability of these acids with silica and the surface tension lowering of the solution. Further, it is evident that Traube's rule as ordinarily stated[2] cannot be applied to adsorption with silica. This fact has also been noted by Holmes and McKelvey.[3]

HYDROLYTIC ADSORPTION

From the work of Bartell and E. J. Miller[4], Miller[5] and Kolthoff[6] with ash free carbon, it has been shown that carbon, properly prepared, adsorbs acids, both organic and inorganic, but does not adsorb inorganic bases. On the other hand, silica, freed from impurities, as used in this work, was found to adsorb inorganic bases, organic acids slightly, but the inorganic acids not at all. Within the range of concentration studied, from 0.1 N to 0.001 N, the Freundlich equation was found to hold for adsorption of bases within the limit of experimental error.

It was observed by Bartell and Miller[7] and was conclusively proven later by Miller[8] that a large number of neutral salts, inorganic as well as organic,

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[1] The results obtained with hydrated silica, containing 4 per cent. water, showed that the total adsorption with bases was considerably greater than with anhydrous silica, with organic acids somewhat greater, but in all cases the order of adsorption was the same as given above. The greater adsorption was probably due to the larger surface area of the hydrated silica, as will be shown in a later paper.

[2] Freundlich: "Colloid and Capillary Chemistry," 195.

[3] J. Phys. Chem., 32, 1522 (1928).

[4] J. Am. Chem. Soc., 44, 1866 (1923); 45, 1106 (1923).

[5] J. Phys. Chem., 30, 1162, 1031 (1926); J. Am. Chem. Soc., 47, 1270 (1925).

[6] Rev. Trav. chim. Pays-Bas, 46, 549 (1927).

[7] J. Am. Chem. Soc., 44, 1866 (1922); 45, 1106 (1923).

[8] J. Am. Chem. Soc., 46, 1150 (1924).

were hydrolytically adsorbed by pure carbon. This follows from the fact that carbon adsorbs the acid preferentially and leaves the basic constituent in the solution. Since silica adsorbs base preferentially, it might be expected that hydrolytic adsorption would likewise occur with this adsorbent with salt solutions, the difference between carbon and silica adsorptions being that in the latter case, it would be the acid instead of base which would be split off and left in solution. This was found to be the case, as is shown by Table IV.

TABLE IV

Hydrolytic Adsorption of Alkali Salts by Pure Silica

Salt (40 cc. solution)		0.01 N Acid set free by 1 gm SiO_2	Salt		0.01 N Acid set free by 1 gm SiO_2
Na formate	.05 N	2.64 cc.	NaCl	2 N	1.88 cc.
Na acetate	.05 N	4.94 cc.	$NaNO_3$	2 N	1.84 cc.
Na propionate	.05 N	5.13 cc.	$NaClO_3$	2 N	1.75 cc.
Na butyrate	.05 N	5.20 cc.	Na_2SO_4	N/4	0.25 cc.
			KCl	2 N	1.60 cc.
Na tartrate	.05 N	3.22 cc.	LiCl	2 N	2.03 cc.
Na benzoate	.05 N	3.91 cc.			
Na oxalate	.05 N	2.20 cc.			
Na salicylate	.05 N	1.26 cc.			

Even though inorganic bases are readily adsorbed and the inorganic acids are not, their salts are apparently but slightly hydrolysed during the adsorption by silica. In the case of 0.02 N solutions the pH value of the solution was in some experiments found to change from 7.0 to 5.2 for the alkali salts of strong inorganic acids. The acid thus liberated is in such small quantity that it can scarcely be titrated with a base. In the case of solutions of salts of the organic acids, the acids of which are adsorbed to a greater extent than the inorganic acids, the results at first thought appear to be inconsistent for the hydrolysis is comparatively high. With 40 cc. of the 0.05 N solutions the acids liberated were in some cases equivalent to about 5 cc. of 0.01 N NaOH. The above results do not appear, to be in agreement with those of Bartell and Miller with carbon. In their work it was shown that the amount of base liberated by carbon was in the same order as the adsorbability of the acids with which the cation was combined. This apparent discrepancy, however, can be explained from the following consideration. Since but a small amount of acid was liberated from the inorganic salts, there must have been an equilibrium involving adsorption and de-sorption of the base, which greatly limited the amount of base which could be held by the silica: Had this not been the case the adsorption of the base would have proceeded to such an extent that a large amount of free acid would have been left in the solution. When acids are liberated, they tend to neutralize the adsorbed bases in a manner according to the strength and adsorbability of the acids. The stronger the acids the more base on the silica surface will be neutralized by them. Since organic acids, as a rule, are weaker than inorganic acids, they are not so effective in the removal of the adsorbed base: hence more hydrolysis will occur. In order to test the above assumption, the following experiment was carried out.

After the silica had been treated with NaOH, the solution of base was poured off and the silica was rinsed twice with conductivity water; twenty-five cc. were used each time. The total amount of base adsorbed was determined by titrating the solution poured off, including also the rinsing water. The amount of water adhering to the silica after rinsing was determined by weighing. Since the amount of base adsorbed by the silica was known, the quantity of water adhering to the silica surface could be determined. A definite volume of different acids (40 cc.) of approximately equal concentration, was then added to the silica and after four hours of shaking the amount of acid neutralized by the adsorbed base was determined. In this manner it was found that inorganic acids removed all the adsorbed base while the organic acids always left some base on the silica even though the acid present was more than necessary to neutralize the base.

TABLE V

Displacement of the Adsorbed NaOH by Different Acids

Acid (40 cc.)	.01N NaOH on SiO_2	Acid taken up by SiO_2	NaOH left on SiO_2
Hydrochloric	29.50 cc.	29.47 cc.	0.03 cc.
Nitric	29.43 cc.	29.43 cc.	0.00 cc.
Formic	29.40 cc.	28.00 cc.	1.40 cc.
Acetic	30.00 cc.	27.40 cc.	2.60 cc.
Propionic	29.40 cc.	26.80 cc.	2.60 cc.
Butyric	29.70 cc.	27.00 cc.	2.70 cc.
Benzoic	29.12 cc.	27.40 cc.	1.72 cc.
Oxalic	29.32 cc.	27.00 cc.	1.32 cc.
Salicylic	29.24 cc.	28.30 cc.	1.04 cc.

From Table V it is seen that the order in which the acids displace the base is just the reverse of the order of the increasing hydrolytic adsorption of their salts. It is also shown that the stronger the acid the more base it will displace. An exception to the last statement is given with salicylic acid which, aside from the inorganic acids, displaced the largest amount of base. If, however, we consider the adsorbability of the different acids, this apparent anomaly disappears, because it was found that salicylic acid is the most highly adsorbed acid among those used.

In his investigation on the adsorption of inorganic salts by carbon, Miller[1] found the adsorption to be purely hydrolytic in nature. None of the salt as such was adsorbed. In this investigation we wished to determine whether the adsorption of neutral salts by silica is also purely hydrolytic. In order to determine this, titration of the acid set free is alone not sufficient, both

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[1] J. Am. Chem. Soc., 46, 1150 (1924).

molecular and hydrolytic adsorption might occur simultaneously and not be differentiated by the titration. It is, therefore, necessary to determine the concentration of the cation and of the anion both before and after the adsorption, in addition to the determination of the free acid present in the solution. If the process be exclusively hydrolytic, the concentration of the cation in solution should decrease in proportion to the increase in acidity of the solution, while the concentration of the anion should remain constant: if, on the other hand, the adsorption be both molecular and hydrolytic, no such proportionality would be found. To test this point 40 cc. of solution of KCl (approximately 1 N) were treated with about three grams of pure silica and the concentrations of both the cation and anion were determined. The potassium was determined by Smith's perchlorate method[1] and the chloride was determined with silver nitrate volumetrically. The results obtained follow: Before adsorption

10 cc. of the KCl solution required 21.06 cc. $AgNO_3$ (0.50 N)
20 cc. of solution gave 2.9138 gms. $KClO_4$
Solution was neutral.

After adsorption
10 cc. of the solution required 21.07 cc. $AgNO_3$
20 cc. of solution gave 2.9118 gms. $KClO_4$
3.30 cc. acid (0.01 N) was set free.

Altogether four samples were used, and similar results were obtained in each case. The discrepancy in the different determinations was well within the limits of accuracy of the method. The amount of hydrochloric acid set free was equivalent to 0.0045 gm. of $KClO_4$, while the decrease in potassium determined by the perchlorate method was equivalent to 0.0040 grams $KClO_4$ (average of four determinations). The concentration of the cation, K, in solution was thus shown to decrease during adsorption by an amount equivalent to the increase in acidity of the solution. The concentration of the Cl ion was shown to remain unchanged. The adsorption of KCl by silica was, then, completely hydrolytic and no KCl as such was adsorbed.

INFLUENCE OF SOLVENT ON ADSORPTION

It is well known that a solvent has a marked influence on adsorption. Different theories have been advanced to account for this influence, but none of them seem to be sufficiently comprehensive. In developing a general theory, one must consider not only the influence of the solvent on the adsorbate, but also its influence on the adsorbent. The first factor is determined by the solubility of the solute and the second factor by the adhesion tension of the solvent against the adsorbent. When an adsorbent is added to a solution, an equilibrium is soon set up between the adsorbed and the unadsorbed portions of the solute. The amount of the solute that will be

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[1] J. Am. Chem. Soc., 47, 762, 774, 1020 (1925).

adsorbed depends first of all on its chemical potential. The relation between solubility and chemical potential has been expressed by W. Lash Miller[1] as follows:

"If the solution of the substance S be prepared of equal concentrations in different solvents, the potential will be greatest for that solution which is nearly saturated; or the greater the solubility of S in any solvent the less the potential for any given concentration." The inverse relation between adsorption and solubility has been emphasized by Patrick and Jones who stated that "no exception has been found to the generalization that greater adsorption always follows lower solubility of the solute adsorbed in the solvent." This statement is also supported by our data from which the following two examples are chosen.

TABLE VI

Adsorption of Benzoic Acid by Silica

From carbon tetrachloride		From benzene	
Equil conc.	x/m	Equil conc.	x/m
0.0383 N	0.75	0.0400 N	0.371
0.0766 N	1.03	0.0470 N	0.405
0.1169 N	1.34	0.120 N	0.57
0.2529 N	1.95	0.196 N	0.67

The solubilities of benzoic acid in carbon tetrachloride and in benzene are 4.18 and 12.43 respectively at 25°.

The above theory, thermodynamically sound as it is, is not sufficient to account for all the facts observed, as for example, Freundlich[2] found that from different solutions of the same concentration carbon adsorbs the same amount of benzoic acid from benzene as from ether, even though the solubilities of the acid in these liquids are 12 and 46 grams respectively. The insufficiency of the solubility relationship is also shown from the familiar fact of removing the adsorbed benzoic acid from carbon by washing the solid with organic liquids. In this case benzene was found to be more efficient in the removal of adsorbed benzoic acid than alcohol even though the latter can dissolve much more of the acid than benzene. This anomaly must be explained by considering the influence of the solvent on the adsorbent.

If the solvent has a high interfacial tension against the solid, it is then possible to cause a marked depression of this tension by adding a solute, thereby a high adsorption will occur. The high adsorption from water is generally explained in this way. Thus Freundlich[3] stated: "Water is characterized by a high surface tension and by a high interfacial tension against other liquids. We may therefore ascribe to it also a high interfacial tension against solids, especially hydrophobic solids. On the other hand, adsorption is low from organic liquids such as benzene, alcohol, etc., in the case of which we may assume for similar reasons a low interfacial tension against solids."

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[1] J. Phys. Chem., 1, 653 (1897).

[2] Z. physik. Chem., 57, 385 (1907).

[3] "Colloid and Capillary Chemistry," 192.

The above generalization does not hold for silica and probably would not hold for other hydrophillic solids. Bartell and Osterhof[1] have shown in their investigation on the adhesion tension of liquids against carbon and silica that while organic liquids have, in general, a low interfacial tension against carbon, they have a high interfacial tension against silica. Therefore silica should adsorb best from organic solvents. For examples, from solutions of the same concentration, with water and carbon tetrachloride as solvents, silica was found to adsorb 0.05 and 0.32 millimoles of benzoic acid respectively.

In order to compare the influence of solubility on adsorption, it is important to use solvents which have the same interfacial tension against the adsorbents. Since, as has been shown in this laboratory, benzene and carbon tetrachloride have approximately the same adhesion tension against silica, it must follow that the interfacial tension against silica must be similar, therefore one is justified in comparing results obtained with these two liquids. If one wishes to study the relation between adhesion tension of the solvent against the solid and the degree of adsorption, it is necessary to use adsorbates which have the same solubility in the solvents in question. In general, we may say that if the solubility of the adsorbate is the same in different solvents, greater adsorption will occur from solutions the solvent of which has a lower adhesion tension against the solid. On the other hand, if the adhesion tensions of the solvents are the same, then greater adsorption will occur from those solvents in which the adsorbate is less soluble.

Summary

1. Hydrolytic adsorption occurs when aqueous salt solutions are treated with pure dehydrated silica prepared from silican tetrachloride. The basic constituent is preferentially adsorbed from such solutions. In general, bases are adsorbed, organic acids are slightly adsorbed and inorganic acids are not adsorbed at all.

2. Inorganic bases are preferentially adsorbed in the order LiOH > NaOH > KOH > NH_4OH. This order is the same as that for the degree of hydration of the cations. The order of adsorption is probably due to the strongly hydrophilic nature of the silica.

3. Organic acids are adsorbed in decreasing amounts in an ascending homologous series, i.e., Formic > Acetic > Propionic > Butyric. This order is more pronounced in adsorption from organic solvents.

4. From solutions of sodium salts of the organic acids hydrolytic adsorption (preferential adsorption of base) occurs in increasing amounts in the ascending homologous series, i. e., Na formate < Na acetate < Na propionate < Na butyrate.

5. Inasmuch as an equilibrium condition exists between the base adsorbed and the acid in solution, the extent of base adsorption is regulated by the acid given to the solution by the hydrolytic adsorption, i.e., by the

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[1] Loc. Cit.

strength of the acid or hydrogen ion concentrations of the solution. This probably accounts for the higher degree of hydrolytic adsorption with salts of organic acids than with salts of inorganic acids.

6. The adsorption of inorganic salts such as KCl by silica is completely hydrolytic, that is, no KCl as such is adsorbed, neither is Cl ion nor HCl adsorbed.

7. The degree of adsorption is determined not only by the specific properties of adsorbent and adsorbate, but is dependent upon the solubility of solute in the solvent and upon the solid-liquid interfacial tension relationships. If the solubility of a given adsorbate is the same in a series of different solvents, greater adsorption will occur from solutions the solvent of which has the lower adhesion tension with the adsorbent.

Chemical Laboratory
University of Michigan
Ann Arbor, Michigan

PROPERTIES OF CARBONIZED TUNGSTEN

BY B. T. BARNES

A study of the formation of the carbides of tungsten was published by Mrs. Andrews[1] several years ago. The rate of carbonization and decarbonization was discussed in a subsequent paper[2] by the same author in collaboration with Dr. Dushman. A recent paper by Skaupy[3] is of interest in that it gives x-ray patterns obtained with tungsten, WC, W_2C, and what is described as a new phase, possibly W_3C, obtained at temperatures above 2400°C. The evidence regarding this new phase presented in his paper is not very conclusive.

The present paper deals with the spectral and total emissivity and melting point of W_2C. No attempt was made to form W_3C, and micro-photographs of filaments carbonized at temperatures from 1950° to 2150°K showed only the W_2C and WC. The spectral emissivity measurements were made on tubular pressed tungsten filaments similar to those used by Worthing with the outside diameter of the tube 30 mils and the inside 20 mils. Holes 4 mils in diameter allowed black body radiation to come out of the central cavity. Pyrometering the holes gave the true temperature and comparing the brightness of the holes with that of the surface gave the spectral emissivity.

For polished uncarbonized filaments the averages of the spectral emissivity values for $\lambda .660\mu$ obtained on ten well-aged filaments were .02 higher than obtained by Worthing. This discrepancy may have been due to imperfect polishing or to the radiation from the hole not being black body radiation. Partial carbonization by heating in acetylene vapor at temperatures from 1950° to 2150°K increased emissivity values for $\lambda = .660\mu$ by .02 on the average. This increase may be largely due to roughening of the surface since microscopic examination showed that the filaments were considerably more pitted after carbonization than before. After polishing one of these carbonized filaments its spectral emissivity was .01 to .02 greater than before carbonization.

Averaging spectral emissivity readings for $\lambda .472\mu$ for seven filaments when uncarbonized gave values .01 greater than those obtained by Worthing. Carbonizing the surface to W_2C increased the emissivity at any given temperature by .03.

Total radiation measurements were made on four 10-mil. filaments before and after carbonization. Two coils of one mil tungsten wire fused on to each filament for potential leads eliminated most of the end loss. It was found that the total emissivity values obtained at 1600°K for the uncarbonized tungsten agreed fairly well with the values published by Forsythe and Worth-

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[1] J. Phys. Chem., **27**, 270 (1923).

[2] J. Phys. Chem., **29**, 462 (1925).

[3] Z. Elektrochemie, **33**, 487 (1927).

ing, but those for temperatures above 2200°K were usually several percent too large. This might possibly be due to conduction by gas given off by the bulb walls and leads. After carbonizing the surface to W_2C and heating for a sufficient length of time to insure that no free carbon remained the total emissivity was considerably higher. With 5% of a 10 mil filament converted to W_2C the increase ranged from .06 at 2000°K to .10 at 1400°K. This initial increase in total emissivity is due partly to a roughening of the surface as may be seen by comparison of the micro-photographs for a carbonized and an uncarbonized filament in Fig. 1. There is an additional increase in total radiation with increased carbonization which may be attributed in part to further roughening of the surface and to the development of cracks in the filament surface but is due chiefly to a radial expansion which amounts to as much as 15% when the filament has been completely carbonized to W_2C.

Fig. 1 A
Surface of uncarbonized tungsten filament, etched by heating. × 940.

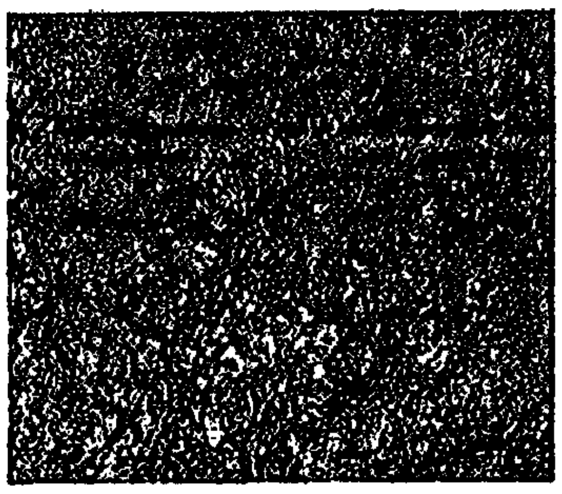

Fig. 1 B
Similar filament after carbonizing. ×940.

The magnitude of this further change depended somewhat on the heating given the filament during carbonization, but the average of the emissivity values uncorrected for radial expansion obtained with 50% of the filament changed to W_2C was about .02 higher than with 5%; and for 90% W_2C the values ranged from .04 to .05 higher than those with 5% W_2C content.

To obtain corrected emissivity values for W_2C the increases produced by carbonization were added to the accepted values for tungsten. Since the best polished filaments when uncarbonized gave values quite close to those published by Forsythe and Worthing this seems a reasonable method of correcting for lack of polish and for any systematic error in matching the pyrometer filament with the image of the small hole, in the case of spectral emissivity measurements. The final values obtained in this manner are given in Fig. 2. The spectral emissivity is the average for partially carbonized filaments and the total emissivity that obtained when a surface layer comprising 5% of a 10 mil filament is carbonized to W_2C. For more completely carbonized filaments the corrected total emissivity and the spectral emissivity were constant within the limits of the measurements. (.01).

Resistance data obtained on the 10-mil filaments used for total radiation measurements were reduced to relative conductances. In Fig. 3 are plotted

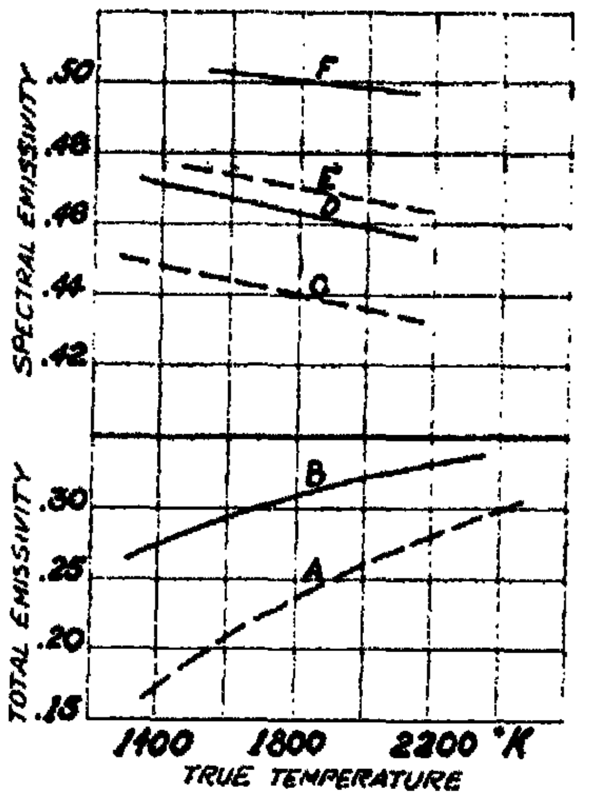

Fig. 2

Total emissivity of tungsten (A) and of W_2C (B). Emissivity for λ.660μ of tungsten (C) and of W_2C (D). Emissivity for λ.472μ of tungsten (E) and of W_2C (F).

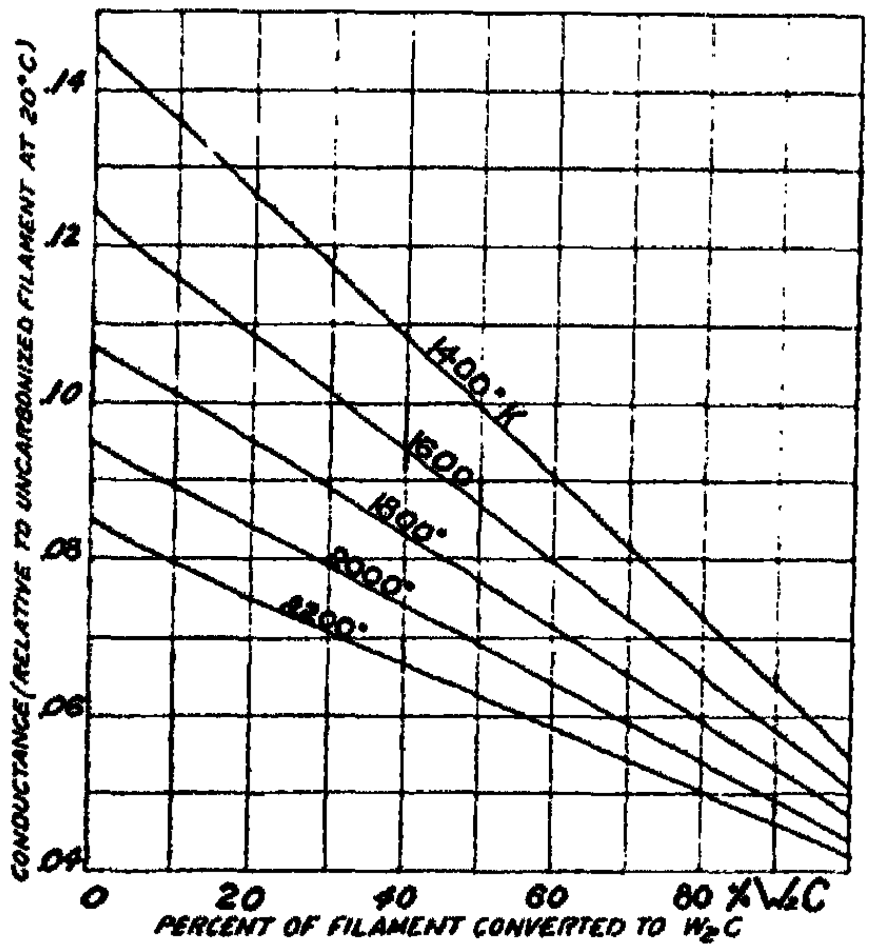

Fig. 3

curves giving the ratio of the conductances of a carbonized filament at true temperatures from 1400° to 2200°K to that of the filament at 20°C when uncarbonized. For percentages of W_2C greater than 50 the curves are only approximately correct, because irregularities of carbonization and cracks developing in the filament caused discrepancies in the measurements. Data on one filament carbonized beyond the W_2C point indicated that the resistance at 2100°K is nearly constant, independent of the proportion of the filament that has been converted to WC, although the cold resistance of WC is about one-fifth that of W_2C, as Mrs. Andrews has shown.

Fig. 4
Filament with sheath of decarbonized tungsten around core of W_2C crystals with decarbonized *striae* crossing them. × 175.

Considerable study was made of the process of carbonization and decarbonization. Tungsten filaments with large crystal grains were partially carbonized and cross-sections made to see if the carbonization proceeded faster along the crystal boundaries. It was found that the carbide layer was usually of fairly uniform thickness, independent of crystal boundaries. Decarbonization is less regular. A filament partially decarbonized by heating to a high temperature in vacuo has occasional completely decarbonized grains scattered through the W_2C and parallel layers of decarbonized tungsten in each W_2C crystal, as well as a sheath of completely decarbonized tungsten on the outside. A cross-section of such a filament is shown in Fig. 4.

A method for determining the melting point of W_2C was developed from the observation that slightly carbonized filaments which had been heated to a high temperature resembled a string of beads because the carbide had melted and collected in drops along the tungsten core. A 10-mil filament with a surface layer of W_2C was heated till the latter melted on a small part of the filament. The temperature was lowered and then gradually raised till the region where the W_2C had melted began to spread. Pyrometer readings were made on the surface which had previously melted. Assuming that the surface had the spectral emissivity of tungsten, the melting point of W_2C* was computed to be 3000°K ± 15°. It seems reasonable to suppose that the surface was decarbonized somewhat during the heating subsequent to melting the W_2C. A microphotograph of the filament surface after melting showed that it was fairly smooth, hence the characteristic emissivity of the material would be unaugmented by surface irregularities. Even if the surface remained W_2C, using the spectral emissivity obtained by extrapolation of the curve for polished carbide would reduce the computed melting point by only 10° to 20°.

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* Strictly speaking, probably an eutectic of W_2C and tungsten.

THE ADSORPTION OF WATER, ETHYL ALCOHOL, ETHYL ACETATE AND ACETIC ACID VAPORS BY TUNGSTIC AND ZIRCONIUM OXIDES; ITS BEARING ON HETEROGENEOUS CATALYSIS

J. N. PEARCE AND M. J. RICE

It has long been known that many oxides act catalytically as dehydrating and dehydrogenating agents. The dehydration of alcohol vapor during its passage through an earthen tube heated to redness was observed by Priestley[1] as long ago as 1783. At a slightly later date Deimann[2] found that alcohol vapor passed over heated alumina and silica is decomposed to ethylene and water and a small amount of hydrogen. Under certain conditions ethyl ether[3] is also formed. Baskerville[4] failed to obtain ethyl ether with thoria at temperatures even as low as 250°, but he did find that the simultaneous dehydration of a phenol and an alcohol by thoria at 400° gives a mixed aliphatic ether.

Sabatier and Mailhe[5] conducted an extended series of experiments using various metallic oxides and several vapors, and observed that in many cases there is a dehydrogenation as well as dehydration. They report thoria to be more active than alumina and state that it behaves exclusively as a dehydrating agent. While alumina is an exceedingly strong dehydrating agent it also possesses some dehydrogenating power. Kramer and Reid,[6] however have shown that under certain conditions thoria may also act as a dehydrogenating agent toward alcohols. They also state that overheating in preparation seems to lessen the activity of the thoria.

Sabatier and Mailhe[5] have found that the specific catalytic action of the oxide is dependent on the temperature of the reaction, since alcohols are converted into ethylenic hydrocarbons by ThO_2, Al_2O_3, and W_2O_3 between 300° and 350°, while ethers are produced at temperatures below 250°. They consider that the mechanism of the process involves the formation of a complex intermediate compound, $ThO(OC_nH_{2n} + 1)_2$. This may either break up to give ethylene and water, or, under other conditions, it may react with another molecule of alcohol to give an ether, regenerating the metallic oxide. Engelder[7] has shown that the presence of water vapor or of hydrogen in the incoming alcohol vapor also determines the ratio of ethylene and hydrogen

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[1] Priestley: Phil. Trans., **73**, 429 (1783).

[2] Deimann: Crell's Ann., **2**, 312, 430 (1795).

[3] Grigorieff: J. Russ. Phys. Chem. Soc., **33**, 173 (1901).

[4] Baskerville: J. Am. Chem. Soc., **35**, 93 (1913).

[5] Sabatier and Mailhe: Compt. rend., **136**, 738, 921, 983 (1903); **146**, 1376 (1908); **148**, 1734 (1909); **150**, 823 (1910); **152**, 358, 494 (1911).

[6] Kramer and Reid: J. Am. Chem. Soc., **43**, 880 (1921).

[7] Engelder: J. Phys. Chem., **21**, 676 (1917).

in the resulting decomposition products. Senderens[8] obtained ethers by passing the vapors of methyl and ethyl alcohols over alumina at temperatures between 240° and 260°, and he represents the reaction as merely one of dehydration. The higher alcohols, however, give either a low yield of ether, or none at all, ethylenic hydrocarbons being the chief products. With W_2O_3 only small amounts of methyl and ethyl ethers are formed and no ether is obtained with ThO_2. By heating acids and esters in the presence of these oxides he has also obtained ketones. He represents the reaction in this case as a dehydration followed by a decomposition; the acid anhydride is first formed and this then breaks up to give the ketone and CO_2. This idea was confirmed by the fact that CO_2 and dimethyl ketone are obtained when acetic anhydride vapor is passed over Al_2O_3 at 300°. In another paper Senderens[9] has shown that both aliphatic and aromatic acids yield ketones when heated in the presence of ThO_2, ZrO_2 and UO_2.

The effect of Al_2O_3, ThO_2 and TiO_2 on ethyl acetate in the neighborhood of 400° is summarized by Sabatier[10] in the following manner:

$$2\,CH_3COOC_2H_5\ (Al_2O_3) = (CH_3)_2CO + 2\,C_2H_4 + CO_2 + H_2O,$$
$$2\,CH_3COOC_2H_5\ (ThO_2) = (CH_3)_2CO + C_2H_4 + CO_2 + C_2H_5OH,\ \text{and}$$
$$CH_3COOC_2H_5\ (TiO_2) = CH_3COOH + C_2H_4.$$

An extended investigation of the activity of oxide catalysts at temperatures between 300° and 400° by Sabatier and Mailhe[11] shows that a majority of oxides promote two reactions simultaneously, one the process of dehydration, the other the process of dehydrogenation. The analysis of the gaseous products obtained in passing the vapor of ethyl alcohol over various oxides at 340° to 350° showed that with certain oxide catalysts ethylene only is produced. In general, however, the effluent gas is a mixture of ethylene and hydrogen in varying proportions depending on the catalyst employed. They have tabulated the different metallic oxides in the order of decreasing power of dehydrating alcohol, thus:

Oxide	$\%C_2H_4$	$\%H_2$	Oxide	$\%C_2H_4$	$\%H_2$
ThO_2	100.00	Trace	U_3O_8	24.0	76.00
Al_2O_3	98.50	1.5	Mo_2O_3	23.0	77.0
W_2O_3	98.5	1.5	Fe_2O_3	14.0	86.0
Cr_2O_3	91.0	9.0	V_2O_3	9.0	91.0
SiO_2	84.0	16.0	ZnO	5.0	95.0
TiO_2	63.0	37.0	MnO	0.0	100.0
BeO	45.0	55.0	SnO	0.0	100.0
ZrO_2	45.0	55.0	CdO	0.0	100.0

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[8] Senderens: Bull., (4), **5**, 480 (1909); Compt. rend., **140**, 995 (1905); **148**, 227, 927 (1909); **150**, 111 (1910); Ann. Chim. Phys., (8) **28**, 243, 322 (1918).

[9] Senderens: Compt. rend., **150**, 702 (1910).

[10] Sabatier: "La Catalyse en Chimie organique," p. 341 (1920).

[11] Sabatier and Mailhe: Ann. Chim. Phys., (8), **20**, 341 (1910).

These data show that ThO_2 behaves almost exclusively as a dehydrating catalyst under the given conditions; its power as a dehydrogenating agent is practically nil. Alumina and tungstic oxides are only slightly less active dehydrating agents. The oxides of tin, manganese and cadmium are exclusively dehydrogenating catalysts, their dehydrating power is entirely suppressed. Between the two extremes the dehydrating and dehydrogenating powers of the metallic oxides vary rapidly. In general, the greater the dehydrating activity of a metallic oxide, the smaller is its dehydrogenating activity toward alcohol.

Adkins and Krause[12] state that the reaction induced by an oxide catalyst is influenced by the method of preparation and is not dependent merely on the metallic element present. They disagree with the intermediate compound theory of Sabatier and Mailhe.[6] In a later paper[13] Adkins suggests that the efficiency of the oxide depends on the character of the surface presented to the vapors, and in so doing he apparently accepts the view presented by Briggs.[14] The latter considers that the activation of charcoal for the adsorption of gases is dependent upon interstices of molecular dimensions formed by the elimination of carbon atoms from the carbon molecule or space lattice. The larger, microscopically visible pores or capillaries have apparently little to do with adsorption. Starting with this idea, Adkins[13] has advanced an hypothesis which considers that the catalytic activity of alumina is conditioned by its molecular porosity, or the distance between the aluminum atoms, and that this part is determined by the size, shape and position of the radicals attached to the aluminum atom when the aluminum compound passes into the solid state of the catalyst. To this end he prepared aluminum oxide by heating aluminum hydroxide and aluminum ethylate. Since the size of the molecules eliminated in the latter case is larger, the porosity should be greater. In turn, the adsorption capacity of the oxide formed from the aluminum ethylate should be correspondingly greater. All of the experimental evidence obtained by Adkins with aluminum catalysts, prepared in various ways, was found to be in complete harmony with this hypothesis. He was able to activate alumina preferentially, either for dehydration or for decarboxylation, by modifying the mode of preparation. In terms of his hypothesis he states that decarboxylation is favored by large molecular pores in alumina and that ethylene formation is favored by small pores.

This idea is also supported by Pease and Yung.[15] They find that alumina dehydrates alcohol at 300° to 400° to give pure ethylene, while ether is produced if the reaction is carried out at 240° to 250°. They also state that the size of the pores determines whether ethylene or ether is produced, large pores favoring the formation of ether, small pores favoring ethylene formation.

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[12] Adkins and Krause: J. Am. Chem. Soc., 44, 385 (1922).

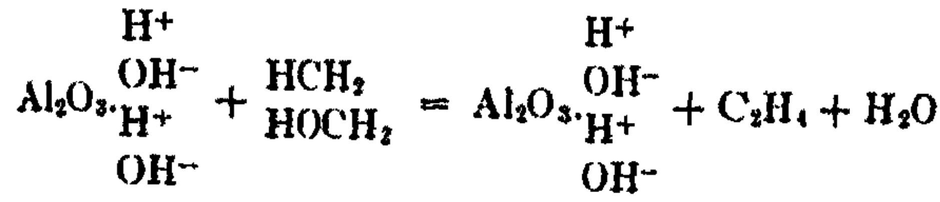
[13] Adkins: J. Am. Chem. Soc., 44, 2175 (1922).

[14] Briggs: Proc. Roy. Soc., 100A, 88 (1921).

[15] Pease and Yung: J. Am. Chem. Soc., 46, 390 (1924).

However, since water is eliminated in either case, this cannot be a wholly satisfactory view.

In discussing the mechanism of catalysis by alumina, Boswell and Bayley,[16] and Boswell and Dilworth[17] have suggested the presence of a stable film of dissociated water in the form of charged H^+ and OH^-. They claim that the great stability of this film is indicated by the fact that it still persists after heating for 20 hours at 500° followed by two days heating over a Meeker burner. Further, that the stability of this film indicates that the H^+ and OH^- are arranged in alternate rows and completely envelope each oxide particle. Upon studying the reaction between C_2H_5OH and Al_2O_3 these authors conclude that the reaction is most satisfactorily represented thus:



$$Al_2O_3.\begin{matrix}H^+\\OH^-\\H^+\\OH^-\end{matrix} + \begin{matrix}HCH_2\\HOCH_2\end{matrix} = Al_2O_3.\begin{matrix}H^+\\OH^-\\H^+\\OH^-\end{matrix} + C_2H_4 + H_2O.$$

It is evident that if this represents the true mechanism of the dehydration of ethyl alcohol by alumina, then we must likewise assume that all oxides which cause the dehydration of alcohol must be covered with a similar film of H^+ and OH^-. The difficulty in applying such a scheme comes when we consider that most of these oxides show also some dehydrogenating activity.

Langmuir[18] has shown that the tendency of a gas or vapor to be adsorbed on the surface of a solid is determined by the rate of evaporation from the surface. Further that this rate depends upon the magnitude of the forces acting between the atoms of the crystal and those of the adsorbed substance. According to him, these forces are of the same nature as those which hold solid bodies together, and we may look upon them as chemical forces. Adsorption is thus due to the unsaturated force fields at the surface of the solid. Selective and irreversible adsorption are due to primary valence forces. The weaker and less specific secondary adsorptions are due to secondary valence forces. From certain assumptions based on his own data, Benton[19] has devised a method of calculating the relative magnitudes of primary and secondary adsorption. He finds that there is no relation between the total adsorption on the surface of an adsorbent and its catalytic activity; on the other hand, the magnitude of the primary adsorptions calculated are in the same order as the catalytic activities of the substances.

In a recent paper Taylor[20] has advanced a theory of adsorption to explain the catalytic activity of solids. While he assumes with Langmuir an unbalanced force at the surface of a solid, he develops the idea of this force in a somewhat different way. According to Taylor, the atoms on a plane surface of a solid are saturated in three dimensions by neighboring atoms. There is

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[16] Boswell and Bayley; J. Phys. Chem., 29, 679 (1925).

[17] Boswell amd Dilworth: J. Phys. Chem., 29, 1489 (1925).

[18] Langmuir: J. Am. Chem. Soc., 38, 2267 (1916).

[19] Benton: J. Am. Chem. Soc., 45, 887 (1923).

[20] Taylor: J. Phys. Chem., 30, 145 (1926).

left, however, one degree of unsaturation directed toward the gaseous phase. It follows then that atoms which lie on the edge of a solid will have two degrees of unsaturation; those on a corner will have three degrees of unsaturation directed toward the gaseous phase. The attractive forces exerted by the atoms of the adsorbent upon the impinging molecules will, therefore, be greatest at the corners and least on the plane surfaces. Thus, points are considered as representing places of preferential adsorption.

That these oxides may possess an extensive capillary structure is also without question. We should expect, therefore, a wide variation in their adsorption power depending not only upon the shape, the diameter and the depth of the capillaries, but also upon the shape and volume of the adsorbed molecules. The possibility that both surface and capillary forces are active only adds to the complexity of the adsorption process.

In order to obtain some insight into the possible mechanism of ester catalysis by metallic oxides, Pearce and Alvarado[21] have measured the adsorption of water, ethyl alcohol, acetic acid and ethyl acetate vapors by thoria and alumina at 99.4°. They find that if we consider the adsorption of vapor by a unit mass of adsorbent, X/m, the results obtained show that alumina is a better adsorbent for water vapor, ethyl alcohol and ethyl acetate than is thoria. Whereas, on the basis of vapor adsorbed by 1 cc. of the oxide, X/V, thoria appears to be the better adsorbent for water vapor at all pressures, and for ethyl alcohol at low pressures. At all pressures the acetic and ethyl acetate vapors are more highly adsorbed by the aluminum oxide. If the adsorption magnitudes are calculated on the basis of equal volumes of the oxide adsorbents, the order of magnitude for the adsorption of water vapor, and for ethyl alcohol at low pressures, is the same as the order of decreasing dehydrating power of the oxides for alcohol. The magnitude of the adsorption of the vapors was found to vary with the nature of the vapor; it is greatest for water vapor and least for ethyl acetate, with alcohol occupying an intermediate position. The adsorption of acetic acid vapor seems to vary more specifically both with the nature of the oxide and with its degree of hydration.

In the present work we have continued the study of the adsorption of these vapors by the oxides of tungsten and zirconium.

Materials

Tungstic Oxide.—A large sample of the C.P. tungstic acid was dissolved in ammonium hydroxide; the solution was boiled to expel the free ammonia, and sufficient nitric acid was added to precipitate the oxide, WO_3. The precipitate was washed by decantation until the wash water showed no traces of nitrates, then filtered through hardened filter and thoroughly washed. The oxide was then dried for 24 hours at 130° and pulverized to pass through a 200-mesh sieve. After a second heating at 250° for 24 hours it was transferred to a glass-stoppered bottle and stored in a desiccator over P_2O_5.

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[21] Pearce and Alvarado: J. Phys. Chem., 29, 256 (1925).

Zirconium Oxide.—The C.P. zirconium nitrate was dissolved in water and precipitated by ammonia. The subsequent treatment was the same as that used in preparing the tungstic oxide.

The method followed in purifying the solvents was the same as that employed in the previous paper.[21]

In order to determine the volume occupied by the adsorbent it was necessary to know the density of each oxide. A sample of the oxide was evacuated to less than 0.0001 mm. at 500° in a bulb provided with a drawn-out capillary. After evacuation the tube was sealed and the bulb weighed. The seal was broken under pure benzene, where it was allowed to remain for a time to allow for the drift; the level of the liquid was brought to a given mark at 25° and the bulb was again weighed. The density values obtained for the ZrO_2 were 5.489, 5.480 and 5.482, the mean being 5.484. For WO_3 the results were 6.924, 6.926 and 6.923, the mean being 6.294.

Apparatus and Manipulation

The apparatus used was similar to that used by Coolidge[22] in his study of the adsorption of vapors by charcoal. It was entirely of Pyrex, and without ground joints, stop-cocks or rubber connections. All of the parts used for measuring the gas volumes were accurately calibrated. With the exception of the vessel holding the liquid source, the whole apparatus was mounted in a large double-walled thermostat. This was electrically heated and electrically controlled at 70° ± 0.05 throughout the whole series of measurements. The temperature of the oxide bulb was kept constant by immersion in a flask containing boiling water. Hence the temperature was subject only to changes due to fluctuations in barometric pressure. The whole apparatus was evacuated by means of a Hyvac pump in series with a mercury vapor condensation pump. The vacuum obtained was read from a McLeod gauge.

In every case a sample of the oxide was weighed by removing the adsorption bulb, weighing empty, and then with the oxide present.. After the bulb was replaced, the oxide was evacuated at 500° and the evacuation was continued until the gauge indicated a pressure of less than 0.00005 mm. The apparatus was then sealed and allowed to stand for 24 hours. If no appreciable pressure developed, the experiment was begun. The exact weight of the dry oxide was determined by subjecting a sample of equal weight to exactly the same heat treatment. All volumes were corrected for dead space, and were reduced to 0°, latitude 45° and sea level.

Results

Since adsorption is a surface phenomenon, it is quite obvious that for a given uniform solid adsorbent, the total magnitude of the unsaturated surface forces, as well as the capillary effects, will be directly proportional to the extent of surface. If it were possible for two different adsorbents to possess identically the same number of unsaturated surface forces per unit area of

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[22] Coolidge: J. Am. Chem. Soc., 46, 596 (1924).

surface, the two adsorbents could approximate equal adsorption capacities, per gram of solid adsorbent, only when they expose equal surfaces. Or, on the other hand, if the surface topographies of the oxides were in every way identical, we might consider the adsorption of a given gas or vapor as a measure of the relative magnitudes of these unbalanced surface forces. It is evident that all such assumptions as these are entirely out of the question when we consider the oxides used in this paper. The densities of the oxides used thus far were Al_2O_3, 2.86; ZrO_2, 5.48; ThO_2, 6.82; WO_3, 6.92. The corresponding specific volumes of the gas-free oxides were 0.349, 0.182, 0.147 and 0.145 cc. respectively. The adsorbents were all prepared in the same general way; in the final step all were pulverized to pass through the same mesh sieve. Assuming that the oxide particles are round and that they have the same diameter and surface topography, which is undoubtedly not true, the surface exposed by one cc. of the various oxides should be approximately the same. The surface exposed by one gram of the oxides should, on the other hand, decrease rapidly in the order of increasing density. In the study of the adsorption of gases and vapors by solid adsorbents it has been the custom, generally, to consider the volume of vapor in cc. (N.T.P.) adsorbed by 1 g. of adsorbent. For the reasons given above we believe that adsorption relations are much better expressed when the magnitudes are expressed in volumes of vapor adsorbed by 1 cc. of the solid oxide.

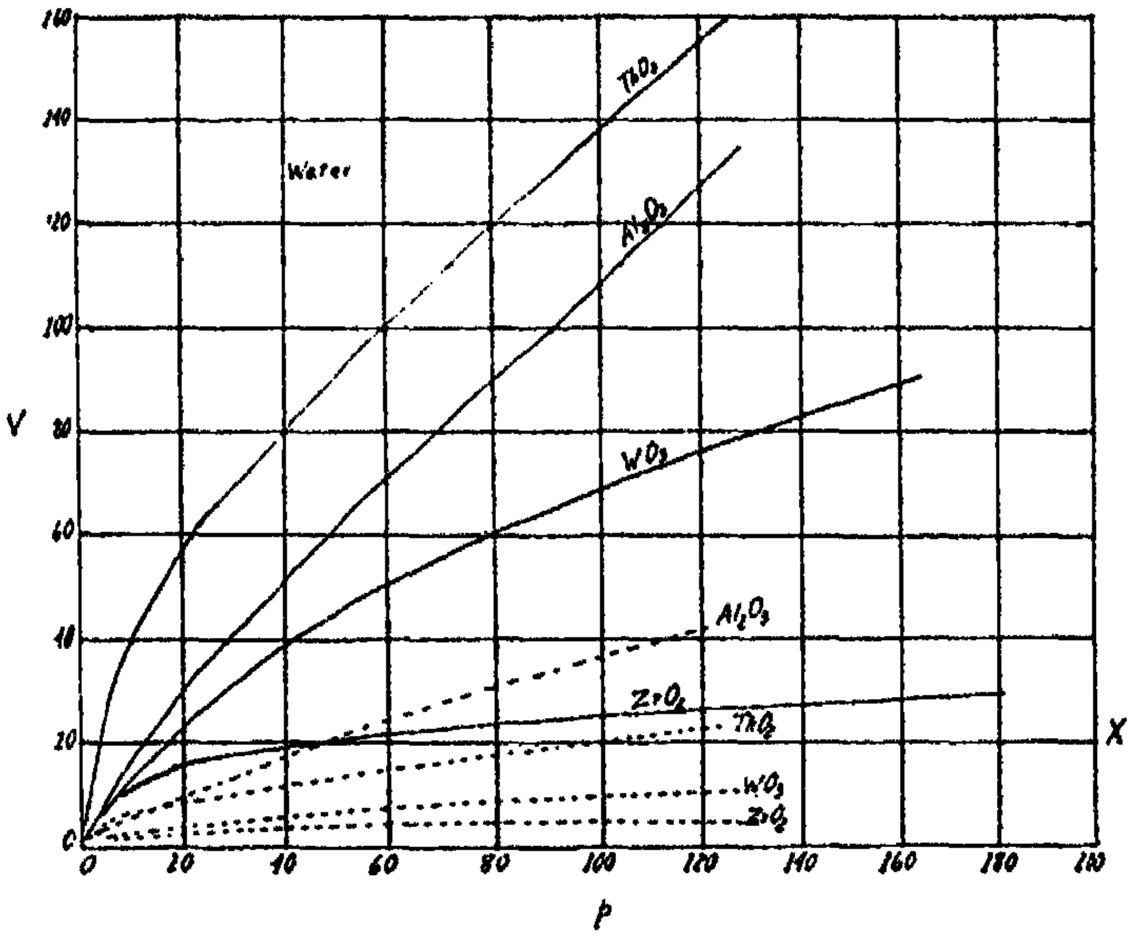

Fig. 1

V ————

X ....

At least two independent series of adsorption data were obtained for each vapor on each oxide. The pressure-concentration data obtained were

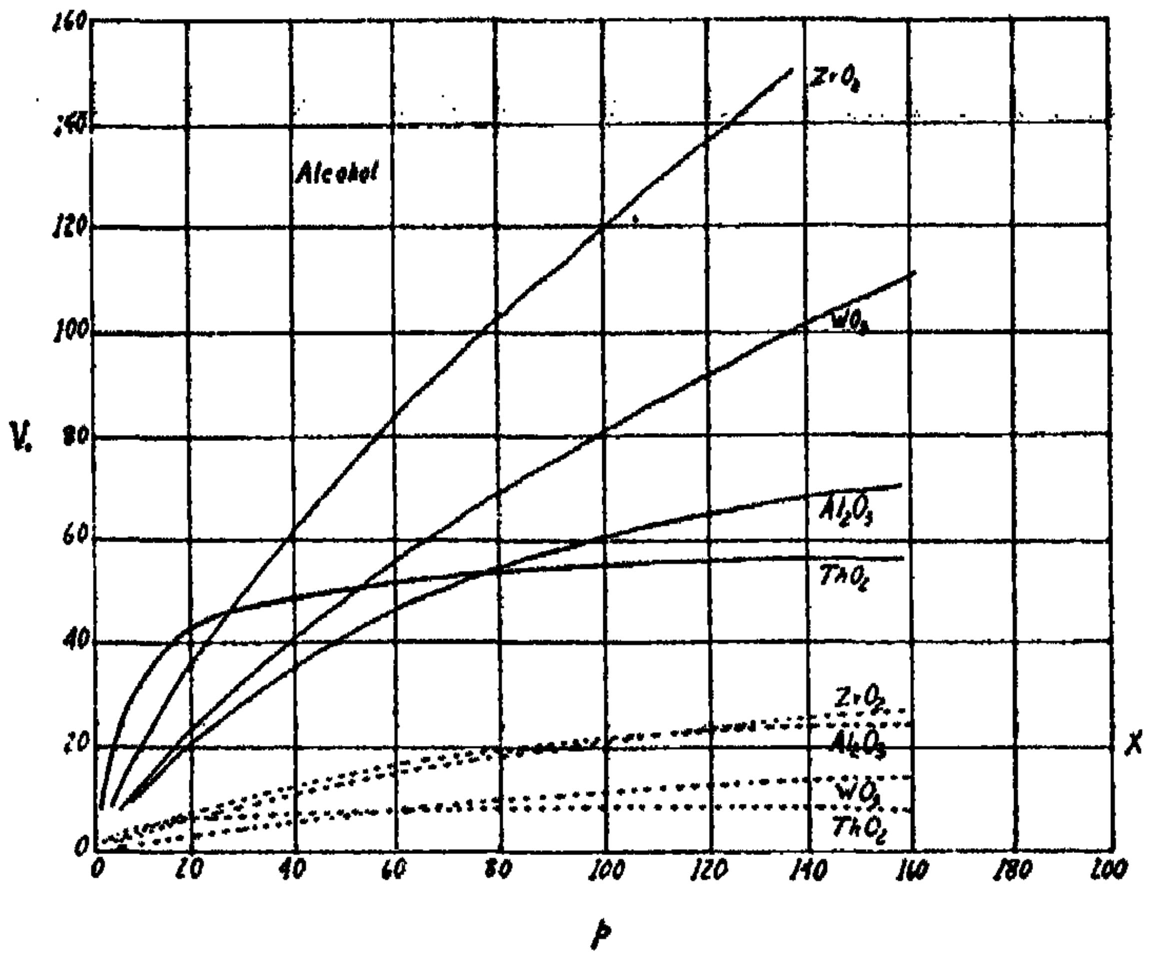
160
140
120
100
80
60
40
20
0
V.
Alcohol
ZrO_2
WO_3
Al_2O_3
ThO_2
ZrO_2
Al_2O_3
WO_3
ThO_2
X
0
20
40
60
80
100
120
140
160
180
200
p

FIG. 2

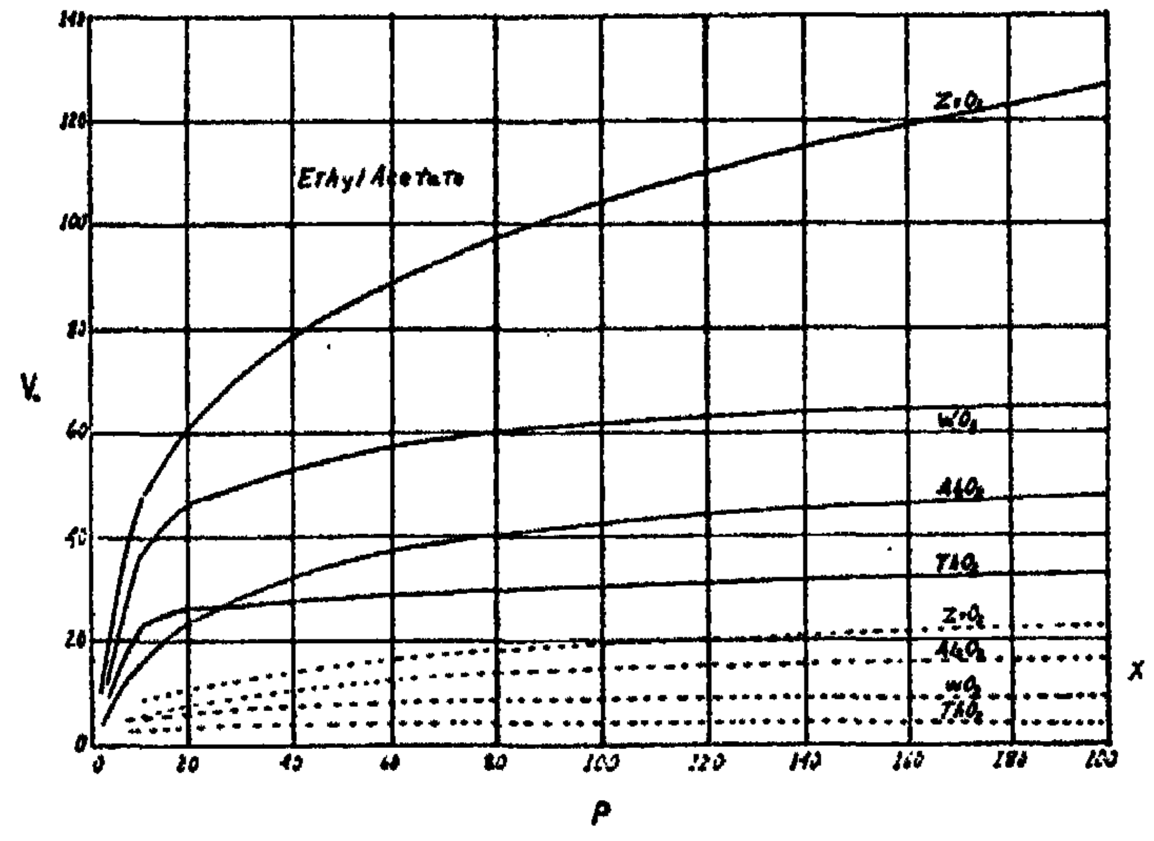
140
120
100
80
60
40
20
0
V.
Ethyl Acetate
ZrO_2
WO_3
Al_2O_3
ThO_2
ZrO_2
Al_2O_3
WO_3
ThO_2
X
0
20
40
60
80
100
120
140
160
180
200
p

FIG. 3

V ————

X ………………

plotted on a large scale and a smooth isotherm was drawn through each set of points.

In the discussion which follows, X and V represent the volume of vapor in cc. (N.T.P.) adsorbed by 1 g. and by 1 cc. of the oxide, respectively. The relative adsorptive powers of ZrO_2 and WO_3 for the four vapors are clearly indicated in Figs. 1 to 4; the corresponding isotherms for the same vapors with ThO_2 and Al_2O_3[21] are included for comparison. In considering adsorption as a possible explanation of heterogeneous catalysis, we are for the present more particularly interested in the relative adsorption of each of the four vapors by each of the four different oxides. These relations are best shown in Figs. 5 to 8.

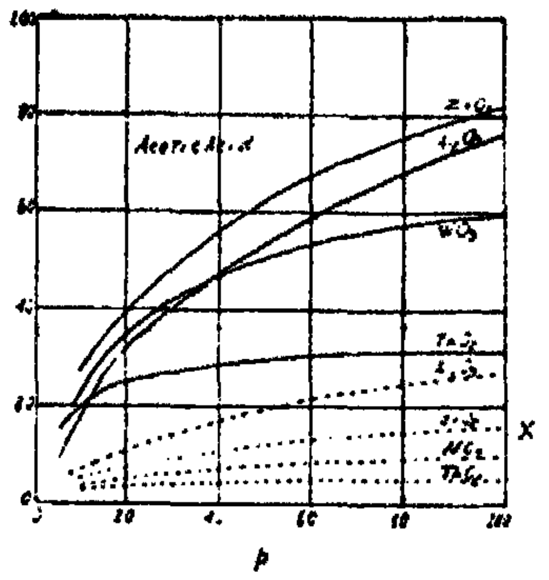

Fig. 4

V ————

X ....

Considering the volume of vapor adsorbed by 1 cc. of oxide, Fig. 1, ThO_2 has the greatest adsorption capacity for water vapor, and this capacity decreases in the order, ThO_2, Al_2O_3, WO_3, ZrO_2. Except for WO_3, this is exactly the order of the dehydrating power of these oxides toward alcohol.[11] While we have used the oxide WO_3 it falls into the same relative position below Al_2O_3 as that given by Sabatier and Mailhe for W_2O_5. The adsorption power of the first three oxides for water vapor increases rapidly with the pressure; that of ZrO_2 increases very slowly for pressures above 30 mm. When considered on the basis of cc. of vapor adsorbed by 1 gram of oxide, X, the same order obtains only for pressures below 15 mm. Above this pressure the adsorptive power of ThO_2 falls below that of Al_2O_3.

Up to about 25 mm. ThO_2 shows the greatest adsorption capacity for ethyl alcohol vapor per 1 cc. of oxide, Fig. 2. The order of decreasing capacity being ThO_2, ZrO_2, WO_3, Al_2O_3. For pressures above 75 mm. the adsorptive capacity of ThO_2 falls below that of Al_2O_3. Above 75 mm. the order of decreasing adsorption is ZrO_2, WO_3, Al_2O_3. This is exactly the reverse of the order of the dehydrating effect of these oxides on ethyl alcohol.

Except for pressures below about 25 mm., Fig. 3, where the adsorption capacity of ThO_2 is greater than that of Al_2O_3, the adsorption of ethyl acetate vapor by 1 cc. of oxide decreases in the order, ZrO_2, WO_3, Al_2O_3, ThO_2. The order is exactly the same as that observed for alcohol vapor at high pressures, and is exactly the reverse of that of the dehydrating power of the oxides.

For pressures less than 10 mm., Fig. 4, the adsorption of acetic acid vapor in decreasing order is ZrO_2, WO_3, ThO_2, Al_2O_3. At about this pressure the adsorptive capacity of Al_2O_3 begins to exceed that of ThO_2; at about 37 mm. it rises above that of WO_3. On the basis of 1 gram of oxide Al_2O_3 is at all pressures the best adsorbent for acetic acid vapor. This is then followed

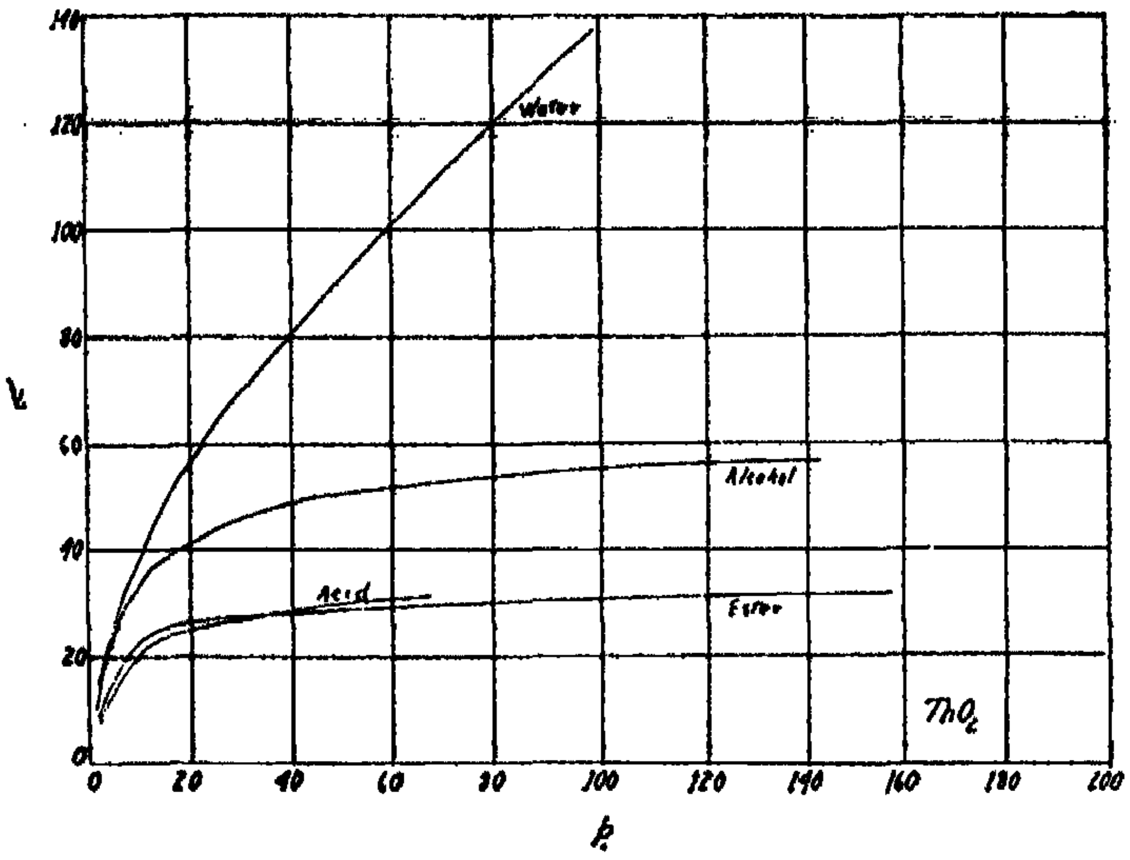

Fig. 5
Adsorption of Vapors on ThO_2

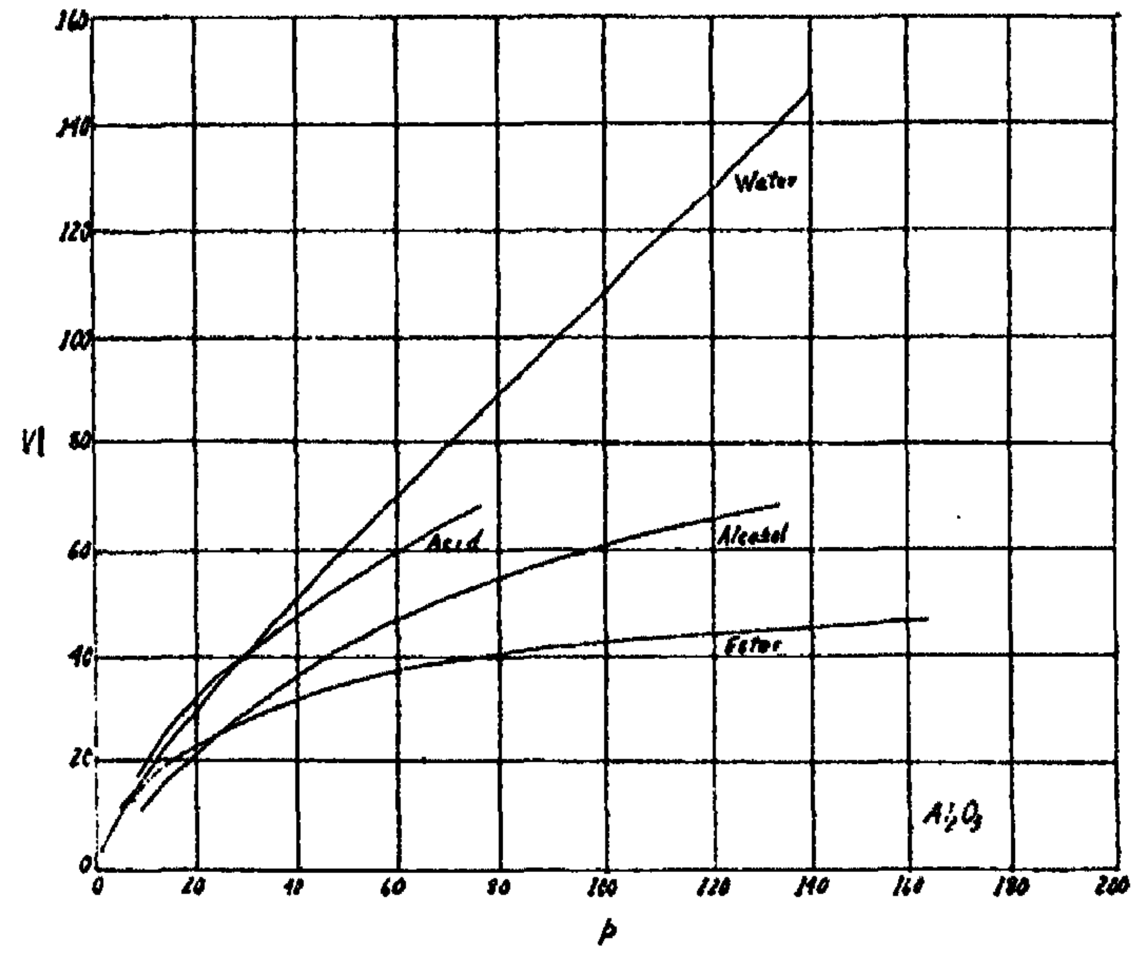

Fig. 6
Adsorption of Vapors on Al_2O_3

by ZrO_2, WO_3 and ThO_2 in the order named. The pronounced acid property of the acetic acid may exert a more or less specific influence, depending on the nature of the adsorbing oxide.

The relations shown in Figs. 5 to 8 appear to show definitely that in the heterogeneous esterification process the adsorption of one or both of the reactants, and possibly of one of the products,—the ester, may be involved. At low pressures the ester and acetic acid vapors are more highly adsorbed by WO_3 and ZrO_2 than are water vapor and alcohol. With both of these oxides, however, the amount of alcohol adsorbed by 1 cc. of oxide increases rapidly with the pressure.

At a given temperature and pressure each oxide will possess a characteristic specific adsorption for each of the four vapors. Unless a vapor is irreversibly adsorbed it may, according to the Mass Law, be displaced by increasing the concentration, or the partial pressure of a second vapor. The relative displacing powers of the different vapors on a given oxide at a given pressure are to a considerable degree at least indicated by the P-V isotherms of Figs. 5 to 8. Unless the surface of an oxide possesses different types of elementary spaces, each type capable of adsorbing molecules of one vapor to the exclusion of molecules of the other three, the water vapor will be most preferentially adsorbed by ThO_2 and to a slightly less extent by Al_2O_3. Since the alcohol at the same pressure is also highly adsorbed, the presence of both the alcohol and water vapors would practically exclude the simultaneous adsorption of acetic acid vapor, and therewith one of the essential reactants of the esterification process. Indeed, if the pressure of the water vapor is so large that the rate of evaporation is less than the rate of condensation, then it is possible for the surface of the catalyst to become so covered with water molecules that even the alcohol would no longer be adsorbed. If such were the case, the dehydration of the alcohol by these oxides would be at most only minimal in quantity. This statement is borne out by the work of Engelder. He found that by increasing the proportion of water vapor in the alcohol passed over TiO_2 the dehydration of alcohol to ethylene is decreased to a marked degree.

In their previous paper, Pearce and Alvarado[21] were inclined to favor the view that in the dehydration of alcohol by ThO_2 and Al_2O_3, the initial step in the process is the formation of the highly adsorbed water vapor and ethylidene. The ethylidene then rearranges to form ethylene. We have found nothing since that would lead us to modify that view. Both ThO_2 and Al_2O_3 are dominantly dehydrating catalysts; they exhibit but little tendency to catalyze the esterification of the aliphatic acids and alcohols.

Nothing has been observed in the literature relative to the esterifying property of ZrO_2. It lies just below TiO_2 in the list of Sabatier and Mailhe. They have found that TiO_2 rapidly catalyzes the esterification process at 280° to 300° with the production of high concentrations of the ester. Whether or not TiO_2 is the best oxide catalyst for this reaction is still a question. With rise in temperature the adsorption of the four vapors by any oxide will de-

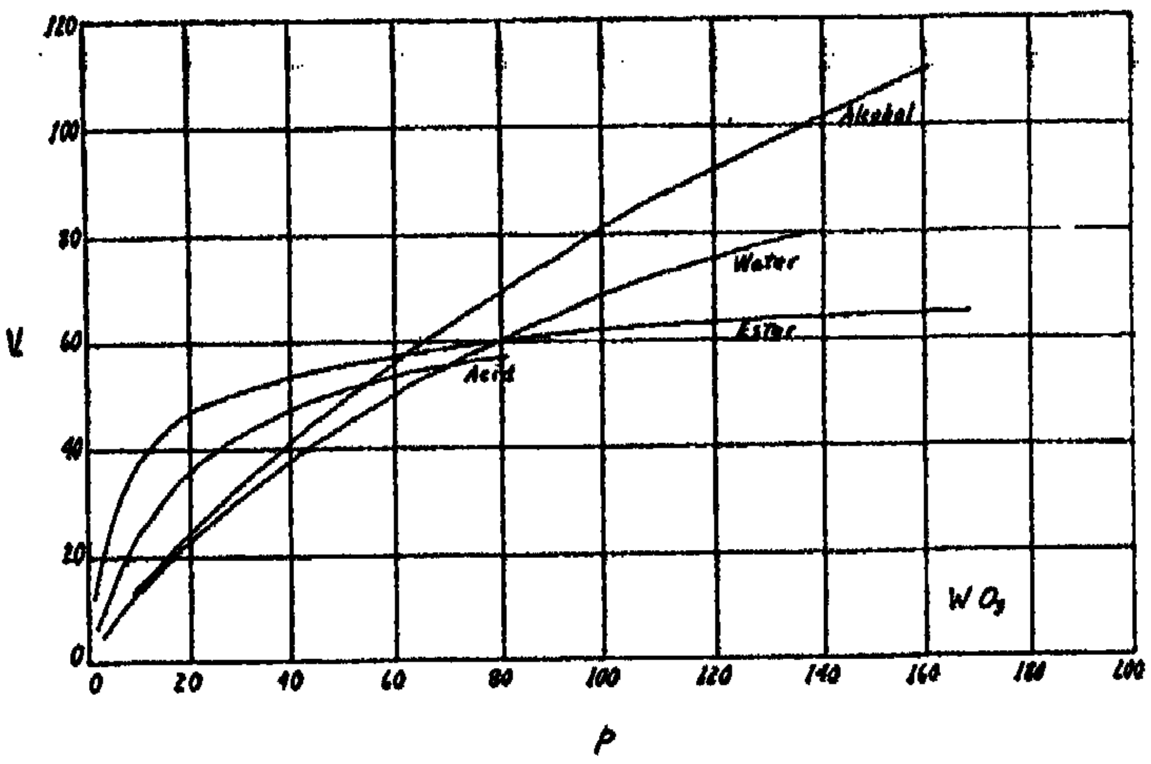

Fig. 7
Adsorption of Vapors on W_2O_5

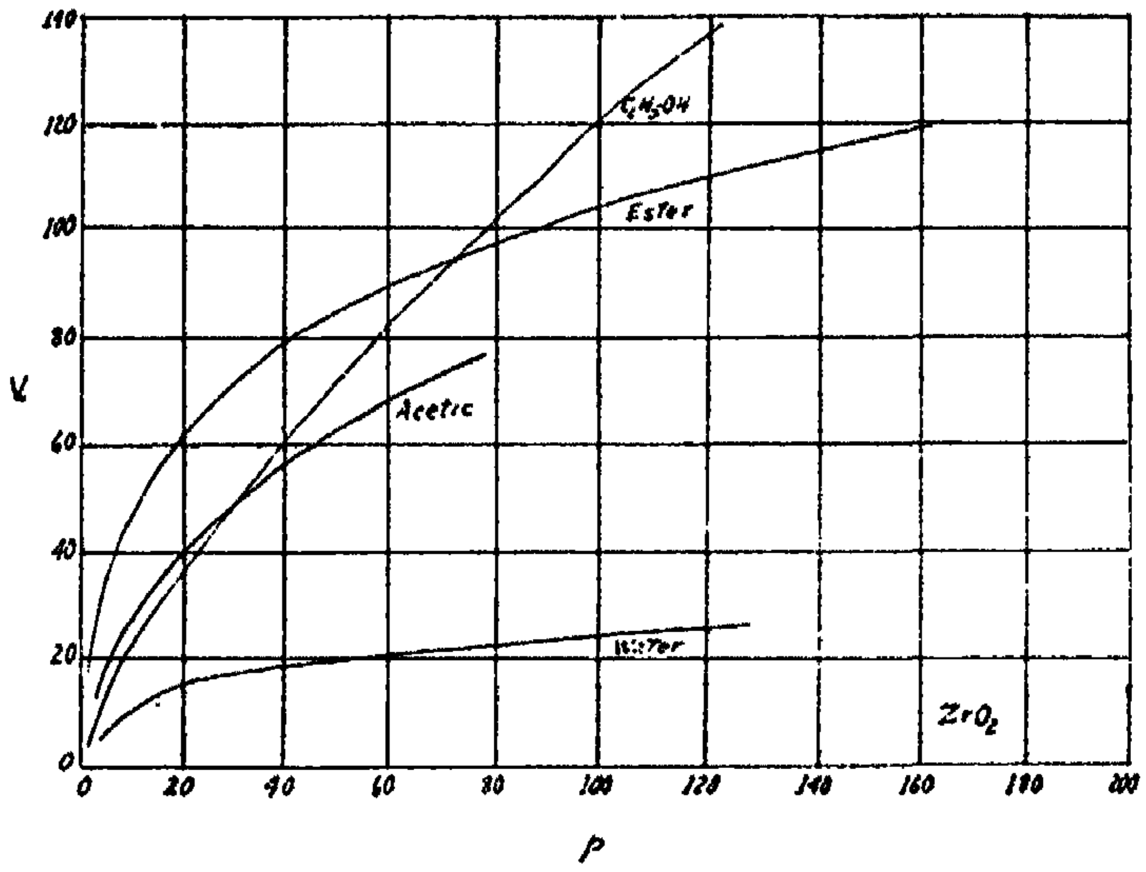

Fig. 8
Adsorption of Vapors on ZrO_2

crease, and obviously at different rates. The amount of each vapor adsorbed under a given pressure at the optimum temperature, say 280°, will be less than at the temperature at which we have made our experiments. The adsorption capacity of ZrO_2 for water vapor should be relatively very much less than its capacity for adsorbing acetic acid and alcohol. The inhibiting power of the water vapor is thus decreased and the reaction proceeds with greater velocity. On the basis of these considerations we may not be far amiss in assuming that the esterifying power of ZrO_2 is of the same order as, or possibly greater than, that of TiO_2.

If we may be allowed to speculate as to the mechanism of esterification, using such catalysts as TiO_2 and ZrO_2, it would seem from the results shown that the initial step consists in the adsorption of both alcohol and acetic acid vapors. Under the conditions of temperature and pressure a stress is produced which weakens the primary valences of the molecules, and metathesis ensues with the formation of the ester and the water vapor. The less strongly adsorbed water is vaporized and the ester is displaced by the adsorption of more acid and alcohol.

Summary

1. The adsorption of water, ethyl alcohol, acetic acid and ethyl acetate vapors by tungsten and zirconium oxides has been studied at 99.4°. The results obtained have been compared with those of a similar study of the adsorption of the same vapors by thoria and alumina.

2. For unit volume of adsorbent the adsorption capacities for water vapor decreases in the order ThO_2, Al_2O_3, WO_3, ZrO_2. This is also the order also of the dehydrating power of these oxides toward alcohol. The order of adsorption for ethyl acetate is exactly the reverse of that for water vapor.

3. The results confirm the view that in the catalytic process both the alcohol and acetic acid vapors must be adsorbed simultaneously. Further, that the catalytic effect increases as the power of the oxide to adsorb water decreases.

Physical Chemistry Laboratory,
The State University of Iowa,
August, 1928.

CRITICAL SOLUTION-TEMPERATURE PHENOMENA IN THE TERNARY SYSTEM PHENOL-THYMOL-WATER

BY KATHLEEN W. WILCOX AND C. R. BAILEY

Thymol and phenol are chemically similar and easily miscible; the overloading of the nucleus in the case of thymol brings a correspondingly low solubility in water, while both substances are capable of forming two liquid layers with this solvent. As a consequence of these conditions, the solubility relationships in the ternary system containing these three components are complicated and of considerable interest, and curves have been obtained which illustrate the interplay of these opposing characteristics.

Materials. (i) Phenol. Detached crystals of absolute phenol were twice distilled and the initial and end fractions rejected. The melting point of the product was 40.8° (uncorrected). This value compares well with the best recent determinations:— 40.92° (corr.) by Hill and Malisoff[1]; 40.85° by Leroux;[2] and 40.8° by Hulett,[3] Rhodes and Markley,[4] and Ferguson.[5]

(ii) Thymol. After crystallisation from acetic acid and drying in a vacuum over caustic soda, the melting point obtained was 50.0°.

The Binary Systems

(1) Phenol-Water. A short discussion of the equilibrium phenomena in this system has been given by one of the authors;[6] the data of importance to the present work are as follows:—m.p. of phenol, 40.8°; critical solution temperature (36.5 per cent. phenol), 65.3°.

(2) Phenol-Thymol. The system has been examined by Paternò and Ampola.[7] It was not re-investigated as the results in the above paper show the presence of a simple eutectic at 7.5° and 51.8 per cent. phenol, and we are not primarily concerned here with solid-liquid equilibria.

(3) Thymol-Water. The solubility of thymol in water is given by Seidell,[8] from 10° to 40° as varying from 0.067 to 0.141 grams per 100 grams solution. As the system does not appear to have been more extensively examined, we determined the complete equilibria, partly by thermal analysis and partly (for co-existing liquids) by the synthetic method in which the critical saturation temperatures are observed for a number of mixtures in

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[1] J. Am. Chem. Soc., **48**, 918 (1926).

[2] Compt. rend., **163**, 361 (1916).

[3] Z. physik. Chem., **28**, 663 (1899).

[4] J. Phys. Chem., **25**, 527 (1921).

[5] J. Phys. Chem., **31**, 757 (1927).

[6] Bailey: J. Chem. Soc., **127**, 1951 (1925).

[7] Gazz., **27**, 481 (1897).

[8] Am. Chem. J., **48**, 453 (1912).

sealed tubes. The results are condensed in Table I and the equilibria illustrated by a curve in Fig. 1; the conditions in the neighbourhood of the melting point of ice cannot be defined on the scale used. The temperatures recorded for the liquid-liquid equilibria are not those of the initial appearance of critical opalescence; the temperature of sudden increase in turbidity which accompanies the separation into two phases is definite and reproducible, and gives results in accordance with the quantitative analysis of the separated phases: the beginning of critical opalescence takes place at a considerably higher temperature in many cases, and although a series of isotherms can be constructed with such data, they do not accurately represent the phase changes (Bailey: l.c.). It was not possible to observe the critical solution temperature for this system as the critical temperature for the vapous-liquid equilibria was reached before complete miscibility was obtained.

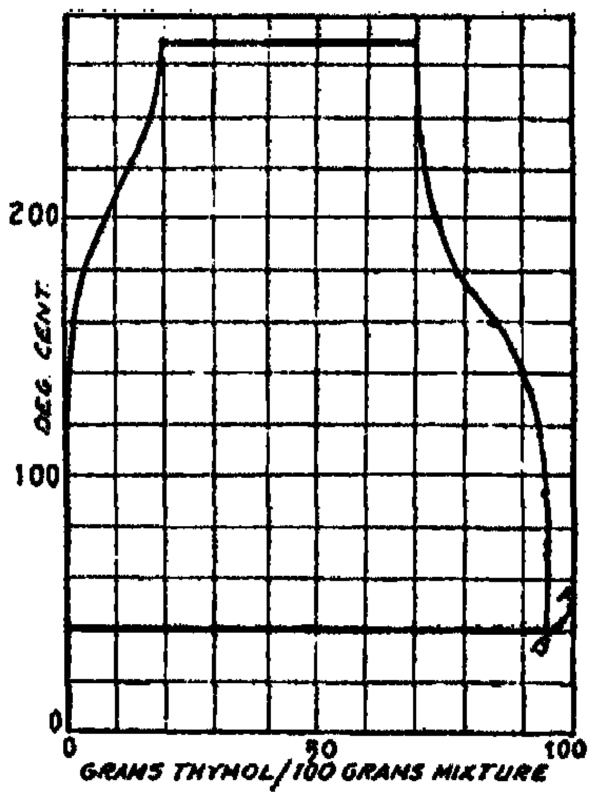

Fig. 1
The Binary System: Thymol-Water.

Table I

Point	% Thymol by weight	Temp.	
A	100.0	50.0°	M.p. of pure thymol
B	95.4	40.0	
C	70.2	270	Critical temperature
C'	20.1	270	
D	0.1	40.0	
E	0.04	−0.05	Eutectic
F	0.0	0.0	M.p. of ice

The form of the curve AB is characteristic in that it is concave upwards, and denotes the imminent formation of two liquid layers,

The Ternary System

Examination was restricted to the liquid-liquid equilibria which were investigated by the synthetic method; standard mixtures of two components were made up and introduced into glass tubes, a known percentage of the third component added, and the tubes sealed. By this means a number of curves for constant relative proportions of the two components were obtained, and in the triangular diagram all such points for any one proportion lie on the straight line joining the opposite vertex to the point of initial composition on the binary axis; it is hence an easy matter to transfer observations made at varying temperatures to the isotherms. Tables II-V give a selection from the available data.

TABLE II

Temp. 250° (corr.)

No.	% Thymol	% Phenol	% Water
1.	71.5	—	28.5
2.	67.3	6.7	26.0
3.	55.0	14.5	30.5
4.	40.0	19.3	40.7
5.	20.1	15.9	64.0
6.	8.9	4.9	86.2
7.	19.0	—	81.0

TABLE III

Temp. 200° (corr.)

No.	% Thymol	% Phenol	% Water
1.	10.0	—	90.0
2.	4.0	4.8	91.2
3.	9.1	18.0	72.9
4.	18.2	26.1	55.7
5.	75.8	8.1	16.1
6.	87.0	1.0	12.0
7.	75.1	—	24.9

TABLE IV

Temp. 65° (corr.)

No.	% Thymol	% Phenol	% Water
1.	0.1	—	99.9
2.	0.1	10.9	89.0
3.	0.1	19.8	80.1
4.	—	32.2	67.8
5.	—	42.0	58.0
6.	0.8	49.2	50.0
7.	0.5	50.2	49.3
8.	3.3	59.2	37.5
9.	6.0	61.0	33.0
10.	18.5	59.5	22.0
11.	47.0	41.0	12.0
12.	55.0	34.5	10.5
13.	73.1	19.4	7.5
14.	93.0	2.4	4.6
15.	94.5	0.5	5.0
16.	95.0	—	5.0

TABLE V

Temp. 15°.

No.	% Thymol	% Phenol	% Water
1.	—	73.1	26.9
2.	1.0	70.0	29.0
3.	2.0	71.0	27.0
4.	9.5	70.2	20.3
5.	80.3	15.9	3.9
6.	94.0	2.3	3.7
7.	95.2	0.6	4.2
8.	95.6	—	4.4

The isotherms are given in Fig. 2, together with the "constant relative proportion lines" from which they are obtained; it will be seen that in order to avoid crowding, certain of the curves have been left uncompleted: this is necessarily the case with temperatures below 65°, as the solubility of thymol in the water-rich mixtures does not rise above 0.1 per cent. It must also be remembered that ternary mixtures containing more than 40.0 per cent. of thymol are generally metastable and would deposit solid thymol if seeded.

The curves obtained are of considerable interest: in that they show markedly the transition from one form of binodal curve to another. We have, for example, at 250° a critical saturation curve which is typical for the addition of a third substance soluble in one only of a pair of partially miscible liquids, the effect of such additions being to raise the saturation temperature; at 120° the curve has changed to a type characteristic of the addition of a substance soluble to a considerable extent in both liquids. Accordingly at high temperatures, phenol reduces the solubility of thymol in water, but at low temperatures increases it. 65° is just below the critical solubility temperature for phenol-water and another set of phenomena make their appearance, resulting in the intersection of two distinct binodal curves, as at 15°. We have again a pronounced change in the solubility relationships of the partially miscible liquids, since at low temperatures thymol increases the solubility of water in phenol through a small range; at higher concentrations or temperatures it reduces it. The heterogeneous field at room temperature is of wide extent, but nevertheless one can elicit from an inspection of the isotherms the striking fact that a mixture of equal parts by weight of water and thymol can be rendered homogeneous by the addition of rather less than twice its own weight of phenol.

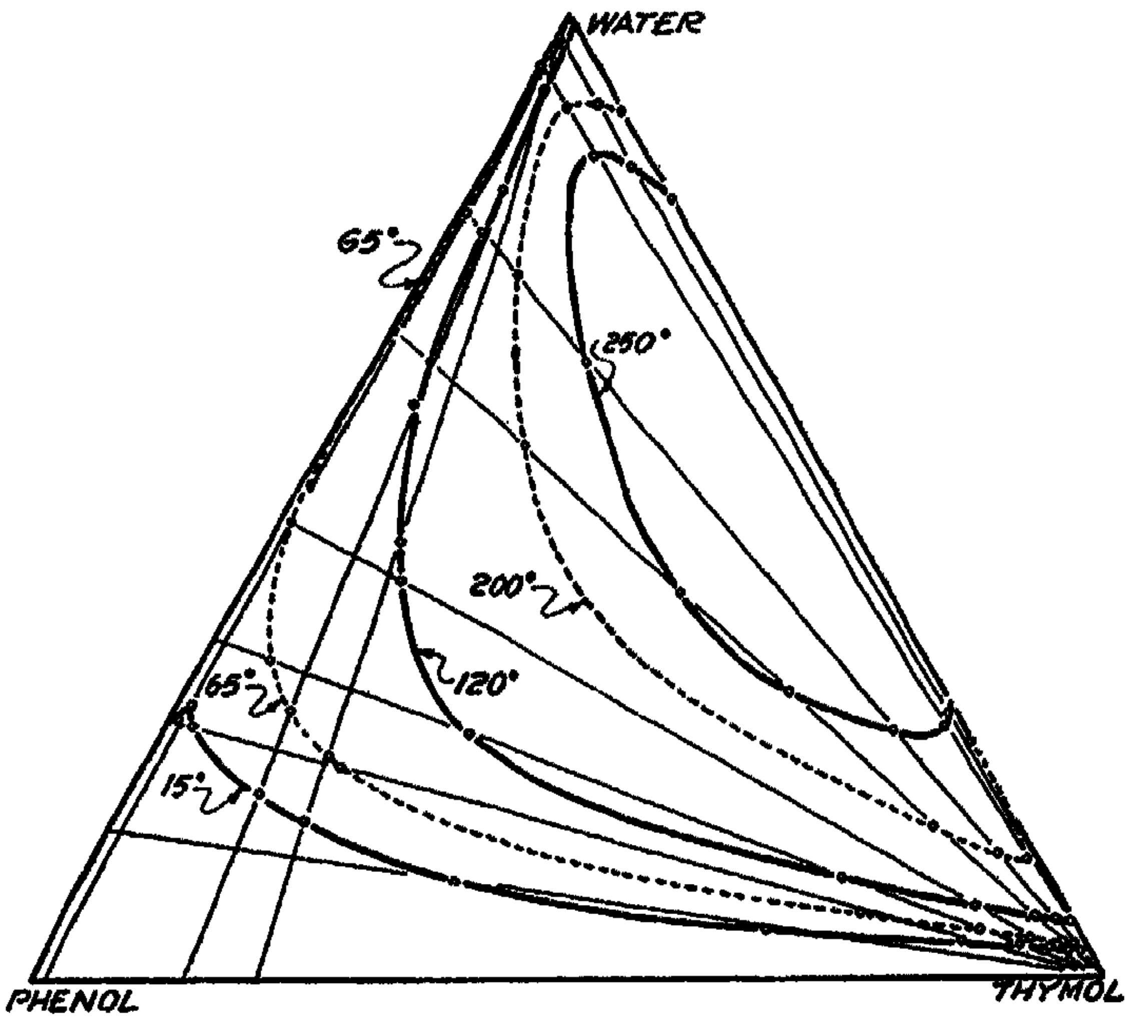

Fig. 2

The authors wish to express their gratitude to the Research Fund Committee of the Chemical Society for a grant which has covered the cost of materials used.

The Sir William Ramsay Laboratories
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University College, London.
December 19, 1928.

THE AQUEOUS SOLUTION OF CUPRIC AND FERROUS SULPHATES

BY F. K. CAMERON AND H. D. CROCKFORD

Introduction. According to Etard[1] a brick-red salt crystallizes from an aqueous solution of ferrous sulphate and cupric sulphate, the composition being represented by the formula, $SO_4Cu.SO_4Fe.2H_2O$. At a high enough temperature it loses all its water and becomes violet, though preserving its crystalline form. Neither salt is oxidized by fuming nitric acid, even at ebullition. We have not been able to confirm any of these observations.

Mixed salts of ferric sulphate and cupric sulphate containing also various proportions of sulphuric acid and water have been described often. But there seems to be little information regarding the solids stable in contact with solutions of ferrous sulphate and cupric sulphate. It it commonly stated that they form mixed crystals, as do all the vitriols.

The Materials used were C. P. grades of J. T. Baker Co. chemicals and the regular drug store Nujol.

Methods of Analysis. Our first analyses of copper were by a volumetric method. Our results seemed to be running consistently high, so the method was abandoned and the copper precipitated electrolytically on platinum. The iron in solution was oxidized by heating to boiling with nitric acid, and removed by precipitating with ammonia, filtering, and weighed after heating the residue in a muffle to red heat for several hours. Sulphates were weighed as the barium salt, and chlorine was weighed as the silver salt. It was found desirable to remove iron before determining copper; and it was, of course, necessary to remove all copper before incinerating the iron precipitates. The procedure followed when both bases were present was to heat the solution to boiling, add a little hydrochloric acid, and then somewhat more barium chloride than necessary to insure complete precipitation of sulphates; filter, and wash with a hot solution of hydrochloric acid, and then with hot water; to the filtrate and washings again brought to boiling, a slight excess of sulphuric acid was added, and the excess of barium precipitated was removed by filtration and discarded. The filtrate was then brought to a vigorous boiling, a little nitric acid added, and boiling continued for 5-10 minutes. On cooling somewhat, concentrated ammonia water in excess was added with continuous stirring. The precipitated oxide of iron was washed on a filter alternately with concentrated ammonia solution and hot distilled water, until no trace of copper could be recognized in the washings. The filtrate and washings were evaporated to a small volume, thus getting rid of the excess of ammonia, acidified with sulphuric acid, and the copper precipitated electrolytically. Resolution and reprecipitation guarded against mechanical inclusions.

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[1] Compt. rend., **87**, 602 (1878).

Cupric Sulphate, Sulphuric Acid, and Water. This system was investigated by Bell and Taber[1] at 25°C, their results being quite satisfactorily confirmed later by Foote.[2] As our work was to be at 30°C a part of the isotherm was determined for this temperature and covering the concentrations in which we were interested. The results are assembled in Table I. It appears that cupric sulphate is somewhat more soluble in aqueous solutions of sulphuric acid at 30°C than at 25°C.

TABLE I

Solubility of Cupric Sulphate in Aqueous Solutions of Sulphuric Acid at 30°C

$CuSO_4$ gms. per 100 gms. H_2O	H_2SO_4 gms. per 100 gms. H_2O	$CuSO_4$ gms. per 100 gms. H_2O	H_2SO_4 gms. per 100 gms. H_2O
20.14	7.38	15.57	16.12*
18.62	17.13	9.81	34.93*
16.22	20.65	16.55	14.61**
14.08	27.76	8.63	37.24**
7.82	49.61		

* Calculated from Bell and Taber: loc. cit.
** from Foote: loc. cit.

Sulphuric acid depresses the solubility of cupric sulphate. In contact with solutions of sulphuric acid up to about 49 per cent of sulphuric, the solid stable is the pentahydrate, $CuSO_4.5H_2O$. As concentration of sulphuric acid increases, the trihydrate, the monohydrate, and finally anhydrous cupric sulphate become in turn the solid phase. No evidence has appeared that solid complexes may appear containing sulphuric acid as well as water and cupric sulphate.

Ferrous Sulphate, Sulphuric Acid, and Water. Wirth[3] has studied the solubility of ferrous sulphate in solutions of sulphuric acid at 25°C finding that the solubility of the salt decreases with increase of acid. Up to solutions about 12th normal, the stable solid in contact with the liquids is ferrous sulphate heptahydrate, $FeSO_4.7H_2O$. As the concentration increases, the solid phase is the monohydrate, $FeSO_4.H_2O$. Wirth's results are given in terms of "normality" of the acid and grams ferrous sulphate ($FeSO_4$) per 100 grams of solution, without the data necessary to compute the two solutes on a common basis. Our results obtained at 30°C are assembled in Table II. Within the range of concentration involved the stable solid was ferrous sulphate heptahydrate.

Kenrick[4] has studied the solid phases stable in this system over a wide range of concentrations. He found that the constant solution, or concentration beyond which ferrous sulphate monohydrate is the stable solid, was

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[1] J. Phys. Chem., 12, 175 (1908).
[2] J. Am. Chem. Soc., 37, 290 (1915).
[3] Z. anorg. Chem., 79, 364 (1913).
[4] J. Phys. Chem., 12, 693 (1908).

about 78 grams of sulphuric acid per hundred grams of water. From Kenrick's data it appears that, as concentration of sulphuric acid increases, at about a concentration of 459 grams of sulphuric acid per 100 grams of water, the compound with the formula 2 $FeSO_4.H_2SO_4$ becomes the solid phase, replacing the monohydrate. Above concentration 855 grams sulphuric acid per 100 grams of water, the stable solid has the formula $FeSO_4.H_2SO_4$, and above concentration 1592 grams sulphuric acid per 100 grams of water the stable solid has the formula $FeSO_4.3H_2SO_4$. We have dealt with no such concentrations in the present investigation. But we consider it possible that similar solids have appeared in our work and that it is desirable to call attention at this point to the facts that ferrous sulphate unites with sulphuric acid in the solid phase, under favorable conditions, whereas cupric sulphate appears not to do so under any conditions.

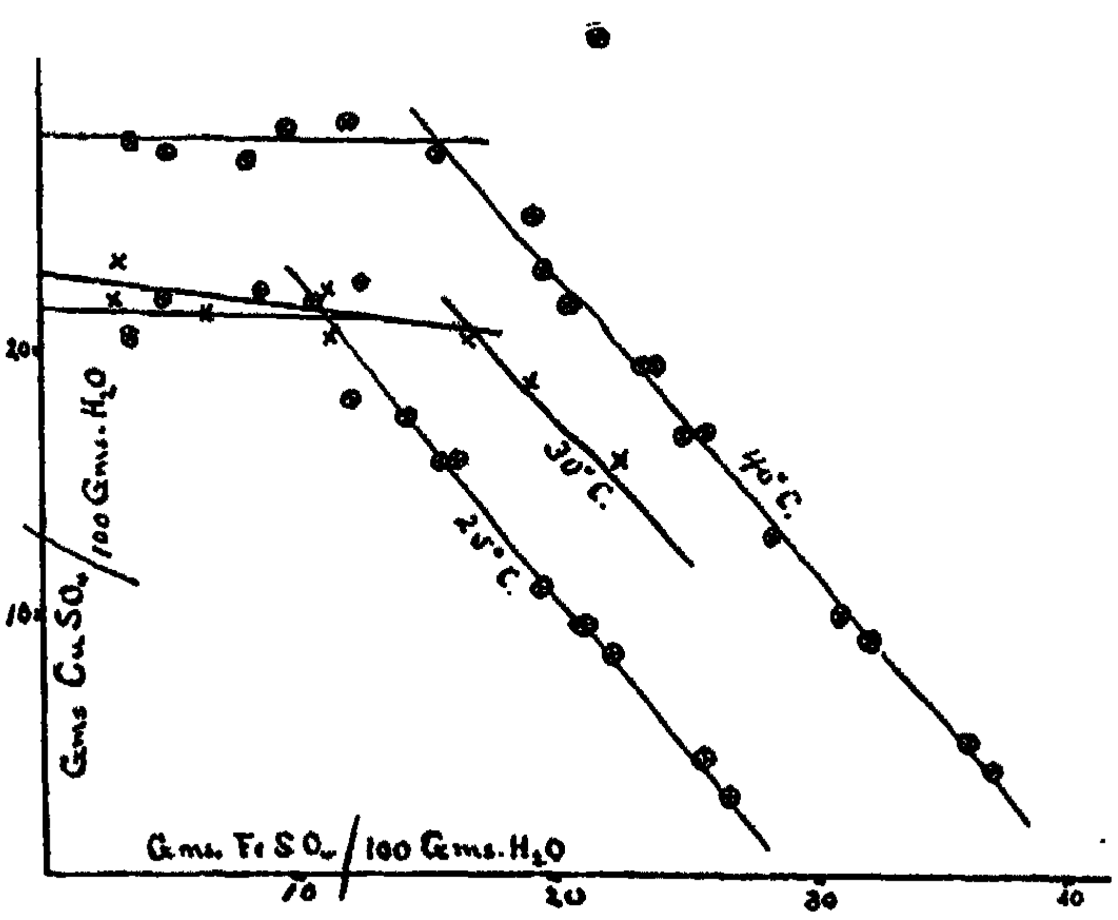

Fig. 1

Solubility isotherms for aqueous solutions of cupric sulphate and ferrous sulphate.

Table II

Solubility of Ferrous Sulphate in Aqueous Solutions of Sulphuric Acid at 30°C

$FeSO_4$ Gms per 100 gms H_2O	H_2SO_4 Gms per 100 gms H_2O	$FeSO_4$ Gms per 100 gms H_2O	H_2SO_4 Gms per 100 gms H_2O
16.89	14.99	19.30	41.85
17.53	19.96	17.43	19.50
18.08	25.20	18.65	31.29
18.56	32.60	17.79	25.57

TABLE III

Mutual Solubilities of Cupric Sulphate and Ferrous Sulphate in Water. Stated in grams dissolved salt per 100 grams water.

25°C*		30°C		40°C*	
$CuSO_4$	$FeSO_4$	$CuSO_4$	$FeSO_4$	$CuSO_4$	$FeSO_4$
21.59	3.44	23.53	3.13	28.07	3.47
22.12	4.94	22.49	11.51	27.70	5.11
22.37	8.93	20.54	17.16	27.39	8.43
22.00	10.96	18.95	19.61	27.75	16.14
22.61	13.08	16.02	22.75	31.68	22.14
18.37	13.55	21.98	3.29	23.41	20.06
17.61	14.64	21.56	6.86	21.92	20.94
15.79	16.67	20.67	11.82	19.73	23.51
15.76	16.04			19.75	23.89
11.18	19.82			17.07	25.83
9.61	21.33			16.89	25.07
8.48	22.28			12.83	28.68
4.33	25.78			10.30	31.46
3.03	26.61			9.12	32.48
				4.81	36.19
				3.71	37.09
				28.57	10.11
				28.78	12.47
				25.16	19.65

* Calculated from data by Agde and Barkholt: loc. cit.

Cupric Sulphate, Ferrous Sulphate, and Water. Agde and Barkholt[1] by studying the change in composition on the cooling of numerous mixtures of cupric sulphate, ferrous sulphate, and water obtained data from which to chart several isotherms for this system. We have recalculated their data for 25°C and 40°C and assembled them in Table III and Fig. 1. At lower concentrations with respect to ferrous sulphate, the stable solid phase is copper sulphate pentahydrate, $CuSO_4.5H_2O$, while the liquid solutions of higher concentration are in equilibrium with members of a series of solid solutions. The limiting member of this series of solutions, at the transition point, probably has the composition, $3CuSO_4.7H_2O.2FeSO_4.7H_2O$. Hydrolysis of the salts had little effect. As long as cupric sulphate pentahydrate alone is in contact with the solutions, increase in content of ferrous sulphate has little effect. It is noteworthy that they attained equilibrium conditions involving the formation of a solid solution so very quickly.

Our experience has not been so happy in attempting to realize this system as one of three components. Stock solutions were prepared by warming an excess of cupric sulphate crystals and cupric oxide in distilled water; and ferrous sulphate crystals with cleaned wire nails and water. From these a series of solutions were prepared, solid cupric sulphate in excess being added

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[1] Z. angew. Chem., 39, 851 (1926).

to the solutions of ferrous sulphate, and an excess of solid ferrous sulphate to the solutions of cupric sulphate. Each member of the series was "seeded" with a few crystals of a solid solution. Prevention of oxidation by air was attempted by superimposing a heavy layer of Nujol. This device was but moderately successful, as, in time, some solid ferric hydrate always appeared. Analysis of five of these solutions in which there showed not more than appreciable amounts of ferric iron are here given. The solutions had been kept in a thermostat at 30°C for 11 days, meanwhile being shaken vigorously at frequent intervals. Examination of the solid phases, carefully dried by pressing between filter papers, was disconcerting. No distinctions in crystal form were observable, even with a hand magnifying glass. But there was a marked gradation in color from blue through the intermediate shades to a strong green. Generally crystals of a quite different color and composition could be picked from the mass corresponding to one and the same solution. The analyses of these samples always showed a discrepancy between the sulphuric acid content as calculated from the metals found, and that actually found. A few typical cases are given in Table IV.

TABLE IV

Composition of Precipitates in contact with Aqueous Solutions of Cupric Sulphate, Ferrous Sulphate, and Hydrogen Sulphate

Color	$CuSO_4$ per cent	$FeSO_4$ per cent	H_2SO_4 per cent	H_2O per cent
Blue	20.64	35.50	− 1.33	45.21
"	22.42	37.04	− .56	41.10
"	20.42	21.33	24.60	33.60
Green	27.64	16.70	20.62	35.03
"	25.81	31.49	9.67	33.02

Three dilute solutions of ferrous sulphate were prepared, and cupric sulphate added in excess. No Nujol was added, but the air was removed by displacement with carbon dioxide. At the expiration of six days the solutions were analyzed and the accompanying solid phases, dried between filter papers, proved to be cupric sulphate pentahydrate containing no detectable amounts of iron. These flasks were then seeded, each with a few crystals of a solid solution. At the end of another period of five days, each flask contained more or less ferric hydroxide and some green crystals as well as blue crystals of cupric sulphate pentahydrate. The green crystals contained both iron and copper. Their color was decidedly different from the bluish color of the seed crystals.

Apparently, with extraordinary care or by good luck, a three-component system containing cupric sulphate, ferrous sulphate, and water can be realized. Ordinarily, however, one deals with a four-component system, and more commonly where hydrogen sulphate may be considered most conveniently as the fourth component.

Cupric Sulphate, Ferrous Sulphate, Sulphuric Acid, and *Water.* A series of solutions was prepared, a part by adding an excess of solid ferrous sulphate to solutions of cupric sulphate, and a part by adding solid cupric sulphate to solutions of ferrous sulphate. To each solution in the series was added the same excess of sulphuric acid. The containers were quite filled and tightly stoppered. Under these conditions there was practically no oxidation of the iron. After being in the thermostat for about three weeks, at a temperature of 30°C, with intermittent but frequent shaking, samples of the solutions approximately of 4.5 grams each, were analyzed, the results being assembled in Table V. The solids in contact with five of these solutions were carefully separated by filtration on a Buchner funnel, quickly dried between heavy filter papers, pulverized and quartered for a subsample for analysis. In each case the whole solid phase was carefully inspected with a hand glass before pulverizing. But while it appeared that characteristic crystals of cupric sulphate pentahydrate were present in each case, it also proved hopeless to separate them mechanically from the remaining crystals. The analysis of the solids are included in Table V.

TABLE V

Composition of Liquid and Solid Phases, at 30°C, in the System of Cupric Sulphate, Ferrous Sulphate, Sulphuric Acid, and Water

	Solution				Solid			
Sample No.	$CuSO_4$ per cent	$FeSO_4$ per cent	H_2SO_4 per cent	H_2O per cent	$CuSO_4$ per cent	$FeSO_4$ per cent	H_2SO_4 per cent	H_2O per cent
1	18.81	3.63	6.21	71.36	34.98	4.63	24.86	35.52
2	16.21	7.17	4.51	72.11	39.38	5.56	18.60	36.56
3	13.99	11.32	4.58	70.01	43.59	7.74	12.58	36.09
4	13.89	10.85	5.49	69.77				
5	13.82	11.24	4.69	70.25				
6	13.67	11.09	5.38	69.86				
7	13.38	11.62	5.06	69.94	26.92	15.24	20.32	37.52
8	13.22	12.09	4.56	70.13				
9	11.09	13.55	5.50	69.86	12.50	18.16	27.04	42.31

Probable Solid Phases:

1 $CuSO_4.5H_2O$ and $FeSO_4:8.31H_2SO_4:28.75H_2O$
2 $CuSO_4.5H_2O$ and $FeSO_4:5.17H_2SO_4:21.75H_2O$
3 $CuSO_4.5H_2O$ and $FeSO_4:2.51H_2SO_4:12.48H_2O$
7 $CuSO_4.5H_2O$ and $FeSO_4:2.06H_2SO_4:12.31H_2O$
9 $CuSO_4.5H_2O$ and $FeSO_4:2.29H_2SO_4:16.36H_2O$

Inspection of the figures in the table shows that the solubility of either salt is depressed by the other and by the sulphuric acid. The solution figures when plotted on the equilateral tetrahedron and projected on the $CuSO_4$-$FeSO_4$-H_2SO_4 triangle fall on or very close to a smooth curve.

In this system of at least four components there must have been two solid phases present, since there was but one liquid and vapor, in each of the containers. It seems most reasonable to assume, although not definitely proven, that one of the solid phases in each case is cupric sulphate pentahydrate,

$CuSO_4.5H_2O$. This assumption made, the composition of the other was computed for each case and the results assembled under Table V. Since there is apparently a continuous and progressive variation in the composition of the solid phase, with the progressive variation in the composition of the liquid phase, we may conclude that the solid phase containing ferrous sulphate also contains sulphuric acid and water in solid solution. Apparently we are dealing with a series of solid solutions, although the data for the solid in contact with solution No. 9 does not accord too well with the others. Another series of solutions was prepared, but designed to cover a wider variation in the concentrations of the components. In this series, the solid phases were not separated from the supernatant liquid by filtration. Hydrochloric acid, about one per cent or a little more, was added to each solution as a "tell tale." After standing at room temperature for about three weeks, being shaken vigorously several times a day, the samples were then immersed in the constant temperature bath for 22 days. Samples of the solutions of about approximately 6.5 grams weight each were withdrawn for analysis. Residues of solid and mother liquor were also taken for analysis at the same time, these residues varying in mass from slightly less than two grams, to over five grams. The samples were each dissolved and made up to 500 cc volume, and analysis made on aliquots. Considerable difficulty was met in making the chlorine determinations. The "chlorine ratio" for liquid and residue was considered sufficiently reliable to be used in but five out of the nine cases. The final computations are assembled in Table VI.

TABLE VI

Composition of Liquid and Solid Phases, at 30°C, in Systems of Cupric Sulphate, Ferrous Sulphate, Sulphuric Acid, and Water

	Solutions				Solids			
Sample No.	$CuSO_4$ per cent	$FeSO_4$ per cent	H_2SO_4 per cent	H_2O per cent	$CuSO_4$ per cent	$FeSO_4$ per cent	H_2SO_4 per cent	H_2O per cent
1	16.05	2.09	5.71	76.14	25.18	3.68	32.51	38.62
2	15.40	3.58	6.16	74.86				
3	13.93	5.39	7.62	73.05				
4	11.80	11.22	9.81	67.16	48.53	7.79	9.60	34.08
5	11.63	11.01	8.56	68.79				
6	9.17	9.68	9.46	71.68	24.06	18.56	21.53	35.84
7	5.86	10.40	11.35	72.40	19.36	22.41	22.23	36.00
8	3.44	11.33	11.13	74.10				
9	1.91	12.41	12.49	73.17	4.01	33.73	21.80	40.45

Probable Solid Phases:

1 $CuSo_4.5H_2O$ and $FeSO_4:13.69H_2SO_4:55.98H_2O$
4 $CuSO_4.5H_2O$ and $FeSO_4:1.90H_2SO_4:7.26H_2O$
6 $CuSO_4.5H_2O$ and $FeSO_4:1.80H_2SO_4:10.12H_2O$
7 $CuSO_4.5H_2O$ and $FeSO_4:1.54H_2SO_4:9.44H_2O$
9 $CuSO_4.5H_2O$ and $FeSO_4:0.99H_2SO_4:9.5H_2O$

These figures suggest the same conclusions as do those in Table V. They are charted in Fig. 2. It will be observed that the data for solution No. 4 falls far from the smooth curve indicated by the data for the other solutions. Whether equilibrium had not been reached in this solution or the analytical work was faulty in determining the excess of acid to be added, it gives an adequate reason for suspecting the correctness of the composition found for the solid solution in contact with this solution. There seems to be no reasonable escape from the conclusion that the solid phases in this system are the pentahydrate of cupric sulphate and one of the members of a series of solid solutions containing ferrous sulphate, sulphuric acid, and water.

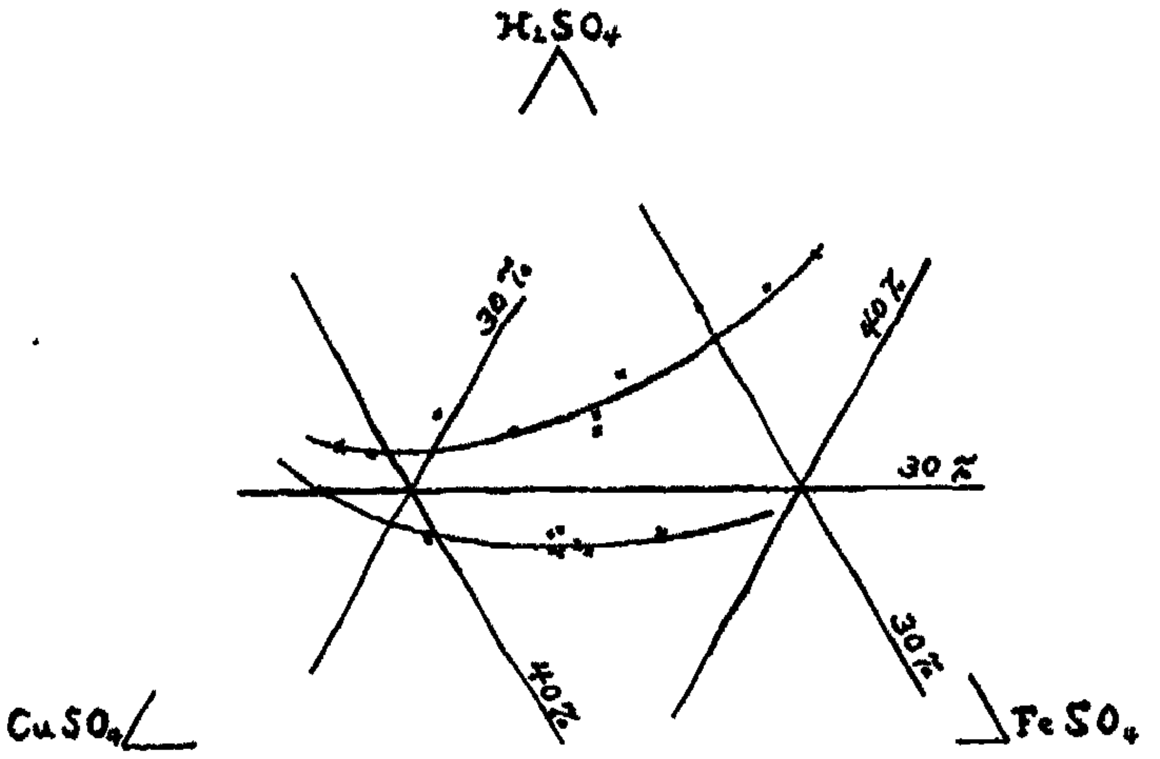

FIG. 2
Solubility at 30° of cupric sulphate and ferrous sulphate in aqueous solutions of sulphuric acid.

Summary. It has been shown that, at 30°C:

1. The solubility of cupric sulphate in water is depressed by sulphuric acid.

2. The solubility of ferrous sulphate in water is depressed by sulphuric acid.

3. Cupric sulphate and ferrous sulphate mutually depress one another's solubility in water. The presence of sulphuric acid augments the depression. Two isotherms have been charted.

4. A satisfactory explanation of the two solid phases in contact with an aqueous solution of cupric sulphate, ferrous sulphate, and sulphuric acid, is that one phase is cupric sulphate pentahydrate, $CuSO_4.5H_2O$, and the other a solid solution of ferrous sulphate, sulphuric acid, and water.

Department of Chemistry,
University of North Carolina.

OXIDATION OF HALOGEN ACIDS BY SULPHURIC ACID*

BY KSENIA PROSKOUHIAKOFF

The manuals of organic preparations insist on the addition of water when making ethyl bromide. Gattermann[1] says: To2 oo grammes (110 c.c.) of concentrated sulphuric acid contained in a round litre-flask, add quickly with constant shaking, without cooling, 90 grammes of alcohol (about 95%). After cooling the mixture to the room temperature, add carefully 75 grammes of ice-water, the cooling to be continued, and then 100 grammes of finely pulverised potassium bromide."

W. A. Noyes[2] says: "Put 100 cc. of concentrated sulphuric acid in a flask, add slowly with constant shaking, but within two or three minutes, 100 cc. of alcohol. Cool thoroughly and pour the mixture into a 400 cc. distilling bulb or flask containing 70 grams of potassium bromide, and 70 cc. of water."

From the mass law relations we know that, other things being equal, there will be less ethyl bromide formed from given amounts of ethyl alcohol and hydrobromic acid the more water is present. The reason for adding water is not obvious and is not given in either of the two books just cited. A run without the addition of water shows that hot sulphuric acid oxidizes hydrobromic acid to bromine when the acid is too concentrated.

It seems desirable to get some idea of the relations between temperature and pressure for visible oxidation. Since iodides are less stable than bromides, the first experiments were made with potassium iodide. A constant volume of 100 cc of a known sulphuric acid solution was placed in a small Erlenmeyer flask and heated to the desired temperature, when two small crystals of potassium iodide were dropped in. The flask was shaken lightly over a white asbestos board, which facilitated the recognition of the iodine color. If no iodine color was visible, the experiment was repeated at about 20° higher; or at about 20° lower if the color of iodine could be recognized. It was soon found that, because of the delay in the appearance of the color, the test had to be made after a definite time interval and thirty seconds was chosen arbitrarily as the standard time.

By repeating the tests at temperatures half-way between those at which free iodine was present and those at which it was absent, it was possible to obtain minimum temperatures for oxidation which are consistent and which are probably accurate to ±3°. The curve begins with 25% sulphuric acid which oxidized the hydriodic acid only at 100° and higher, and was extended to 50% acid which reacts at a little above room temperature. The data for hydriodic acid and similar data for hydrobromic acid are given in Table I and are plotted in Fig. 1.

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* This work was done as part of the senior thesis under Professor Bancroft.

[1] "The Practical Methods of Organic Chemistry," 131 (1918).

[2] "Organic Chemistry for the Laboratory," 109 (1897).

TABLE I

Oxidation of Hydriodic and Hydrobromic Acids

Hydriodic Acid		Hydrobromic Acid	
% H_2SO_4	Temp.	% H_2SO_4	Temp.
25	100°	60	169°
30	60	70	100
35	50	80	46
40	45	90	35
50	36		

Since mercuric sulphate is an efficient catalyst in the oxidation of naphthalene by sulphuric acid, it was thought desirable to see whether mercuric sulphate would lower the temperature of oxidation of hydriodic acid. Experiments similar to those already described were made with potassium iodide crystals and 100 cc 30% sulphuric acid to which there had been added about 0.045 g mercuric sulphate. No liberation of iodine could be detected at 60°. In some cases a red precipitate was formed which looked like mercuric iodide. In order to make sure that iodine did not form a colorless compound in such a solution under these experimental conditions, a crystal of iodine was dropped into a solution of 30% acid and mercuric sulphate. No reaction was apparent. This is strong presumptive evidence that no iodine is formed and that the hydriodic acid is converted into mercuric iodide.

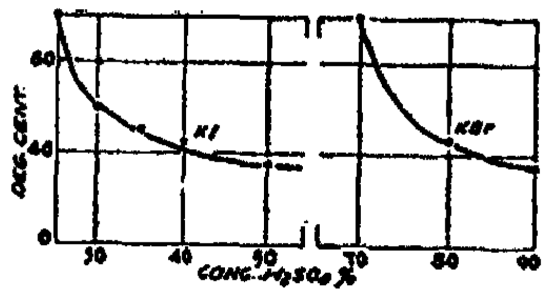

FIG. 1
Oxidation Curves

It was decided to determine the composition of the precipitate, and there were therefore added amounts of potassium iodide slightly greater than that necessary to convert the mercuric sulphate into mercuric iodide. The results were unsatisfactory because the turbid precipitate made it difficult to tell definitely whether there was free iodine present or not. Similar tests were made, adding the potassium iodide very slowly; but the color of iodine was not apparent until so much iodide had been added that the precipitate dissolved. The amount added was considerably more than was theoretically necessary either for mercuric iodide or for H_2HgI_4.

Finally, a somewhat larger amount of powdered mercuric sulphate was taken and a little more than enough potassium iodide to form mercuric iodide. This was kept for a few minutes at 62° and was then permitted to stand (covered) over night at room temperature. After the precipitate had settled, the color of iodine was clearly visible in the supernatant solution. A confirmatory starch test gave the characteristic blue color.

The general results of this paper are:

1. With 100 cc H_2SO_4 and two crystals of potassium iodide, iodine can be detected in thirty seconds at 100°, 60°, 50°, 45°, and 36° with 25%, 30%, 35%,

40%, and 50% sulphuric acid respectively. With hydrobromic acid the corresponding oxidation temperatures are 169°, 110°, 46°, and 36° with 60%, 79%, 80%, and 90% sulphuric acid respectively.

2. The difference in the ease of oxidation of hydriodic acid and hydrobromic acid is shown by the fact that at 100° a 25% H_2SO_4 will oxidize hydriodic acid, while a 70% H_2SO_4 is necessary to oxidize hydrobromic acid.

3. Mercuric sulphate does not act as a catalyst for the oxidation of hydriodic acid between 36° and 100°. Mercuric sulphate reacts with the hydriodic acid to form insoluble mercuric iodide before the sulphuric acid can oxidize the hydriodic acid to iodine. The rate of oxidation must therefore be the slower of the two reactions.

Cornell University.

A CONTRIBUTION TO OUR KNOWLEDGE OF DISINFECTANT ACTION. III

Unsaturated Compounds as Germicides

2534

BY HENRY DOUGLAS CHEESEWORTH AND E. ASHLEY COOPER

The object of this investigation has been to obtain further knowledge concerning the relationship between chemical constitution and germicidal power by means of a comparative study of the toxic action of unsaturated and saturated compounds upon micro-organisms, e.g. bacteria and protozoa.

Bactericidal power has been measured in this investigation by two methods.

(I) the Chick-Martin[1] method, by which disinfectant action is measured over comparatively short periods, e.g. 30 minutes.

(II) the inhibitory method,[2] which measures the capacity of a substance to restrain bacterial growth over a longer period of 48 hours.

By these methods the activity of the following groups of compounds has been studied:

(I) aliphatic unsaturated compounds and related saturated derivatives.

(II) the phenols, and cyclohexanols.

The results are described in Section I of this paper. Section II deals with the physico-chemical aspect of the subject.

I. Germicidal Action

The germicidal efficacy of representative compounds is expressed in terms of bactericidal concentrations in Tables I-IV.

TABLE I

Action of Disinfectants upon B. Coli communis
(by the method of Chick and Martin)

C = minimum concentration killing B. Coli in 30 mins. at 20°C

Disinfectant	C	Disinfectant	C
Phenol	1 : 130	Tri-chlor-ethylene in 25% alcohol	>1 : 700
Cyclohexanol	1 : 32	Butyric acid	1 : 85
p-Cresol	1 : 325	Crotonic acid	1 : 87
p-Methyl Cyclohexanol	1 : 127	Succinic acid	1 : 55
o-Methyl Cyclohexanol	1 : 117	Maleic acid	1 : 550
m-Methyl Cyclohexanol	1 : 110	Fumaric acid	<1 : 800
Benzyl alcohol	1 : 65		
Tetra-chlor-ethane in 25% alcohol	1 : 900		

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[1] Chick and Martin: J. Hygiene, **8**, 654 (1908).

[2] Cooper and Forstner: Biochem. J., **18**, 941 (1924).

TABLE II

Minimum Concentrations inhibiting B. Coli at 37°C
C = minimum inhibiting concentration

Disinfectant	C	Disinfectant	C
Phenol	1 : 575	Propyl alcohol	1 : 70
Cyclohexanol	1 : 250	Allylamine	1 : 650
m-Cresol	1 : 1170	Propylamine	1 : 5000
m-Methyl-Cyclohexanol	1 : 525	Butyric acid	1 : 475
Benzyl alcohol	1 : 250	Crotonic acid	1 : 1100
Allyl alcohol	1 : 85	p-Chlor-phenol	1 : 4000

TABLE III

Action of Disinfectants upon B. Fluorescens non Liquifaciens

Disinfectant	Method	Germicidal Concentrations
Phenol	Inhibitory	1 : 1100
	Chick-Martin	1 : 190
Cyclohexanol	Chick-Martin	1 : 95
Benzyl alcohol	Chick-Martin	1 : 75
Propyl alcohol	Inhibitory	>1 : 80
Allyl alcohol	Inhibitory	1 : 95
Allylamine	Inhibitory	1 : 1000
Propylamine	Inhibitory	1 : 8000

TABLE IV

Comparison of the germicidal action of phenol, cyclohexanol, and other substances under various conditions

(a) with B. Coli (Chick-Martin method)

	Temp.	Period of disinfection	Germicidal strength	Phenol Ratio
Phenol	20°C	½ hour	1 : 130	.25
Cyclohexanol			1 : 32	
Phenol	20°C	2 hours	1 : 135	.45
Cyclohexanol			1 : 61	
Phenol	37°C	½ hour	1 : 220	.37
Cyclohexanol			1 : 82	

(b) B. Fluorescens non Liquifaciens and B. Proteus Vulgaris.
(Chick-Martin method).

	B. Fluor. non Liq.	Phenol Ratio	B. Prot. Vulg.	Phenol Ratio
Phenol	1 : 190	.5	1 : 166	.3
Cyclohexanol	1 : 95		1 : 55	

(c) Inhibitory Method at 20°C and 37°C B. Coli

	Inhibition at 37°C	Inhibition at 20°C
Phenol	1 : 575	1 : 750
Cyclohexanol	1 : 250	1 : 215
m-Cresol	1 : 1170	1 : 1250
m-Methyl Cyclohexanol	1 : 525	1 : 475
Benzyl alcohol	1 : 250	1 : 280
Crotonic acid	1 : 1100	1 : 750
Butyric acid	1 : 475	1 : 525

A survey of the results indicates that allyl alcohol is more active than the corresponding saturated propyl alcohol, crotonic acid more active than butyric acid, and maleic and fumaric acids are superior to succinic acid in bactericidal power. The phenols are also more efficacious than the cyclohexanols. The superiority of the phenols over the cyclohexanols in germicidal power has been previously noted by Cooper and Mason,[1] and by Schaeffer and Tilley.[2] The additional data furnished in the present paper show that the phenols are from two to four times more effective as germicides than the corresponding cyclohexanols according to the test-organism and experimental conditions employed. This serious collapse in germicidal power as a result of the hydrogenation of the benzene nucleus is remarkable, in view of the fact that benzene and its derivatives are not regarded as typical unsaturated substances.

There are, furthermore, exceptions to the rule that unsaturated compounds are stronger disinfectants than the saturated analogues. Thus, allylamine is very much less effective than propylamine; but this may be accounted for by the fact that the unsaturated amine is the weaker base. Trichlorethylene is less germicidal than tetrachlorethane, so that it would seem that the additional chlorine atom more than counterbalances the effect of the loss in unsaturated character. Benzyl alcohol is an unexpectedly weak disinfectant, having only one-fifth the efficacy of the isomeric cresols. The former is also less active than the methyl-cyclohexanols. This indicates that the attachment of the hydroxyl group to the side-chain is even more unfavourable to germicidal power than hydrogenation of the aromatic nucleus.

Protozoa:

The work was now extended to the animal kingdom: the minimum lethal concentration of the fore-mentioned compounds was determined for paramoecium. It is a ciliated organism of sufficient size to be distinctly visible under a low-power microscope, and this portion of the work was therefore performed microscopically.

The organism was grown in hay infusion and subcultured to a fresh medium every month, by the transference of a few c.c. of the liquid and a

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[1] Cooper and Mason: J. Hygiene, 26, 118 (1927).

[2] Schaeffer and Tilley: J. Bact., 14, 259 (1927).

little of the solid grass. It was not necessary to sterilise either media or apparatus in this work, since the appearance and size of the paramoecium renders it easily distinguishable from all other organisms present.

The technique of the method is as follows:—The tests were performed at room temperature; the standard time of disinfection was two minutes. One drop of the culture, from a standard dropping pipette, was placed on a microscope slide. At least twenty to thirty organisms should be present to obtain consistent results, since the individual resistance of different organisms varies somewhat. To the drop of the culture was added one drop of the disinfectant solution, and the slide gently sloped backwards and forwards for one minute to ensure complete mixing. It was then examined under the microscope for a further minute. This procedure was repeated with various concentrations of the disinfectant until the limiting concentration was reached, at which the organisms were killed just within the standard time. The concentration of the disinfectant when mixed with the drop of culture is of course already half the strength of the solution that was prepared.

The results (Table V) show the same general relation between saturated and unsaturated compounds, already described in the bacteriological work, Allylamine, however, is more toxic to protozoa than propylamine, the converse having been observed in the case of bacteria.

Table V

Minimum Concentrations killing paramoecium in 2 minutes

C = minimum killing concentrations

Phenols and Alcohols	C	Acids and Bases	C
Phenol	1 : 800	Fumaric acid	1 : 4500
Cyclohexanol	1 : 200	Maleic acid	1 : 2400
o-Cresol	1 : 1000	Itaconic acid	1 : 2200
o-Methyl Cyclohexanol	1 : 285	Citraconic acid	1 : 1400
Benzyl alcohol	1 : 250	Mesaconic acid	1 : 4700
Propyl alcohol	1 : 15	Crotonic acid	1 : 2400
Allyl alcohol	1 : 30	Butyric acid	1 : 1600
Resorcinol	1 : 300	Allylamine	1 : 2500
p-Chlorphenol	1 : 3000	Propylamine	1 : 1500

Fumaric acid proved to have a greater toxic effect than maleic acid on both protozoa, and bacteria, although the *cis* acid is the stronger acid. Similar results were obtained with the corresponding homologues, mesaconic and citraconic acids. As regards toxicity to the lowest forms of life, configuration may thus be of more significance than ionisation.

II. Action of Certain Compounds on Proteins and Lipins

The factors governing the disinfectant action of a compound are numerous and complex. Permeability through a membrane (the cell wall), the power of coagulating the cell-proteins, and the partition coefficient between water and protein are all concerned. According to Lepeschkin,[1] the severing of the combination of the protein and lipin constituents of the protoplasm into its components, constitutes the death of the cell. Experiments have therefore been devised, employing certain of the foregoing compounds, for the purpose of explaining their germicidal action on physicochemical grounds.

Precipitation of Egg Albumin.

The first series of these experiments consisted in measuring the precipitating action of various compounds on egg albumin.

A 10% solution of egg albumin was prepared and to 2 c.c. of this solution 8 c.c. of varying concentrations of the disinfectants were added, and well mixed. The immediate effect was noticed, and the observations were also made after definite intervals of time. The results are set out in Table VI.

TABLE VI

Precipitation of Egg albumin

Concentrations causing precipitation

	Immediately	¼ hr.	½ hr.	1 hr.
Phenol	>.8%	>.8%	>.8%	·7%
Cyclohexanol	>3·3	—	—	>3·3
m-Cresol	·7	·5	·5	<.05
o-Cresol	·7	·5	·3	<.05
o-Methyl Cyclohexanol	>.8	—	>.8	·5
p-Methyl Cyclohexanol	>.8	—	>.8	·5

TABLE VII

Precipitation of .54% Lecitho Vitellin

Concentrations causing precipitation

	Immediate action	¼ hr.	1 hr.
Phenol	1 : 250	1 : 290	1 : 450
Cyclohexanol	1 : 50	—	—
o-Cresol	1 : 420	1 : 750	1 : 750
m-Cresol	1 : 420	1 : 600	—
p-Cresol	1 : 420	1 : 600	1 : 600
Benzyl alcohol	>1 : 62	1 : 66	1 : 78
Resorcinol	1 : 150	1 : 280	1 : 500
Quinol	1 : 90	1 : 270	1 : 330
p-Chlor phenol	1 : 670	—	—
Picric acid	1 : 50	1 : 10,000	—
Propyl alcohol	>1 : 12.5	—	1 : 16
Allyl alcohol	1 : 125	1 : 650	1 : 650

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[1] Lepeschkin: Biochem. Z., 171, 126 (1926).

The results show a certain degree of correspondence with the differences already observed in the case of bactericidal power. Thus, the cresols are more powerful than phenol as disinfectants, and are also more efficacious protein precipitants. The cyclohexanols, on the other hand, are inert germicides and are at the same time observed to be weak precipitants. A preliminary experiment also shewed that allyl alcohol is superior to the saturated propyl alcohol in precipitating action, but this is considered in greater detail in the next series of experiments.

TABLE VIII

Phenomena exhibited in the precipitation of .54% Lecitho Vitellin by Allyl alcohol solutions

— indicates no precipitate

\+ indicates precipitate.

Concentrations of Allyl alcohol	Precipitates observed			Precipitates observed			
	immediately	½ hr.	1 hr.	immediately	½ hr.	1 hr.	
1 : 71	—	—	—	—	—	+	very slight precipitates
1 : 83	—	—	—	—	—	+	
1 : 100	+	+	+	+	+	+	very thick precipitate which has settled.
1 : 150	—	+	+	—	+	+	precipitates which remain in suspension for several hours.
1 : 200	—	+	+	—	+	+	
1 : 250	—	+	+	—	+	+	
1 : 330	—	+	+	—	+	+	very thick precipitates which have settled within the first ¾ hour.
1 : 500	—	—	+	—	+	+	
1 : 750	—	—	—	—	—	+	
1 : 800	—	—	—	—	—	—	no sign of precipitate after 2 hrs. standing
1 : 1000	—	—	—	—	—	—	

On further standing, there are also concentration-zones at which the precipitate remains suspended and does not settle out as a coagulum. These zones are indicated in detail in Table VIII.

Precipitation of lecitho-vitellin.

Lecitho-vitellin was prepared from egg-yolk by extraction with 10% sodium chloride solution. The extract was freed from coloring matter by treatment with ether, and the lecitho-vitellin purified by precipitation through dilution with excess of water, in which the substance is insoluble. A solution in 10% sodium chloride was used, and the precipitation tests were carried out as in the foregoing case of albumin. The results are given in Table VII. Control experiments shewed that the lecitho-vitellin was not precipitated through dilution alone under the experimental conditions.

The relative precipitating power of the selected disinfectants is in much the same order as their bactericidal action. Allyl alcohol is more effective than propyl alcohol; phenol exceeds cyclohexanol; and benzyl alcohol is less active than the isomeric cresols.

On long standing, allyl alcohol, however, shows unexpected precipitating power, being even more active than the phenols, although it has never been observed to attain the bactericidal strength of the latter. Allyl alcohol, furthermore, behaves altogether anomalously, insomuch as, unlike all the other compounds examined, it exhibits zones of precipitating activity. This is demonstrated by the results in Table VIII. Thus, only a concentration of 1% possesses any immediate precipitating action on lecitho-vitellin, stronger and weaker solutions being without effect. After 15 minutes contact, only concentrations below 1% precipitate, the minimum effective concentration being apparently 1 in 650.

Distribution of Allyl Alcohol between Water and Protein Phases

With the object of throwing light on the germicidal and precipitating action of allyl alcohol, and its superiority over propyl alcohol, a study was next instituted of its absorption by proteins and the influence of concentration thereon. Aqueous solutions of allyl alcohol of different strengths were left in contact with weighed amounts of an insoluble protein until equilibrium was reached. The aqueous phase was filtered off, and the residual amount of allyl alcohol therein was found by estimating the quantity in 10 c.c. The method of estimation used was that of bromination,[1] the bromine being liberated by acid from a solution containing potassium bromate and bromide.

The protein employed was coagulated egg albumin. This was prepared by coagulation of a solution of egg albumin by heating on a water bath. It was filtered, pressed, and dried at 100°C until the weight was constant. It was then ground to a fine powder, and 1 gram introduced into each of a number of dry wide-necked bottles. 25 c.c. of allyl alcohol solution were now added to each. Preliminary tests showed that equilibrium was not reached until contact had been maintained for three days. The experiments were conducted at 20°C.

The results (Table IX) shew that over a range of concentration from 2-8% the distribution-ratio tends to be constant and is thus a partition-coefficient,

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[1] Stritar: Monatsheft, 39, 619 (1918).

the allyl alcohol being therefore simply dissolved in the protein without any evidence of either molecular association or chemical combination. The allyl alcohol is approximately 3.7 times as soluble in albumin as in water. Previous experimental work[1] has shewn on the other hand that phenol was 12 times as soluble in albumin as in water. The superiority of phenol over allyl alcohol as a germicide thus appears to be associated with its greater solubility in the protein-constituents of the cell.

TABLE IX

Distribution of allyl alcohol between protein and water

1 gram of protein and 25 c.c. of solution were employed at each concentration.

Initial concentration of allyl alcohol %	Final concentration of allyl alcohol %	Amount taken up by 1 gm. protein	Distribution-ratio*	
8%	7%	·25 gms.	3·6	3·7
6%	5·2 %	·20 "	3·8	
4%	3·44%	·14 "	4·0	
2%	1·76%	·06 "	3·4	

* Amount of allyl alcohol taken up by 1 gm. protein divided by amount in 1 gm. of water.

In conclusion, it is suggested that the bactericidal and protozocidal action of allyl alcohol is not due to a specific chemical interaction with the cell-proteins, (such as an additive reaction through the unsaturated group), but is associated with its physico-chemical (denaturating) action on their colloidal suspensions. This view is supported by the fact that no evidence of a chemical interaction between allyl alcohol and amino-acids in aqueous solution could be obtained.

A similar attempt was made to study the distribution of benzyl-alcohol between water and proteins in order to explain its inferior bactericidal power in comparison with its isomers, the cresols. Difficulties were met with, however, in the estimation in dilute aqueous solution.

Bromination gave results too low, the method tried being similar to that previously described. Attempts were next made with oxidation methods by means of permanganate, none of which, however, could be performed quantitatively. Oxidation with potassium bichromate also was not satisfactory, and this work has been left for the time-being.

Summary

1. Unsaturated compounds in general tend to possess a higher bactericidal and protozocidal action than the corresponding saturated compounds. This is illustrated by the cases of allyl and propyl alcohol, unsaturated and saturated fatty acids, and phenols and cyclohexanols.

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[1] Cooper and Mason: J. Phys. Chem., 32, 868 (1928).

2. Benzyl alcohol is a much weaker germicide than the isomeric cresols and even than the methyl-cyclohexanols. The attachment of the hydroxyl group to a cyclic structure is thus more favourable to high germicidal power than its presence in the side chain.

3. Fumaric acid exerts a nore powerful action both upon bacteria and protozoa than the 'cis' acid, maleic acid, although the latter is the stronger acid. Configuration is thus a more important factor than ionization.

4. In general, unsaturated hydroxy-compounds possess a greater precipitating action on proteins and lecitho-protein, than the corresponding saturated substances. The cresols are also more efficacious than their isomer, benzyl alcohol.

5. By a quantitative study of the action of allyl alcohol on proteins, no evidence has been obtained of any chemical interaction through the unsaturated grouping.

It is suggested, therefore, that the superiority of unsaturated substances as germicides is associated with their greater physico-chemical capacity to induce precipitation or denaturation in colloid suspensions.

A similar explanation is advanced to account for the greater bactericidal activity of the cresols over benzyl alcohol.

Chemical Department.
University of Birmingham.
January 25, 1929.

COPPER OXIDE IN THE BORAX BEAD*

BY WILDER D. BANCROFT AND R. L. NUGENT

Under the oxidizing conditions that have been described[1] for manganese in borax melts, copper gives a beautiful, clear, blue glass. When the proportion of boric oxide in the melt is increased gradually, the blue first changes to a light apple green. With further increase of boric oxide, there is a separation of a reddish solid, which is presumably cuprous oxide. The same phenomenon occurs on changing a copper-borax bead from the oxidizing flame to the reducing flame. The natural assumption is that the change from blue to green is due to a reduction of a cupric compound to a cuprous one. With increase in the relative amount of boric acid, more of the cuprous compound is formed, until red cuprous oxide separates due to its insolubility in melts high in boric oxide.

The first thing to be done in order to verify this assumption was to find a method of determining the ratio of cuprous to cupric compounds in borax glasses. The glasses were dissolved in a solution of ferric sulphate and sulphuric acid. The cuprous compound present in the borax glasses reduces the ferric salt to ferrous salt and this latter can then be determined by titration with permanganate. Since it is not convenient to weigh out ferric sulphate direct, we started with ferrous sulphate and converted it into ferric sulphate. To 150 cc water there were added 50 cc sulphuric acid and 10 g $FeSO_4.7H_2O$. The ferrous sulphate was oxidized to ferric sulphate by means of three percent hydrogen peroxide, the excess of the oxidizing agent being removed by boiling and the resulting solution diluted with an equal volume of water. The final titration was made with 0.025 normal permanganate. A synthetic mixture of 0.0504 g cuprous oxide and 0.0496 g cupric oxide, containing therefore 0.0448 g cuprous copper, showed 0.00447 g cuprous copper by this method of analysis.

When 0.05 g cupric oxide was heated in three grams of borax in the usual manner, analysis showed the presence of 15 percent cuprous copper in the melt. With three grams of a mixture containing 4.6 mol percent sodium oxide—an excess of boric oxide—the percentage of cuprous copper rose to about 21 percent. With an excess of alkali—1.6 mols sodium oxide to 1 mol boric oxide—the percentage of cuprous copper dropped to about 4. This indicates a shift of the cuprous-cupric equilibrium to the cupric side with the increase in alkalinity of the borax glass, which is similar to the behavior of the manganese oxides in borax glasses. These figures for copper have not

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* This work is part of the programme now being carried out at Cornell University under a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] Bancroft and Nugent: J. Phys. Chem., 33, 481 (1929).

been checked as much as we should have liked and the absolute values may need correcting. There is no question, however, about the trend of the equilibrium with alkalinity.

The green of copper glasses is evidently due to a mixture of cuprous and cupric compounds. This confirms and explains the results obtained previously by Sir Herbert Jackson.[1] "If the proportion of cuprous oxide introduced into the glass be about 8 per cent., the whole of it dissolves in the glass at the temperature of 1000°C, at which the glass is made. If the glass be chilled quickly from this temperature, no colour except the almost unavoidable green colour due to the oxidation of part of the copper will be seen; the glass is a nearly colourless transparent one. On reheating this glass it is possible to produce, according to the temperatures to which the glass is raised and the length of time during which it is heated, comparatively large crystals or aggregations of crystals of red cuprous oxide, smaller crystals of the same form, or particles so small as not to be recognized as crystals under the microscope. Along with these are frequently obtained definite crystals of the yellow form, clouds of yellow particles, and if the reheating be gentle, the particles of yellow cuprous oxide are so small as to be irrevealable by the microscope, and what is obtained is a clear yellow transparent glass. Here, then, from two forms of one and the same oxide of copper, we have a range of colours associated with the proportions in which the two forms are mixed in the glass and with the size of their particles. What is the inner nature of the difference between the red and yellow forms, which may account for their difference in colour, is yet to be made out."

There is some evidence that there are not two forms of cuprous oxide; but that the color varies from yellow to red as the particles become coarser.[2] Sir Herbert Jackson implies that the green color is due solely to the cupric salt; but our experiments are conclusive that the green is always due to a mixture of cupric and cuprous salts. Our experiments do not show whether the green is due to a mixture of the blue of the cupric salt with the yellow or the red of the cuprous compound. Probably all possible gradations can be obtained by varying the temperature and time of annealing.

The fact that the green is due to a mixture of cupric and cuprous compounds accounts for another observation by Sir Herbert Jackson. "The colours produced by cupric oxide in glasses and glazes need not be dealt with in detail, as there is much common knowledge about these. One or two points not in common knowledge may, however, be emphasised. In a glass of the same composition, cupric oxide may give a very marked blue colour if the glass is made at a comparatively low temperature (1000° C. to 1100°C.); whereas with the same concentration of copper and the same glass made at a higher temperature, about 1300°C., for example, there is a very marked green shade in the blue. It is worth pointing out that the blue low-temperature glass is green while hot."

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[1] Nature, 120, 264 (1927).

[2] Bancroft: "Applied Colloid Chemistry," 243 (1926).

The higher the temperature the larger will be the proportion of cuprous oxide when the other conditions remain the same, because the tendency of cupric oxide to dissociate increases with rising temperature. We cannot at present explain why the blue low-temperature glass is green while hot; but this is not an isolated phenomenon. We know why the ruby is red and not green;[1] but we cannot explain why the red ruby is green at temperatures above about 300°. It is possible that the change from green to blue on cooling the copper oxide glass is due to oxidation of cuprous oxide at the lower temperatures.

It is not denied that one can get green crystals or solutions of cupric salts. Cupric chloride is a case in point. Sir Herbert Jackson is wrong, however, in saying that copper sulphate with one of water is colorless. When one eliminates the scattered reflection, the salt is green. In unpublished work by Mr. Rogers in the Cornell Laboratory it has been shown that for cupric salts the radical $Cu.3H_2O$ is always blue while the radicals $Cu.2H_2O$ and $Cu.H_2O$ are always green. Nothing analogous to this has yet been discovered in the borax bead and the close parallelism between color and degree of reduction with the oxides of manganese and of copper makes it practically certain that the green color in copper glasses is due to the admixture of a cuprous compound and not to the presence of a green modification of a cupric compound.

Sir Herbert Jackson has done one experiment which parallels our work to some extent, though the results are not so clear cut and there are no analyses. "A small quantity of cupric oxide does not dissolve in fused boric anhydride, but forms a white borate which is dispersed through the fused mass. [He means a colorless borate which makes the mass white.] The addition of an alkali will bring about solution and give a clear blue transparent glassy mass. The most striking example is to take boric anhydride and the alkali lithium oxide in, say, three different proportions, such as one molecule of lithium oxide to one, four, and ten of boric anhydride. With 0.5 percent cupric oxide the first is a fine deep blue; the second is a paler blue; the third is still paler; and if the proportion of alkali oxide be lowered until there is only just sufficient to bring about complete solution of the cupric oxide in the mass, there is but little colour to be seen at all."

The deepening of the blue color for the same amount of cupric oxide with increasing amount of alkali is in agreement with our results. The difference is that there was apparently no green formed with the smaller amounts of alkali and no precipitation of cuprous oxide in the absence of alkali. The concentration of copper oxide in Sir Herbert Jackson's experiments was less than half what it was in our work and there may have been a difference in the rate of cooling. Granger[2] found that increasing the copper oxide content changed the color from blue toward green. If we write the reaction $4CuO = 2Cu_2O + O_2$, it is evident that the glass should be less green the more dilute

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[1] Stillwell: J. Phys. Chem., 30, 1441 (1926).

[2] Compt. rend., 157, 935 (1913).

the solution. We have confirmed this result. Increasing the copper content in a borax bead changed the color from a light blue to a deep green and the bead was full of a yellow substance, presumably cuprous oxide.

The question of the rate of cooling as affecting the color comes up in reference to another matter. "I must not deal further with cupric oxide glasses except to mention that, unlike cuprous oxide glasses, copper glasses, and many other coloured glasses, such as gold glasses, selenium glasses, cadmium sulphide glasses, and opal glasses, cupric oxide glasses cannot be rendered colourless by sudden chilling, nor, indeed, can the tint of these glasses be modified to any noticeable extent in this way. An attempt to explain this difference which seems to divide colouring agents generally into two classes, would involve a very lengthy account of the various phenomena which have been observed, and would, moreover, be to a considerable extent little more than a re-statement of facts which would involve differentiation between the meanings of such terms as 'solution,' 'chemical combination,' and 'dispersion,' and would lead to much argument. I must content myself with this short and incomplete account of the modes of behaviour of copper and its oxides in glasses and glazes."

It would have taken fewer words to have said that we know that one group of colouring agents forms colloidal solutions and that the other group occurs in true solution either as oxides or as compounds.[1] It is helpful to take one step forward whenever possible.

These experiments enable us to understand the general behavior of cupric oxide in various glazes. Speaking broadly, cupric oxide gives a blue in alkaline glazes and green in lead glazes.[2] "With an oxidizing atmosphere, copper in alkaline glazes gives a beautiful azure blue known by the name of turquoise blue. It becomes intense green in boracic or plumbiferous glazes." There is no suggestion of any change in the nature of the oxide. When discussing Egyptian pottery Birch[3] says: "When the object had assumed the intended shape, the glaze was laid on. It was composed of silica—probably a finely ground or triturated sand, and soda, to which were added certain metallic oxides to produce the colour required. For the fine celestial blue, which is still the admiration of all who view it, and scarcely rivalled after thirty centuries of human experience, an oxide of copper was employed. The green glaze, which, in many instances, seems to be the blue changed by the effect of time, is also stated to have been produced by another oxide of the same metal. The red glaze, but rarely seen, is conjectured to be a protoxide of copper; the violet, to be formed by an oxide of manganese [Mn_2O_3], although capable of being produced by [colloidal] gold. Yellow was, perhaps, made with [colloidal] silver; the white glaze with tin, or a white earth. No very recent analysis has, however, been made; and it is to be regretted that we are compelled to acquiesce in the conjectures of archaeologists, rather

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[1] Bancroft: "Applied Colloid Chemistry," 438 (1926).

[2] Bourry: "A Treatise on Ceramic Industries," 249 (1911).

[3] "History of Ancient Pottery," 48 (1873).

than to adopt the tests of chemists. Of these colours the celestial blue [CuO] is the predominant one, the rest being occasional varieties, used for objects made in the Greek and Roman epochs, when foreign ideas and tastes had superseded the genuine national feelings."

In the next chapter, p. 90, Birch says: "The analysis, made in the Museum of Practical Geology, of the colours of the enamel employed in this brick [from Nimrûd], shows that the opaque white was produced with tin, the yellow with antimoniate of lead, the brown with iron, the blue and green with copper. The flux and glazes consisted of silicate of soda aided by lead."

In the Introduction, p. 4, Birch says: "The desire of rendering terra-cotta less porous, and of producing vases capable of retaining liquids, gave rise to the covering of it with a vitreous enamel or glaze. The invention of glass has been hitherto generally attributed to the Phoenicians: but opaque glasses or enamels, as old as the Eighteenth dynasty, and enamelled objects as early as the Fourth, have been found in Egypt. The employment of copper to produce a brilliant blue-colored enamel was very early both in Babylonia and Assyria, but the use of tin for a white enamel, as recently discovered in the enamelled bricks and vases of Babylonia and Assyria, anticipated by many centuries the rediscovery of that process in Europe in the fifteenth century, and shows the early application of metallic oxides."

There are a number of interesting paragraphs in the article[1] on ceramics. "It is surprising to note that some of the very earliest glazes were coloured glasses containing copper or iron (the green, turquoise, and yellow glazes of the ancient Egyptians and Assyrians). Marvellous work was wrought in these few materials, but the era of the finest pottery-colour dawns with the Persian, Syrian, and Egyptian work that preceded the Crusades. By this time the art of glazing pottery with a clear soda-lime glaze had been thoroughly learnt. Vases, tiles, etc., shaped in good plastic clay, were covered with a white, highly siliceous coating fit to receive glazes of this type, and giving the best possible ground for the painted colours then known. With this rudimentary technique the potters of the countries south and east of the Mediterranean produced, between the ninth and the sixteenth centuries of our era, a type of pottery that remains ideal from the point of view of colour; for, with nothing more than the greens given by oxide of copper and iron, the turquoise of pure copper, the deep yet vivid blue of cobalt, the beautiful uncertain purple of manganese, and in certain districts the rich red of Armenian bole, they achieved colour schemes that have never been surpassed in their brilliant yet harmonious richness."

"The art of making a pottery consisting of a siliceous, sandy body coated with a vitreous copper glaze seems to have been known unexpectedly early, possibly even as early as the period immediately preceding the 1st dynasty (4000 B.C.). Under the XIIth dynasty pottery made of this characteristic Egyptian faience seems to have come into general use, and it continued in use down to the days of the Romans, and is the ancestor of the glazed ware

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[1] Encyclopaedia Britannica, 5, 706, 708, 710, 711, 726, 737 (1910).

of the Arabs and their modern successors. The oldest of Egyptian glazed ware is found usually in the shape of beads, plaques, etc.—rarely in the form of pottery vessels. The colour is usually a light blue which may turn either white or green; but beads of the grey-black manganese colour are found."

"Characteristic of the Parthian period is a coarse green glazed pottery of which the slipper-shaped coffins of the time were made. This glaze possibly contains a small amount of lead; in appearance it is not unlike the contemporary, translucent, blue glaze of Egypt. The Egyptian glaze certainly spread in to western Asia, and we find the last specimens of it in the tiles from the destroyed city of Rhagae in Persia, which may be as late as the 13th century A.D. The lead glazes, unknown in Egypt till the late Roman period, may be of Asiatic origin, though this important point is by no means clear."

"There is abundant evidence that pottery was made in the Egypt of the Roman times and later with rich turquoise blue and yellow glazes, though the potters had learned to produce this glaze on a material containing more clay and less sand than that used in earlier days. We know also that they had learned that the addition of lead oxide to a glaze enabled such glaze to be applied on vessels formed from clay, which was sufficiently plastic to be shaped on the wheel. . . . Oxides of copper or iron were added to the lead glaze, and the resulting green or yellow glazes were applied to plain vases or to vessels decorated with moulded reliefs. . . . We have already spoken of the prevalent use of coloured glazes in all the countries of the nearer East—from Egypt to Persia—from remote times, either as the sole colour decoration or in conjunction with modelled or painted ornament. The fragments from Rai and Fostat include rich turquoise glazes (derived from the ancient Egyptians), deep and light-green glazes containing lead and copper, imitations of ancient Chinese celadon-green, a brownish-purple glaze, a coffee-brown glaze, and a deep cobalt-blue glaze."

For the majolica glazes "pigments were compounded from metallic oxides or earths· the yellow, from antimoniate of lead, which was mixed with oxide of iron to give orange; the green, from oxide of copper (the turquoise tint given to the Egyptian and Syrian glazes by oxide of copper is impossible with a glaze of lead and tin); and the greens were made by mixing oxide of copper with oxide of antimony or oxide of iron; blue from oxide of cobalt, used in the form of a blue glass; brownish-purple, from manganese; black, from mixtures of other colours; and the rare red or reddish brown, of Faenza and Cafaggiolo was probably the same Armenian bole that was used so magnificently by the makers of the Turkish pottery, but on the white enamel ground this colour was most treacherous and uncertain. It must be remembered that many of these colours owe their tint to the lead used in their composition, or to the grounds containing oxides of lead and tin on which they were painted."

There are many passages by Burton[1] which emphasize the conditions for forming blue or green with copper, though not understanding the chemical changes accompanying the color changes.

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[1] "Porcelain," 36, 38, 73, 75, 80, 82, 135 (1906).

"Oxide of copper with a flux or glaze rich in lead gives various shades of green; but when it is dissolved in a glaze consisting of alkaline or earthy silicates, it produces all those wonderful blue-green tints which the potter calls 'Turquoise.' This beautiful tint of this turquoise is, however, destroyed by the addition of lead oxide or by firing to a high temperature. On the other hand, if the green or blue glazes obtained from copper oxide are fixed in a reducing atmosphere the colour changes to a marvellous red, which may be either brilliant and vivid, as in the finest red *Lang-yao* glazes of the Chinese, or opaque and liver-coloured as in those tints more commonly known as *Sang-de-Boeuf*. It has been customary to speak of these green, blue, and red tints obtained from oxide of copper as due to the formation of different silicates of copper. Such a view is hardly tenable, however, for there is nothing to show that the copper-compound exists in any different state of oxidation when it gives a green tint in a lead glaze or flux, or a blue tint in an alkaline mixture; while as to the red, copper-glazes, it seems probable that the tint may be due to the presence of metallic copper in a state of excessively fine subdivision, and not to an oxide of copper at all. Speaking generally, too, it is wiser not to assume that any particular porcelain colour is due to the presence of a definite silicate of the metal, for it may more probably be due only to the solution of some simple or complex metallic compound in a mixture of glassy silicates, borates, etc."

"Certain coloured glazes can only be obtained either with glazes of special compositions or under definite firing conditions. The famous glaze, first made by the early Egyptians on their highly siliceous bodies, which is known to us as turquoise, is obtained from oxide of copper. But this especial tint can only be developed in glazes rich in soda and lime, and, moreover, the fine blue tint which is its special distinction is destroyed at a high temperature. In the same way oxide of manganese will produce a beautiful purple colour comparable in depth and intensity to this turquoise, but only in an alkaline glaze fired at a comparatively low temperature. The appearance of glazes of fine turquoise and rich purple on Chinese porcelain is positive proof that the body of such pieces must have been first fired to the biscuit condition to make the ware translucent, and that the glazes themselves were subsequently fired at a much lower temperature. It will be noted that this involves a departure from the ordinary Chinese method of porcelain-making, and yet we have ample evidence from some such pieces as are described on page 66, that this practice was followed as early as the fifteenth century, before any porcelains had been made in Europe at all.

"Another coloured glaze, made in the same way, is coloured with a yellow made from antimoniate of lead (the Naples yellow of the painter), which is also incapable of enduring the temperature needed to fire the body of Chinese porcelain; yet there can be no doubt that this yellow glaze, described by the Chinese as 'Mi-se' or 'millet-coloured,' made its appearance at a very early period.[1]

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[1] Dr. Bushell states that this glass was first invented under the Sung dynasty.

"We may also mention that the Chinese made another yellow glaze, coloured with oxide of iron alone, but this was only invented at a later date when the porcelain body was exceedingly white and translucent, and the glazes highly refined. This is what is commonly known as 'Imperial' yellow, and was first used on pieces of excessive thinness which are either perfectly plain or have designs incised in the paste.

"It will be seen, therefore, that many of these glazes, especially the turquoise, purple, antimony-yellow, and clear iron-yellow, afford indubitable proof that the Chinese first fired their porcelain to the biscuit condition, and then glazed it at a lower temperature, whenever it suited their purposes so to do."

"Originally, the enamel-colours appear to have been merely applied as thin ground-washes to enhance the value of the decoration painted in underglaze blue, but the brightness and the jewel-like quality of the enamels, as well as the precision and delicacy with which they could be handled, soon brought them into more extended use, and we get the earliest pieces of the decoration so well known under its French title of *famille verte*, because of the predominance of a fine green-enamel, made from oxide of copper with a lead flux, which shines with the greatest brilliancy. Chinese porcelain decorated with on-glaze colours in which green predominates as here described, is almost invariably called 'Ming' porcelain by the dealers; but the true collector will not need to be told that ninety-nine per cent. of such pieces now to be met with are of much later date than the close of the Ming epoch."

The Chinese attribute to Lang t'ing-tso, Viceroy of Kiang-si, the province in which Ching-tê-chên is situated, two of the most beautiful of all their glazes, both of which bear the name of Lang-yao. "The first and the rarest of these is of a blue-green color, known as apple-green, while the second is the famous blood-red, which collectors are agreed is the crowning achievement in all that class of copper-red glazes, best known under their French title of *Sang-de-Boeuf*. . . . It may perhaps be added that the two glazes, the green and the red *Lang-yao*, are apparently identical in composition, the remarkable difference in appearance being due to the fact that the green was fired in an oxidising and the red in a reducing kiln-atmosphere."

"In the earliest glazed pieces that we know—say of Sung and Yuan times—the colouring substance was dissolved in the crude glaze and fired along with it. The first advance, said, by Dr. Bushell to belong to the later Sung times, was that of first biscuiting the porcelain and then firing at a lower temperature glazes of the alkaline type used by the Persian and Syrian potters so as to obtain the turquoise tint from copper and the violet-purple from manganese. This plan has been followed at all subsequent periods, and in the reign of K'ang-hsi the turquoise-coloured glazes, distinguished by the Chinese as 'peacock green' and 'kingfisher blue,' according as the tone is more green or blue (a change which can easily be effected by a slight difference in the firing temperature), were produced with surpassing excellence."

The experiments which we have done with borates agree exactly with the results obtained empirically by the Egyptians, the Chinese, and their followers.

It is possible of course to obtain a green from blue cupric oxide and the yellow of ferric oxide or lead antimoniate. Apart from this we get blue with alkalies and at low temperatures, and green with lead oxide and at high temperatures. At high temperatures cupric oxide will dissociate more readily to cuprous oxide with the consequent formation of a green color. We have shown that at the same temperature there is less cuprous oxide in the melt the more alkaline it is. The experiments with the oxides of manganese[1] showed reduction was greater when lead oxide replaced sodium oxide and the same thing will hold for copper oxide.

Laurie[2] has prepared a crystalline, blue, double silicate of lime and copper, $CaO.CuO.4SiO_2$, which has an inversion point at 850°-900°, the inverted material turning green at about 900°. It has not yet been shown that the green glass contains cuprous oxide; but one can predict with great safety that it will.

There is really nothing new about all this. It is contained, implicitly at least, in some work by Percy,[3] who is a bit hard reading because he reverses the ordinary nomenclature and calls cuprous oxide dioxide of copper, and cupric oxide protoxide of copper, although using the modern formulas. His atomic weights are different, because he takes the atomic weight of copper as 31.648.

"Protoxide of copper, CuO, is the oxide which forms the base in ordinary salts of copper. According to Berthier, it melts at a white heat. It is as easily reduced as the dioxide, and by the same reducing agents. Favre and Maumené state that when protoxide of copper is exposed to about the melting-point of copper, oxygen is given off in a regular stream, which, having once ceased, will not again occur, though the heat may be increased.[4] In four experiments the loss of oxygen varied from 8.0 to 8.2 per cent. [as against nearly nine for the theoretical loss.] The product, which was melted, was black, and consisted of $2\ Cu_2O + CuO$. I had long previously found that when protoxide of copper was exposed in a clay crucible to a high temperature in a common assay furnace, it became brown and formed a sintered mass; but I was not sure that the reduction was the simple effect of heat, and thought that probably the partial reduction might have been caused by the gases of the furnace. . . .

"Berthier heated the following mixture of protoxide of copper and silica:

$3CuO$ = 0.421 gramme.
$4SiO_2$ = 0.579 do.

The product was only semi-fused and blood-red in colour, which proves that the protoxide [CuO] had been reduced to the dioxide [Cu_2O].

"This experiment has been repeated by R. Smith. The proportions employed were 1160 grains of protoxide of copper and 840 of silica. The mixture

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[1] Bancroft and Nugent: J. Phys. Chem., 33, 481 (1929).
[2] Proc. Roy. Soc., 89A, 418 (1924).
[3] "Metallurgy," 243 (1861).
[4] Berzelius: Jahresber., 1846, 184.

was exposed in a fine-grained crucible to a high temperature during two hours. The product was fritted, and very similar in appearance to that obtained by heating a mixture of dioxide of copper and silica. Its upper surface was black, and where it was in contact with the crucible it was orange-coloured. In order to be certain that the gases of the furnace in which the crucible was heated had not contributed to effect the reduction of the protoxide to the dioxide, the following experiment was made in a muffle, in which the atmosphere was oxidizing:—

$3CuO$ = 580 grains
$2SiO_2$ = 440 do.

"The materials were then intimately mixed, and the mixture was exposed in an uncovered platinum dish to a strong red heat in a muffle during 3½ hours. A sound, such as is produced by the evolution of bubbles of gas from a thick liquid was perceived during the process. The dish with its contents was left to cool in the muffle. The product was detached in one piece from the platinum; it was somewhat compact, semi-fused, opaque, and brown-red; the upper surface was black and porous. The platinum dish was attacked where it had been in contact with the mass. About half the product was again exposed during 5½ hours in the same platinum dish in a muffle to a degree of heat approaching whiteness. No perceptible change occurred, except the blackening of the surface of the mass. From the preceding experiments it may be concluded that, under the influence of silica, protoxide of copper [CuO] is reduced to dioxide of copper [Cu_2O]. . . .

"The experiment was made by R. Smith of heating protoxide of copper [CuO] with silica and alumina.

$3CuO$ = 120 grains
Al_2O_3 = 52 do.
$2SiO_3$ = 92 do.

The mixture was heated in a fine-grained crucible in the same furnace, and during the same time, with the crucible in experiment 2, p. 244. The product was melted, compact, and of a greenish-orange colour like that obtained in experiment 2 [where the charge contained dioxide of copper, Cu_2O]. . . .

"The following experiment on borate of copper was made by Berthier:—

CuO = 9.91 grammes.
$2BO_3$ = 14.72 do.

The mixture melted easily without intumescence. The product was tenacious, opaque, and red-brown in colour, spotted with blue. It contained cavities in which were brilliant prismatic crystals, some red and others of the finest blue colour. Part of the protoxide of copper must have been reduced to dioxide.

"The following experiment was made by R. Smith:—

$3CuO$ = 240 grains
$2BO_3$ = 140 do.

The mixture was heated in an open Cornish crucible in a muffle, and in about twenty minutes fused easily at a red-heat; the product was a dark, greenish-coloured glass when seen by transmitted light, but it was blue and iridescent on the surface. . . .

"*Dioxide of copper heated with protoxide of lead.* Experiments by R. Smith.

$$Cu_2O = 720 \text{ grains}$$
$$PbO = 1120 \text{ do.}$$

The mixture melted at a low red heat; it attacked and traversed the substance of the crucible with great rapidity. The product is crystalline and reddish brown-black.

$$Cu_2O = 720 \text{ grains}$$
$$2PbO = 2240 \text{ do.}$$

The mixture melted as in the last experiment, and the product had nearly the same characteristics; its upper surface was coated with a black film having a semi-metallic lustre. It follows from these results that dioxide of copper is not in any degree oxidized when heated with protoxide of lead; for, otherwise, metallic lead would have been separated.

"*Protoxide of copper heated with protoxide of lead.* Experiments by R. Smith

$$CuO = 400 \text{ grains}$$
$$PbO = 1120 \text{ do.}$$

The mixture melted into a compact, hard, dull slag; its upper surface was black, crystalline, and metallic in lustre; the colour of its fractured surface varied from brown to black from below upwards.

$$CuO = 200 \text{ grains}$$
$$2PbO = 1120 \text{ do.}$$

The mixture melted into a crystalline, shining, dark-green slag, much softer than the last, and more resembling fused protoxide of lead in appearance; its upper surface was smooth, black, and semi-metallic in lustre."

While Percy does not call attention to the fact, the green color in the experiment just cited shows that there is more cupric oxide when the ratio of plumbous oxide is increased. The significance of Percy's work seems to have been overlooked hitherto. Mellor[1] says that "copper oxide dissolves in fused silicates producing blue or green glasses. The alkali silicates tinted by copper are blue." The statement on the next page that the hydrated silicates are blue and the anhydrous ones are green is inaccurate as it stands, because dioptase and 'idealized' chrysocolla are both green, while $CaO.CuO.4SiO_2$ is blue. Thorpe[2] says that copper borate is readily obtained by treating a soluble borate with copper chloride or sulphate. It is blue, and used in certain oil paints and also in the colouring of porcelain."

Sir Herbert Jackson[3] has been misled by the apparently striking analogy between the colors of cupric salts in aqueous solutions and those in glasses. "It would lead us into too much detail to do more than direct attention to the possible analogies between the action of water in solutions of cupric salts

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[1] "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," **6**, 340 (1925).

[2] "A Dictionary of Applied Chemistry," **1**, 645 (1921).

[3] Nature, **120**, 265 (1927).

and the action of the oxides of the alkali metals in glasses coloured by cupric oxide. The change from blue to green just mentioned in the case of the low-temperature cupric oxide glasses calls to mind the fact that a green solution of cupric chloride, which becomes blue when sufficient water has been added, becomes green again on heating it. A study of the changes of colour which can be produced in aqueous solutions and salts, and of the methods of modifying these colours, has been of great assistance to me in shortening the experimental work necessary to arrive at the compositions of a number of glasses in which it was desired to produce certain colours either with copper or colouring agents."

This seems to be a case of a bad working hypothesis being better than none. We can have green aqueous solutions and green hydrated salts which contain no cuprous salt. The green copper glasses always contain cuprous oxide, so far as we now know. There is, therefore, no real parallelism. Lasareff and Lazarev[1] have compared the color of a blue borax glass with that of a copper sulphate solution. If we take the absorption for 590 mμ as unity in both cases, the absorption for 470–550 mμ is much greater in the case of the borax glass. The authors draw the conclusion that the color in the copper oxide glasses is different from the color of the ions and is not due to these.

It is possible, however, to duplicate, in aqueous solutions some of the results obtained by Sir Herbert Jackson and by ourselves in fused melts. It has long been known[2] that metallic copper can be obtained by using a high current density with a copper-wire anode in sulphuric acid. Cuprous sulphate is formed at the anode, which then decomposes to metallic copper and cupric sulphate. Mr. L. V. Redman called our attention to the fact that, if we substitute a moderately concentrated solution of copper sulphate for the sulphuric acid, the decomposition of the cuprous sulphate gives a brilliant green color at the anode by reflected light. We have confirmed this; but have not analyzed the precipitate to see whether it is metallic copper, cuprous oxide, or a mixture of the two. By transmitted light the solution is blue. This system seems worth studying in more detail. When the temperature is allowed to rise, the quality of the precipitate changes and the color of the solution becomes a dark olive-green by reflected light. So far as one can judge by the description, this duplicates pretty closely a glaze obtained by Sir Herbert Jackson.[3]

"With many glasses made at a high temperature, cupric oxide gives an olive-green colour. Without going so far as to say that the dusky shade in the green is invariably due to some reduction of the cupric oxide to the lower oxide of copper, there is evidence of this in certain instances which I have come across. To take one: in making trials for a glass which was intended to be of a green colour with only a slight tinge of olive in it, and of a sufficiently

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[1] Compt. rend., **185**, 855 (1927).

[2] Fischer: Z. Elektrochemie, **9**, 507 (1903).

[3] Nature, **120**, 266 (1928).

light shade to enable the light of a candle flame to be seen through a one-inch thickness of the glass, the furnace conditions happened to change so that the glass was exposed to a reducing atmosphere. The resulting glass was so black that a bright June sun was invisible through a piece of the glass one-fortieth of an inch thick. Such a state of affairs might be considered to come about by the glass being a mixture of red copper glass with a green cupric oxide glass, through which mixture but little light could be transmitted. Now red glass owing its colour to finely dispersed metallic copper is rendered colourless by fusing it and chilling it quickly. The black glass referred to might therefore be expected to become green if fused and chilled quickly; but it did not change from its intense black colour. This just gives a hint of the possibility of a cuproso-cupric compound being present in the glass analogous to, though not so definite as ferroso-ferric oxide, the well-known black iron scale.

"Again an analogy with solutions helps a little. If to a colourless solution of cuprous chloride in hydrochloric acid there be added a transparent green solution of cupric chloride, the mixture turns black. Although dusky greens and the black glass just referred to might be accounted for by varying mixtures of red and green glass, the colour of this solution could scarcely be accounted for in the same way. Moreover in experimenting with red copper glasses, and studying the way in which the red colour can be prevented from developing by sudden chilling and can be produced by subsequent heating, I have repeatedly noticed that, instead of obtaining a clear colourless glass in bulbs made from the red glass and chilled quickly, the bulb has been sometimes of a dusky hue and sometimes of a definite neutral tint. As no other colouring agent but copper was present in these glasses, I am inclined to attribute the neutral shade to a cuproso-cupric compound which is stable in the glass and is analogous to the compound formed when the cuprous and cupric chloride solutions are mixed, rather than to a physical mixture of red and green glasses."

This seems to be equivalent to explaining one unknown in terms of another. There is no independent evidence of any cuproso-cupric oxide which might be black in glass and the argument starts from what we believe to be an erroneous assumption, that the green in copper oxide glazes is not due to the presence of cuprous oxide. There could not of course be any cuproso-cupric oxide in a concentrated hydrochloric acid solution, so Sir Herbert Jackson must be postulating a cuproso-cupric chloride in the aqueous solution. Mellor[1] says: "Cuprocupric chloride is said to be present in the brown-coloured solution formed when cupric chloride in acetone is allowed to stand; when a hydrochloric acid solution of cuprous chloride is oxidized; when an aqueous solution of cupric chloride solution is reduced on or at the cathode; when an aqueous solution of cupric chloride is electrolyzed. There is every sign that the alleged cuprocupric chloride is a mixture of the two chlorides."

Anhydrous cupric chloride is yellowish-brown, dissolves in methyl alcohol to form a brown solution, and gives a yellow color with aqueous hydrochloric

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[1] "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 3, 159 (1923).

acid. Nobody knows whether cupric chloride increases the tendency of cuprous chloride to hydrolyze. While we do not yet know the actual cause of the black color in the aqueous solution of cupric chloride, cuprous chloride, and hydrochloric acid, it is certainly not justifiable at present to postulate a cuproso-cupric chloride. It should not be difficult to clear up this point.

Granger found that glasses containing boric oxide and copper oxide had a very deep color and were almost opaque, the glass seeming blackish even by reflected light.

We have shown how the new technique described in these two papers has simplified the question of the colors of manganese and copper oxides in glasses. It seems to us that all problems pertaining to the colors of glazes could be worked out easily and economically by studying the behavior of borax or phosphate beads. Of course the results would then have to be translated into terms of glasses; but that would be relatively simple so soon as one knew exactly what one was trying to do. In any soluble glass, it would be a simple matter to differentiate analytically between metallic copper and cuprous oxide. One could even analyze for all three substances, metallic copper, cuprous oxide, and cupric oxide if it were necessary.

The direct experimenting with glasses is evidently not easy. Fuwa[1] has made a great many experiments on copper oxide in glasses and his results, as given in the abstract are both negative and misleading. On addition of metallic copper, cuprous oxide, or cupric oxide, he obtained colored glasses varying from light to dark blue. In general cupric oxide gave the deepest colors and copper the palest colors. This cannot be true if equilibrium was reached because the composition of the copper products in a given glass depends only on the amount of copper, the temperature, and the oxygen pressure. Familiarity with the phase rule would have enabled him to avoid this error.

Fuwa also added oxidizing agents and reducing agents. With $Cu(NO_3)_2 6H_2O$—which he certainly did not have in the molten glass—he obtained a deeper blue than when he added cupric oxide alone. Addition of one percent potassium nitrate gave him a still deeper blue. Here again he could not have reached equilibrium. What he had done was to over-oxidize the melt. Addition of five percent potassium tartrate to a one percent cupric oxide melt gave reddish colors. He must have reduced beyond the green stage.

Granger's experiments[2] are nearly as disappointing. He recognizes that cupric oxide gives a better blue with more alkali; but he does not find the difference between lead and soda glazes which all potters have found since the time of the early Egyptians. The most probable explanation for his results is that his glasses oxidized at all temperatures, thus throwing his results out. This is made practically certain by one experiment in which a film of copper formed on the surface of a chill-cast piece of glass, while the mass of the glass was blue. Unless the metallic copper was formed by the reaction

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[1] Chem. Abs., 19, 478 (1925).

[2] Compt. rend., 157, 935 (1913).

of the molten glass with the metal mold—and he does not mention that possibility—the cupric oxide must have been pretty well dissociated at the high temperatures and his glass should have come out either green or red.

Granger considers that the color depends on the ratio of cupric oxide to bases and not on the silica content. This may be true; but his experiments do not justify the conclusion. Since he gets a blue when he should get a green, the change due to the silica content may be within his experimental error. He does find that presence of boric acid increases the tendency of the glass to turn green and he finds a similar effect with alumina, which we had not tried, our experimental work having been finished before we read Granger's article.

1. It is possible to determine cuprous oxide and cupric oxide in borate glasses by treating with acidified ferric sulphate and titrating the ferrous sulphate formed by oxidation of the cuprous oxide.

2. It would also be possible, though it did not come within the scope of this paper, to determine metallic copper and cuprous oxide in the same way and thus decide whether a given red color was due to copper or to cuprous oxide.

3. When copper oxide is used to color a boric acid glass, there is some reduction to cuprous oxide. The percentage of cupric oxide in the melt increases with increasing alkalinity and decreases with rising temperature.

4. When lead oxide is substituted for sodium oxide, the percentage of cuprous oxide increases.

5. Cupric oxide gives a blue color to glasses; the green color is due to the presence of cuprous oxide. It is for this reason that copper oxide gives a blue in alkaline glazes and a green in lead glazes. Our results confirm those of Percy and of Sir Herbert Jackson, and are in agreement with those of the potters of all countries.

6. While green glazes can be and have been made with blue cupric oxide and yellow ferric oxide or lead antimoniate, the copper greens are not usually so made.

7. The blue of $CaO.CuO.4SiO_2$ is in accord with the theory; but it has not yet been shown that the green color of the glass obtained by heating above 900° is due to presence of cuprous oxide.

8. While there is a very strong apparent analogy between the blues and greens of cupric salts in aqueous solutions and the blues and greens in glazes, this analogy is superficial and misleading. The green of cupric salts in presence of water depends so far as we now know, on there being not more than two molecules of water attached to the copper. In the glazes the green is due to the presence of cuprous oxide and is never, so far as we now know, a color of cupric oxide. Dioptase and chrysocolla appear to belong in one group and Egyptian blue, $CaO.CuO.4SiO_2$, in the other.

9. It should be both easy and economical to make a preliminary study of all questions concerning the colors of glazes in borate beads.

10. So far as the color of glass is affected by aluminum oxide, stannic oxide, titanium oxide, arsenious oxide, zirconium oxide, cuprous oxide, calcium phosphate, gold, copper, selenium, tellurium, and cadmium sulphide, these substances appear to be in colloidal suspension. So far as the color of glass is affected by cupric oxide, chromic oxide, cobaltous oxide, ferrous oxide, ferric oxide, manganic oxide, and antimony oxide, these substances appear to be in true solution. This statement is not in conflict with the fact that, under certain circumstances, it is possible to have ferric oxide and ferroferric oxides in colloidal suspension, as in the obsidians.

Cornell University

THE EFFECT OF SALTS ON WEAK ELECTROLYTES

III. Interaction of Certain Weak Electrolytes

BY HENRY S. SIMMS*

I. Introduction

In the two previous papers[1] it was shown that the ionic activity of weak electrolytes in dilute solutions is markedly affected by the presence of strong electrolytes. NaCl was found in general to give effects on weak acids in agreement with the limiting Debye-Hückel equation (providing we modify it to allow for the distance between charges in divalent acids). The anomalous effects produced by Mg^{++} and $SO_4^{=}$ were studied. Amines and ampholytes were found to be abnormal with all salts.

It has also been shown[2] that in the case of oxalic acid the large effect of $MgCl_2$ is antagonized by the addition of NaCl or KCl. Likewise[3] the effect (in the opposite direction) of Na_2SO_4 is antagonized by NaCl or KCl. In either case, large additions of NaCl or KCl tend to produce the effect of these salts alone, drowning out the effects of the anomalous salts. These antagonisms follow equations indicating a mechanism involving a mass action effect.

Similarly NaCl, KCl and $MgCl_2$ each lower the pH of gelatin solution (original pH 7.367) when present alone; but the addition of a small amount of a second salt raises the pH; more of the second salt lowers the pH; and still more again raises the pH of the solution. For details one must consult the original paper.[4]

Exactly the same phenomena are produced by the addition of salts to glycine solutions[5] showing that this salt antagonism is unquestionably non-colloidal in character.

On the assumption that such anomalies are due to inactivation of a weak electrolyte by a strong electrolyte, it seems advisable to determine whether one weak electrolyte may be inactivated by another weak electrolyte.

II. Effect of Glycine on H_3PO_4 Titration with Salts

In the present paper we find, first, that the presence of glycine causes a drop in P_{K_2}' of H_3PO_4. This drop increases with addition of salt, being greatest at zero ionic strength (extrapolated). (See Fig. 1).

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* From the Department of Animal Pathology of the Rockefeller Institute for Medical Research, Princeton, N. J.

[1] Simms: J. Phys. Chem., 32, 1121, 1495 (1928).

[2] Simms: J. Gen. Physiol., 12, 241 (1928).

[3] Simms: J. Gen. Physiol., 12, 259 (1928).

[4] Simms: J. Gen. Physiol., 13, 511 (1929).

[5] Simms: (Unpublished).

III. Effect of Various Amounts of Glycine on $HPO_4^{=}$ Activity

This indicates that the glycine inactivates the phosphate diion ($HPO_4^{=}$) perhaps by means of a loose combination. In order to study this we prepared solutions of H_3PO_4 with 1.4 equivalents of NaOH containing varying amounts of glycine. The results are plotted in Fig. 2 where it is evident that the effect on the P_K' reaches a maximum and then decreases per increment of glycine added. This is, however, only an indirect measure of the effect on the activity.

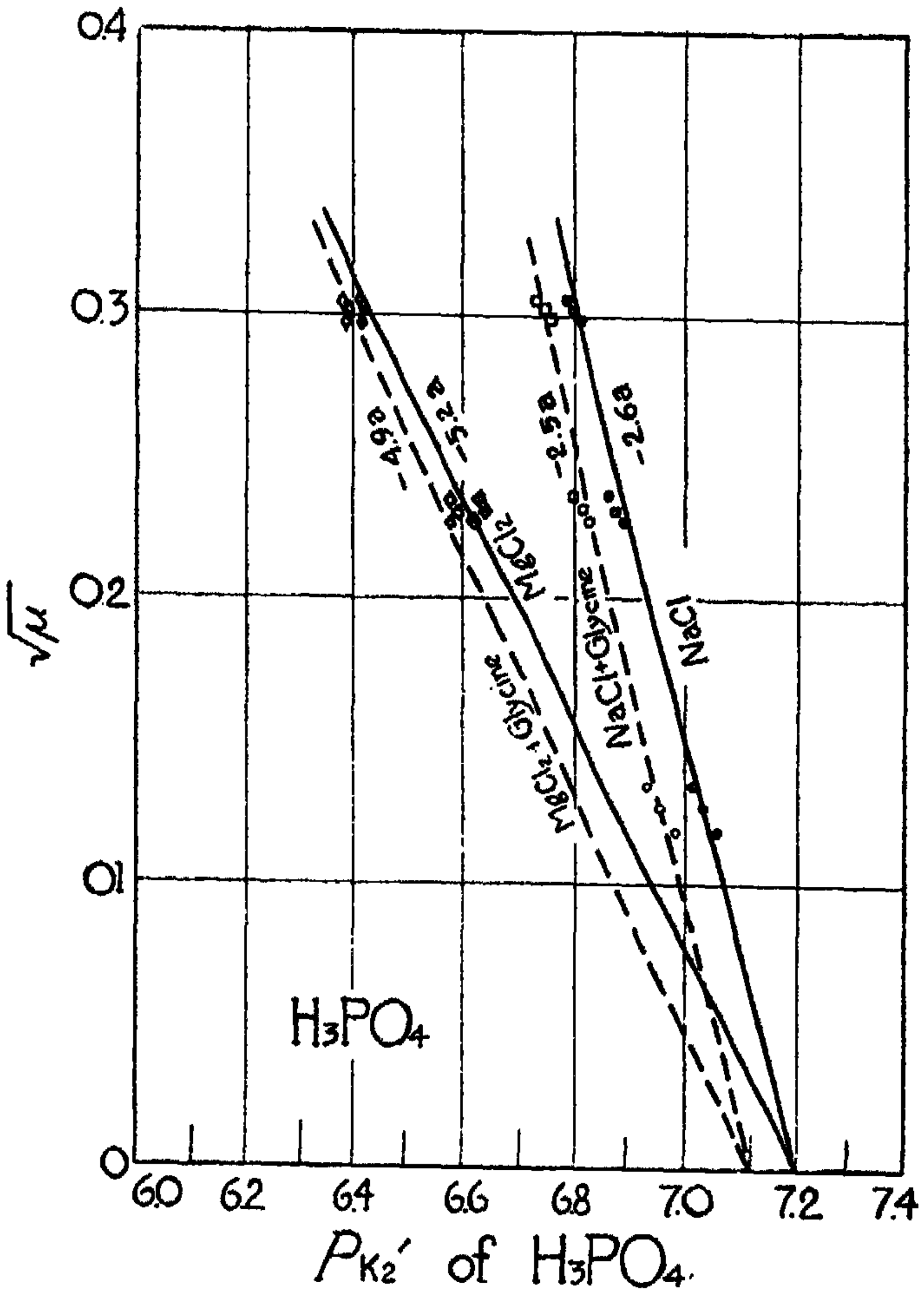

Fig. 1

Effect of Glycine on Pk'_2 of H_3PO_4 in the presence of salts.

If we calculate the remaining activity *f* of $HPO_4^{=}$ ion (see Table II) the fraction inactivated by glycine is (1 − *f*). Plotting *f* against *log* c_G (*i.e.*, log

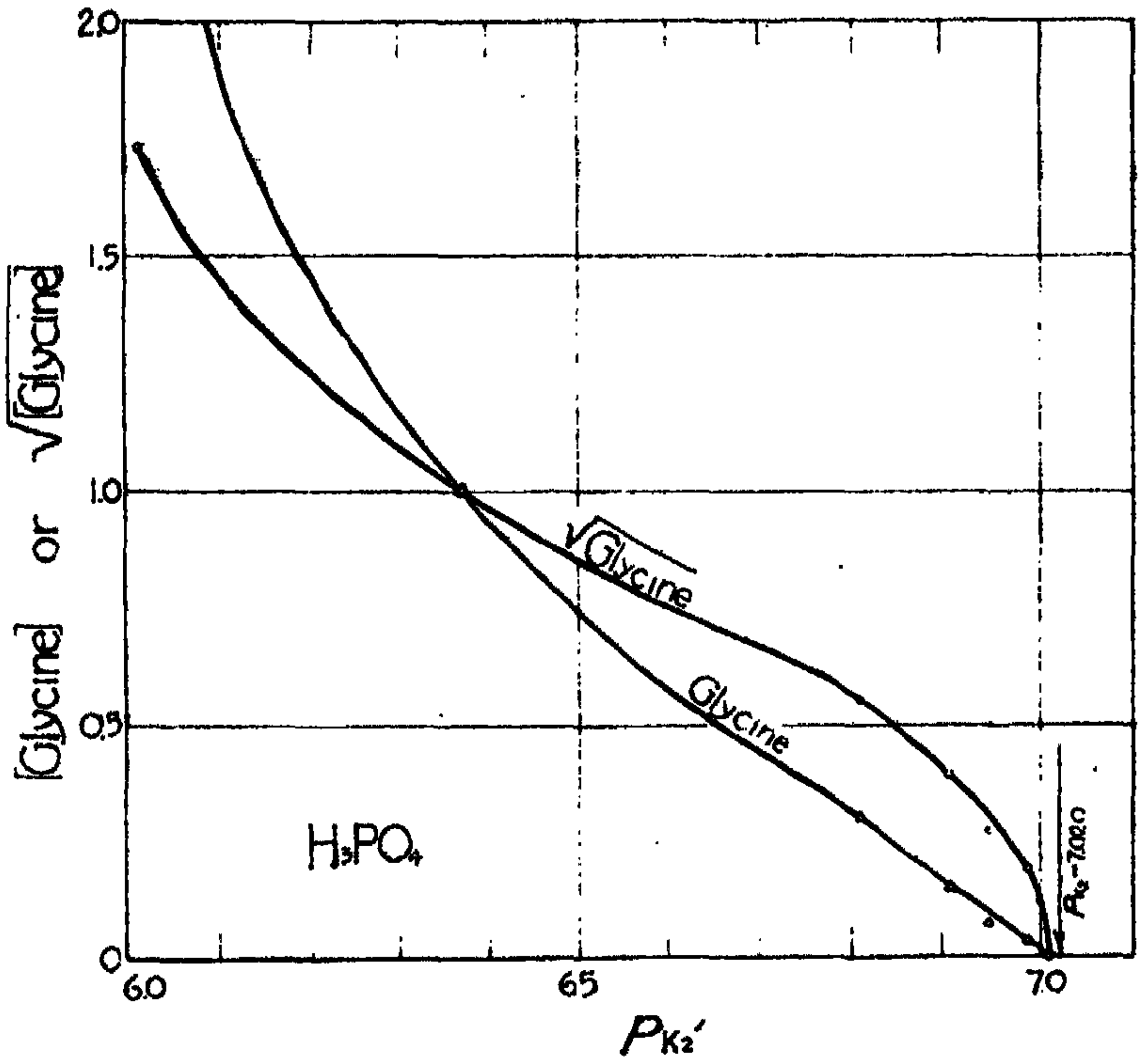

FIG. 2
Effect of glycine on Pk'_2 of H_3PO_4 (where Pk'_2 = log f + 7.620).

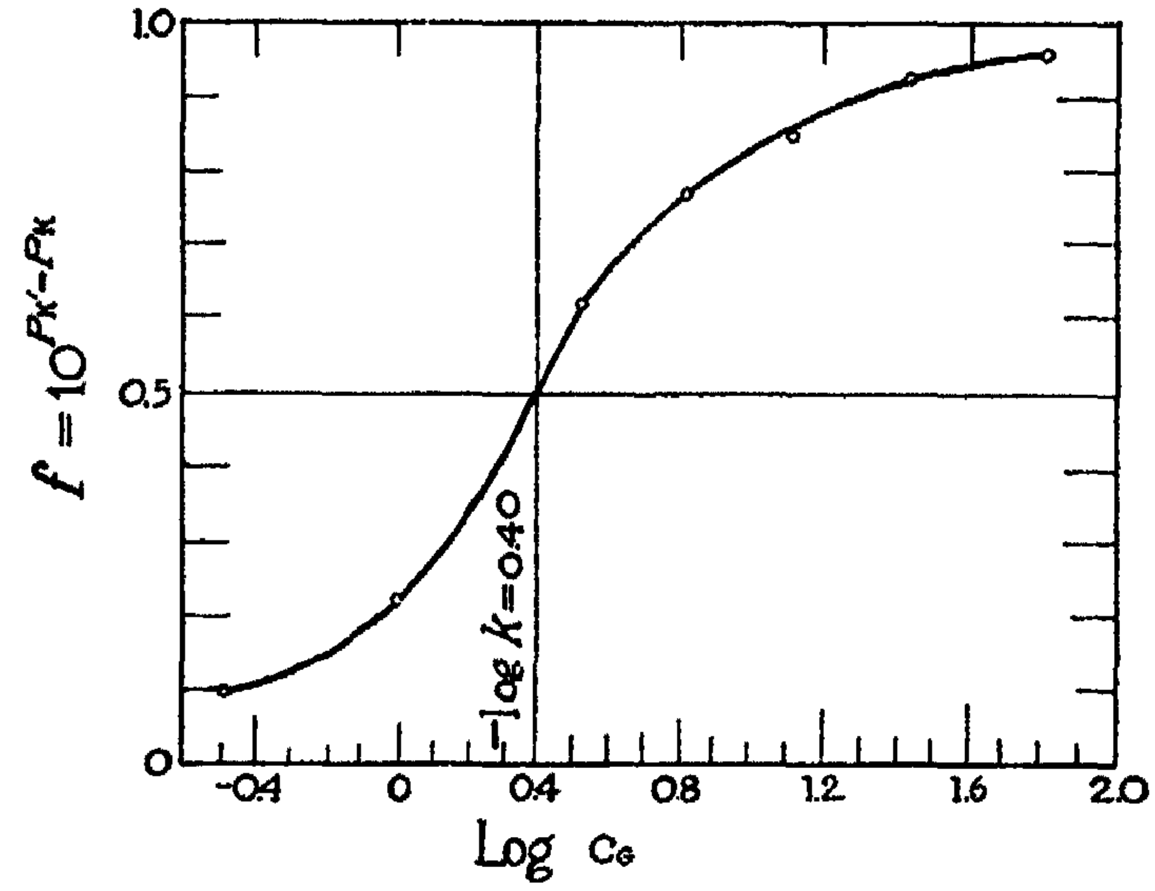

FIG. 3
Plot of $HPO_4^{=}$ activity against log of glycine concentration.

of the glycine concentration) gives a symmetrical S-shaped curve indicating a mass action mechanism. (Fig. 3).

We may moreover calculate a mass action constant k from the equation:

$$k = \frac{[\text{Glycine}] \times [\text{HPO}_4^{=}]}{[\text{Combined}]} = c_G \frac{f}{1 - f} = 0.40$$

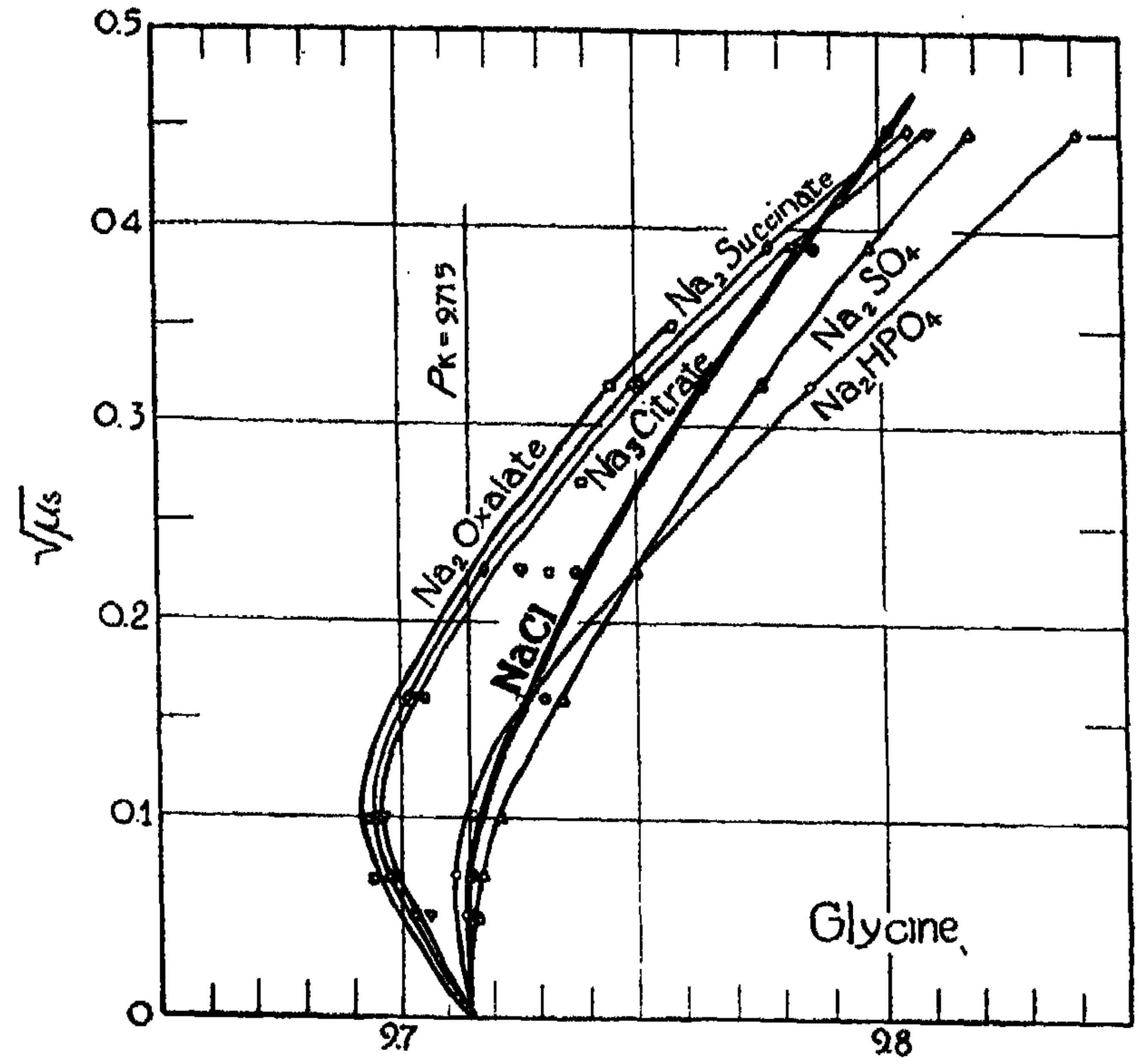

Fig. 4

Effect of salts on Pk'₂ of glycine. μ_s is the ionic strength due to added salts. The abscissas are Pk' values corrected for the normal deviation expressed by the limiting Debye-Hückel equation.

where the free $\text{HPO}_4^{=}$ equals $f\alpha_p c_p$ and the combined $\text{HPO}_4^{=}$ equals $(1 - f)\alpha_p c_p$, see Table II. It will be observed that it is the neutral (zwitterion) form of glycine which does the inactivating. Correction was made for the degree of ionization of glycine in each solution.

IV. Effect of Phosphate and Other Polyvalent Anions on Glycine

One would expect from the above that if $\text{HPO}_4^{=}$ inactivates neutral glycine, then the reverse should be true and the presence of phosphate should affect the ionization of glycine. This is found to be so. In Fig. 4, if we compare the NaHPO_4 curve with that of NaCl, it will be seen that Na_2HPO_4

raises P_{K_2}' of glycine to an extent depending on the amount of phosphate. The direction of the effect agrees with the above assumption that $HPO_4^=$ and *neutral* glycine inactivate each other.

To determine if this effect is specific for phosphates, we substituted Na_2SO_4 (since H_2SO_4 is the only other suitable inorganic divalent acid and since it is known to produce anomalous effects). The curve for Na_2SO_4 in Fig. 4 shows that $SO_4^=$ ion produces the same result as $HPO_4^=$ ion. It therefore appears that $SO_4^=$ also inactivates neutral glycine.

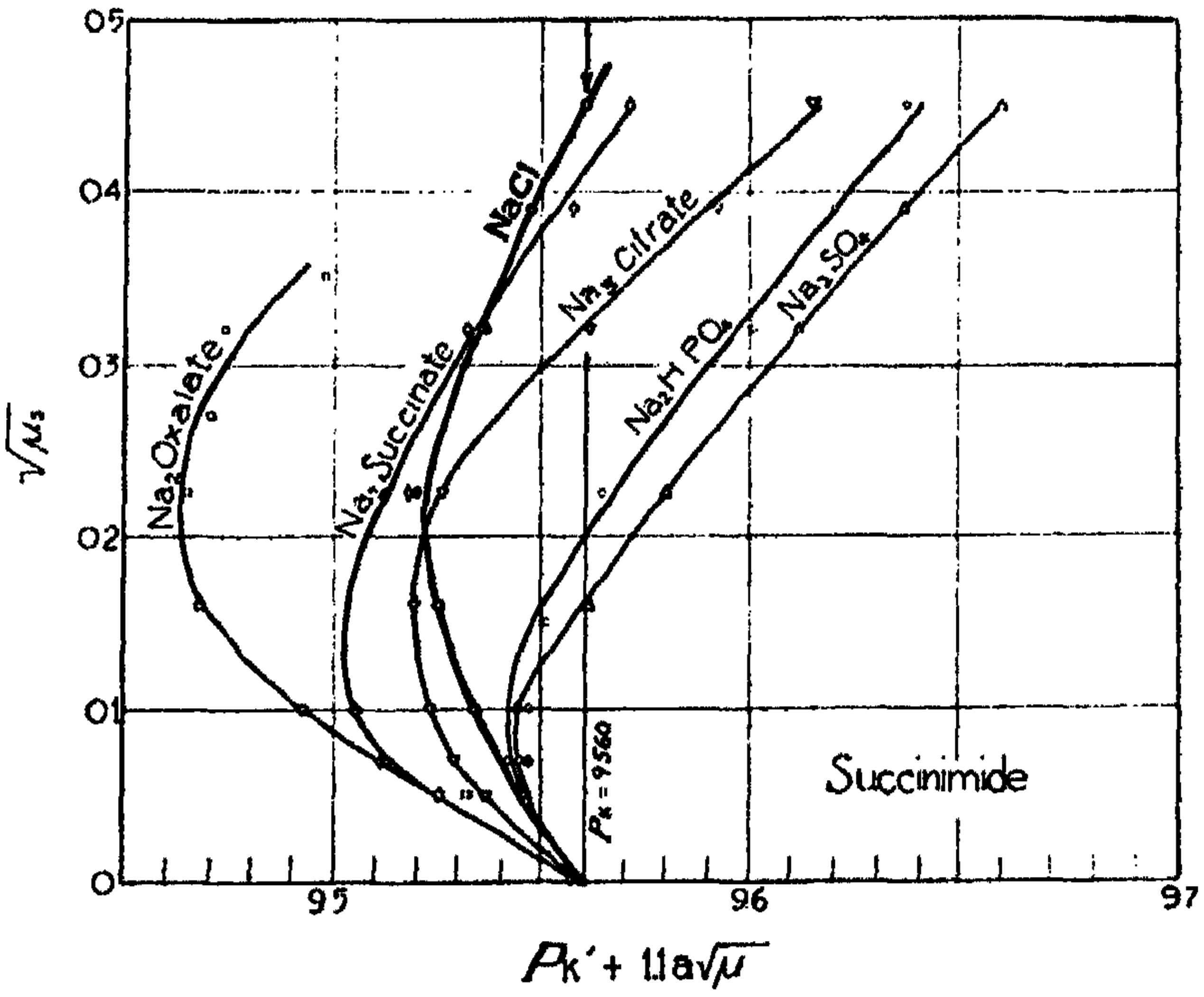

Fig. 5
Effect of salts on Pk′ of succinimide

If this effect is dependent upon the electrostatic charge on the sulfate and phosphate ions it is to be expected that the polyanions of organic acids should also produce the same effect. A study of glycine in the presence of the sodium salts of oxalic, succinic and citric acids shows that these salts *in very dilute solution* (0.01μ) behave *oppositely*, but in higher concentration (0.1μ) behave the *same* as $SO_4^=$ and $HPO_4^=$ ions.

A more careful examination of the Na_2HPO_4 curve shows that in very dilute solution it too tends to have the opposite effect to that in higher concentration. Apparently all these salts have the same effect (of raising P_{K_2}' of glycine) in the higher concentrations (studied up to 0.2μ) but that they differ in their tendency to produce the opposite effect at lower concentration (about 0.01μ). The order of the latter effect is:

oxalate > succinate > citrate > phosphate > sulfate.

V. Effect of Polyvalent Anions on Succinimide

Succinimide is a very weak acid ($P_K = 9.560$) ionizing in the P_H range suitable for studying its effect with $HPO_4^=$. We have already seen that $SO_4^=$ produces anomalous effects on both P_{K_1}' and P_{K_2}' of divalent weak acids (such as malonic[1] and oxalic[2]). With succinimide we may study a monovalent weak acid not only with sulfate but also with phosphate diions, and furthermore with the diions of weak acids.

The results are shown in Fig. 5. The curves of Na_2HPO_4 and Na_2SO_4 show that their effect on succinimide is very similar to their effect on glycine (Fig. 4). Furthermore, the organic salts have a similar, but more marked, effect on succinimide.

There is a gradual transition in the shape of the curves as we pass from sulfate, to phosphate, to citrate, to succinate, and to oxalate. The differences are quantitative rather than qualitative. It would appear that the same effect is produced by all these ions in less dilute solutions but that they differ in their behavior in more dilute solutions (0.01μ).

VI. Conclusions

The observations do not warrant any definite explanation. Glycine causes a drop in P_{K_2}' of H_3PO_4 (the effect being decreased by addition of salts). Na_2HPO_4 causes a rise in P_{K_2}' of glycine. These results suggest that neutral glycine and the phosphate diion ($HPO_4^=$) inactivate each other. On this basis a consistent mass action constant can be calculated.

The assumption of such a mechanism necessitates that we also assume that the diions of sulfates, succinates, and oxalates and the triion of citrates, all inactivate neutral glycine and nonionized succinimide (and other weak acids; and, to a less extent, monoions of divalent weak acids).

These observations may find their explanation in the work of LaMer and his collaborators[6] who explain some anomalies of polyvalent ions on the basis of neglected terms in the Debye-Hückel equation.

In more dilute solution (0.01μ) the salts of divalent anions tend to produce an effect opposite to the above effect at 0.2μ. The order of this effect is the same with either glycine or succinide, namely: oxalate > succinate > citrate > phosphate > sulfate This order is rather strange since the size of the ion and the distance between the charges of oxalate diion are about the same as with phosphate and sulfate diions; while succinate and citrate ions are larger ions and have more remote charges[1]; furthermore the citrate ion has a higher charge.

VII. Experimental

The experimental methods are fully described in previous papers. The data are given in Tables I to IV.

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[6] LaMer, King and Mason: J. Am. Chem. Soc., **49**, 363; LaMer and Mason: 410 (1927).

TABLE I

Effect of Glycine on P_{K_2}' of Phosphoric Acid in the Presence of Salts (0.0100 M NaH_2PO_4 plus NaOH, and 0.0750μ (C.—) or 0.0375μ (D.—) of NaCl or $MgCl_2$; each solution being measured both without glycine and in the presence of 0.075 molar glycine)

Salt	$\frac{b-a}{c}$	$\sqrt{\mu}$	Without glycine		With glycine	
			P_H	P_{K_2}'	P_H	P_{K_2}'
C.–$MgCl_2$	1.196	0.298	5.809	6.421	5.783	6.395
D.–$MgCl_2$	1.196	.227	6.012	6.624	5.974	6.586
No salt	1.196	.118	6.445	7.057	6.370	6.982
D.–NaCl	1.196	.227	8.287	6.899	6.223	6.835
C.–NaCl	1.196	.298	6.206	6.818	6.147	6.759
C.–$MgCl_2$	1.294	.302	6.045	6.427	6.017	6.399
D.–$MgCl_2$	1.294	.231	6.259	6.641	6.216	6.608
No salt	1.294	.126	6.651	7.033	6.577	6.959
D.–NaCl	1.294	.231	6.501	6.883	6.440	6.822
C.–NaCl	1.294	.302	6.423	6.805	6.367	6.749
C.–$MgCl_2$	1.392	.305	6.228	6.419	6.193	6.384
D.–$MgCl_2$	1.392	.236	6.440	6.631	6.396	6.587
No salt	1.392	.134	6.824	7.015	6.749	6.940
D.–NaCl	1.392	.236	6.682	6.873	6.611	6.802
C.–NaCl	1.392	.305	6.600	6.791	6.541	6.732

TABLE II

Effect of Glycine on $HPO_4^{=}$ Activity as shown by P_{K_2}' Values of Phosphoric Acid,—Calculation of Inactivation Constant k. (0.0100 M NaH_2PO_4 plus 0.400 equivalents of NaOH plus various amounts of glycine)

Glycine concentration c_G	P_H	α_P	P_{K_2}'	f	k
0	6.832	0.400	7.008		
0.0150	6.822	.398	7.002	0.959	0.37
.0375	6.802	.395	6.987	.927	.48
.075	6.756	.391	6.948	.85	.42
.150	6.705	.385	6.908	.77	.45
.300	6.580	.370	6.811	.62	.49
1.00	6.137	.369	6.369	.22	.29
3.00	5.77	.361	6.02	.10	.33
		Average			0.40

The degree of dissociation into $HPO_4^{=}$ is given by

$$\alpha_P = b' - 1 - \frac{c_G}{c_P}\alpha_G$$

where b' is the corrected equivalents of base (1.400); c_G and c_P are the concentrations of glycine and phosphate, respectively; and α_G is the degree of dissociation of glycine (P_{K_2}' taken as 9.68).

TABLE III

Effect of the Sodium Salts of Four Dianions and One Trianion on P_{K_2}' of Glycine

The effect of NaCl is given for comparison

(0.0100 *M* glycine with 0.315 equivalent of NaOH (for NaCl, Na_2SO_4 or Na_2HPO_4, or 0.300 equivalent with the other salts) and various amounts of respective salts; $P_{K_2} = 9.715$)

		With NaCl		With Na_2SO_4		With Na_2HPO_4		Na_2 oxalate		Na_2 succinate		Na_3 citrate	
μ_s*	$a\sqrt{\mu}$**	P_H	P_K'	P_H	P_K'	P_H	P_K'	P_H	P_K'	P_H	P_K'	P_H	P_K'
0	0.027	9.350	9.688	9.350	9.688	9.350	9.688	9.316	9.686	9.316	9.686	9.316	9.686
0.0025	.037	9.340	9.678	9.343	9.680	9.367	9.678	9.296	9.666	9.296	9.666	9.299	9.669
.0050	.045	9.333	9.671	9.335	9.673	9.347	9.667	9.279	9.649	9.283	9.653	9.284	9.654
.0100	.056			9.323	9.666	9.323	9.660	9.267	9.637	9.269	9.639	9.270	9.640
.025	.083	9.311	9.649	9.315	9.653	9.306	9.644	9.258	9.623	9.250	9.620	9.252	9.622
.050	.114	9.286	9.624	9.298	9.636	9.298	9.636	9.238	9 608	9.235	9.605	9.242	9.612
.075	.138							9.221	9.591				
.100	.159	9.267	9.605	9.279	9.617	9.289	9.627	9.216	9.586	9.221	9.591	9.221	9.591
.125	.177							9.211	9.581				
.150	.194	9.255	9.593	9.266	9.604	9.286	9.264			9.214	9.584	9.221	9.591
.200	.224	9.240	9.578	9.257	9.595	9.279	9.617			9.212	9.582	9.217	9.587

* μ_s is the *ionic strength* due to added salt. The *concentration* of Na_2SO_4 or Na_2HPO_4 equals $\mu_s/3.00$; of sodium oxalate, $\mu_s/2.75$; of sodium succinate $\mu_s/2.65$; and of sodium citrate $\mu_s/4.8$.

** $a\sqrt{\mu} = 0.495\sqrt{\mu_o + \mu_s}$ where $\mu_o = 0.0031$ is the ionic strength without added salt.

TABLE IV

Effect of Salts of Dianions and Trianions on P_K' of Succinimide
(0.0100 M succinimide with 0.250 equivalent of NaOH (with NaCl 0.255 equivalents were added) and various amounts of salts; $P_K = 9.560$)

		With NaCl		With Na_2SO_4		Na_2HPO_4		Na_2 oxalate		Na_2 succinate		Na_3 citrate	
μ_s*	$a\sqrt{\mu}$**	P_H	P_K'	P_H	P_K'	P_H	P_K'	P_H	P_K'	P_H	P_K'	P_H	P_K'
0	0.025	9.055	9.521	9.055	9.531	9.055	9.531	9.057	9.533	9.056	9.532	9.054	9.530
0.0025	.035	9.052	9.518	9.032	9.508	9.032	9.508	9.018	9.494	9.011	9.476	9.022	9.498
.005	.043	9.035	9.501	9.020	9.496	9.023	9.499	8.991	9.467	8.989	9.465	9.007	9.483
.010	.055	9.007	9.473	9.010	9.486	9.007	9.483	8.956	9.432	8.969	9.445	8.986	9.462
.025	.082	8.969	9.440	8.985	9.461	8.995	9.471	8.902	9.378	8.937	9.413	8.954	9.430
.050	.114	8.929	9.395	8.963	9.439	8.979	9.455	8.864	9.340	8.917	9.393	8.925	9.401
.075	.138							8.842	9.318				
.100	.159	8.895	9.361	8.951	9.427	8.961	9.437	8.822	9.298	8.881	9.357	8.910	9.386
.125	.177							8.827	9.303				
.150	.195	8.868	9.334	8.931	9.407	8.947	9.423			8.868	9.344	8.903	9.379
.200	.223	8.848	9.314	8.915	9.391	8.938	9.414			8.849	9.325	8.893	9.364

* μ_s is the ionic strength due to added salt. The concentration of Na_2SO_4 or Na_2HPO_4 equals $\mu_s/3.00$; of sodium oxalate, $\mu_s/2.75$; of sodium succinate, $\mu_s/2.65$; and of sodium citrate, $\mu_s/4.8$.

** $a\sqrt{\mu} = 0.495\sqrt{\mu_o + \mu_s}$ where $\mu_o = 0.0025$ is the ionic strength without added salt.

$$P_{K_2}' = P_H - \log \frac{\alpha_P}{1 - \alpha_P}$$

f is calculated from: $f = 10^{P_K' - P_K}$ where $P_K = 7.020$

k is calculated from: $k = c_0 \frac{f}{1-f}$ where $1 - f$ is the fraction of $HPO_4^{=}$ inactivated by glycine.

VII. Summary

1. The presence of glycine *lowers* the value of P_{K_2}' of H_3PO_4, this effect being antagonized by increasing concentrations of salts.

2. With increasing amounts of glycine the drop in $HPO_4^{=}$ activity per increment of glycine added is found to reach and pass a maximum, indicating that neutral glycine inactivates $HPO_4^{=}$ ion. This obeys a mass action formula: $k = C_G \frac{f}{1\text{-}f}$ where $1\text{-}f$ is the fraction of $HPO_4{=}$ inactivated by glycine, and C_G is the concentration of glycine.

3. Na_2HPO_4 was correspondingly found to *increase* P_{K_2}' of glycine (as would be expected). A similar effect on glycine is produced by Na_2SO_4.

4. In concentrations approaching 0.2μ sodium oxalate, sodium succinate and sodium citrate give curves parallel to that of Na_2HPO_4, in their tendency to increase P_{K_2}' of glycine. However 0.01μ of these salts tend to decrease P_{K_2}' of glycine in the order:

oxalate > succinate > citrate > phosphate > sulfate

This order does not agree with the size of the respective ions or with the distance between the charges.

5. The above salts produce the same effects on P_K' of succinimide (a weak acid) as they do on P_{K_2}' of glycine. The curves are qualitatively the same; are in the same sequence; but are more separated.

A MECHANICAL MODEL OF AN ASYMMETRIC CARBON ATOM

BY H. G. TANNER

It has been pointed out by Le Bel and van't Hoff independently that optically active liquids and vapors were usually composed of molecules containing a chemically asymmetric carbon atom. Most of the experimental work which has followed their publications has been strictly chemical in its aspect. The evidence, taken as a whole, is very convincing that the optical rotational effect is localized about certain atoms rather than molecules. However, the fact that a molecule possesses an atom asymmetric from the chemical point of view is alone incapable of explaining such data as the variation of optical rotation with temperature, concentration, solvent, wavelength, etc. Light is an electromagnetic phenomenon, and since chemical formulas do not express electromagnetic characteristics of matter, an explanation of optical rotation can never be based upon purely chemical reasoning. On the other hand, the presence of a chemically asymmetric carbon atom in a molecule will without doubt remain a very practical indication of optical rotation.

Numerous physical and mathematical theories have been offered in explanation of optical rotation. In all cases an asymmetric structure of some sort has been assumed. This paper describes the construction and functioning of a mechanical model of an "asymmetric" carbon atom, the analogy being based upon the single postulate that electrodynamical asymmetry of the four valence "bonds" is responsible for the optical activity of the "asymmetric" carbon atom. It is hoped that through the study of this mechanical model a clearer understanding of optical rotation generally as well as specifically can eventually be evolved.

Valence bond electrons are known to function as electrical oscillators. Let the four valence "bonds" about a carbon atom be asymmetric in their tendencies to oscillate. When light disturbs such a system the four "bonds" will be forced to oscillate at the frequency of the incident light. By hypothesis their maxima of reaction will return to the central point at slightly different time intervals. This will cause a change in the phase relationships of the incident wave, and thereby orient the plane of vibration.

Although the valence "bond" itself may be regarded as an electrical oscillator, it is actually only a part of a complex electrical system. Its electrical freedom is undoubtedly determined to a large extent by the atomic structures on each "end." The "bond" is the connection between two complex electrical systems which include not only the contiguous atoms but all of the atoms of each radicle, should they be complex radicles. Position of the atom in a radicle would also be expected to affect the electrical characteristics of the "bond" between the radicle and the asymmetric carbon atom. The importance of chemical asymmetry in conjunction with optical rotation is thus explainable by this theory. It seems reasonable to suppose too, that attractions of solute and solvent molecules, temperature, etc., would affect the electrical characteristics of each of the four radicles about the carbon atom more or less independently. If therefore, the oscillatory characteristics of the valence "bonds" joining the asymmetric carbon atom with its radicles be functions of the electrical stresses and strains in the latter, and if optical rotation depends upon these oscillatory characteristics, then a qualitative explanation can be offered for most and perhaps all of the data concerning optically active solutions.

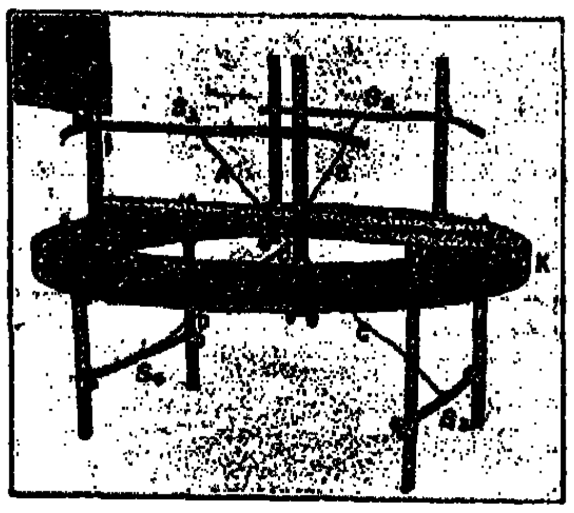

FIG. 1

If the above theory is to be tested by the construction and study of a model it would be desirable from the standpoint of directness to employ a model that would function electrically. This would necessitate the use of short radio waves as the beam of "light," and perhaps an asymmetric set of antennae to serve as the "asymmetric" carbon atom. Such an arrangement, however, would be very inconvenient of manipulation, and the functioning of this "atom" would have to be made visible by indirect means. For reasons, therefore, of simplicity, convenience, and visibility a mechanical analogy was adopted instead.

The accompanying photograph shows the atom model detached from the flexible "wave-cable" which passed vertically through the center of the "atom." Four springs S_1, S_2, S_3, and S_4, are stretched between steel posts appropriately arranged in a wood ring, K. The springs may be adjusted to any desired degree of tension, and are held by sliding sleeve clamps. Usually they were adjusted so as to be distinctly asymmetric in their degree of tension. Judged by the sounds emitted when plucked their fundamental frequencies lay between 10 and 150 per second.

Attached to the centers of these springs are four stiff wires A, B, C, and D. These wires meet at the central point O, (corresponding to the asymmetric carbon atom kernel), at which point they were attached by adhesive tape to the "wave-cable" (not shown). For convenience in defining directions these wires will subsequently be termed "valence wires" since they have the directions of the conventional carbon valence "bonds."

The cable in which the waves were produced was 13 meters in length. made of No. 16 B. and S. gauge steel wire closely wound into a helix 9 mm. in diameter. The upper end was attached to the mechanism for producing the waves. A reciprocating motion produced the linearly ("plane") polarized waves. A frequency of 150 per minute was used. The wavelength was approximately 2 meters. When circularly polarized waves were desired the cable was attached by means of a ball bearing support to a horizontal wheel which could be rotated at any desired speed in either direction. In the experiments described below only one speed, 150 rpm, was used. The ball bearing support prevented the cable being twisted when the wheel was rotated.

The "atom" was affixed about midway down the length of the cable. Originally it was intended that several asymmetric "atoms" be "strung" on the cable in order that racemization effects could be studied, but it was found that the cable was of insufficient length to permit the effects of more than one "atom" to be observed satisfactorily. About half of the length of the cable was required for the waves to become true in form, and the remainder was required for their observation after having passed through the "atom".

Much difficulty was encountered in preventing reflection of waves from the lower end of the cable. The trouble was finally overcome by wrapping the last three meters of its length with "electricians' friction tape" and surrounding it with a sheet metal cone of gentle taper. The cable terminated in the apex of the cone and the latter was anchored to the basement floor. Waves entering this cone were very effectively absorbed.

When linear waves were being used the "atom" rested upon a wood frame of such construction as to allow the "atom" to be tilted through an angle of 60° or oriented around a vertical axis 180°.

Using linear waves, and setting the "atom" in a horizontal position as shown in the photograph, the following observations were made.

(1) Waves passed through without orientation or change of form if the plane of the incident beam coincided with either of two planes of the "atom" containing AOB or COD respectively. These are planes of easy vibration and are two of the six planes of geometrical symmetry of the "atom." Undoubtedly the other four would act similarly.

(2) When the plane of the incident beam did not coincide with either of these two above mentioned planes of the "atom" the emergent wave was elliptical in shape, and the major axis of the ellipse was oriented relative to the plane of the incident beam. The direction of orientation was sometimes clockwise and sometimes counterclockwise.

(3) The direction of rotation of the emergent elliptical wave was always the same as the direction of the orientation of its major axis.

(4) If the springs S_3 and S_4 were weaker than S_1 and S_2, and the plane of the incident waves was midway (in either pair of quadrants) between the planes AOB and COD, the emergent wave had its major axis oriented toward COD. If S_1 and S_2 were made the weaker pair of springs, and the incident beam in the same position as before, the emergent wave had its major axis oriented toward AOB.

Although the emergent wave in each case was oriented toward the plane of greater "weakness" in the "atom," it would be unsafe to draw a general conclusion until the effect has been studied with resonance considerations, for it may be that the wave would be oriented toward a plane through the "atom" in which there is a greater approach toward resonance.

(5) Moderate changes in the angles between the "valence wires" produced no observed change in behavior. Perhaps there was so much distortion of these angles when the "atom" was in motion that distortion in the stationary shape of the "atom" was of negligible consequence.

Since the incident wave was oriented clockwise by the "atom" in some positions, counterclockwise in other positions, and not at all in still other positions,[1] in order to determine whether or not the mechanism was asymmetric in its transmissive characteristics, the sum of the tendencies to orient the waves in each direction had to be determined. Direct measurements of the angles of orientation for many different positions of the "atom" relative to the plane of the incident beam were attempted, but their accuracy was insufficient to warrant conclusions. A more sensitive test was therefore devised. This test was an application of Fresnel's corollary[2] that an optically active substance should transmit with greater ease circularly polarized light rotating in one direction than light rotating in the reverse direction.

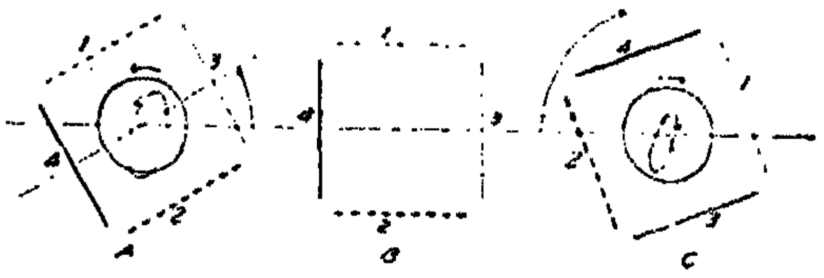

FIG. 2

If matter be not perfectly transparent circularly polarized light will tend to rotate matter, and the greater the resistance offered to transmission the greater will be the torque. It follows from Fresnel's corollary, therefore, that an optically active atom (molecule) should have a greater tendency to be rotated by circular light of one direction than of the other.

To determine the relative resistances of the mechanical "atom" for the transmission of the two oppositely rotating circular waves the "atom" was suspended by four vertical strings two meters long. The arc through which the "atom" itself was rotated became a measure of the resistance for the transmission of circular waves.

Fig. 2 shows diagramatically the positions which the "atom" assumed when circular waves of the two directions were passed through it. The projections are made as though the plane of the paper passed horizontally through the center of the "atom." The solid lines of the square represent the two upper springs, and the dashed lines the two lower springs. They are numbered in the order of their tension, number 1 being the spring under greatest tension. The inscribed eccentric ellipse is an approximate projection of the path traversed by the point of attachment of the "valence wires" to the cable.

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[1] A similar behavior for an optically active molecule was hypothesized by J. F. W. Herschel many years ago. Trans. Cambridge Phil. Soc., 1, 43 (1822).

[2] Fresnel: Ann. Chim. Phys., 25, 147 (1825).

This line therefore describes the form of the emergent wave also. The circle represents the incident wave form. Arrows indicate directions when looking downward along the line of wave propagation.

When counterclockwise circular waves were used the "atom" was rotated through an arc of 30°, as indicated by A. B shows the position of the springs and the "atom" when at rest. C indicates the effects of clockwise waves. In this case the "atom" was oriented 70°. These data conform with the deduction from Fresnel's corollary surprisingly well.

Additional evidence that the mechanism was functioning asymmetrically toward the two species of circular waves came from the observation that there was more confusion in the incident beam (due to reflection from the "atom") when clockwise waves were used than when counterclockwise waves were employed. The latter proceeded through the "atom" smoothly and with less diminution in amplitude.

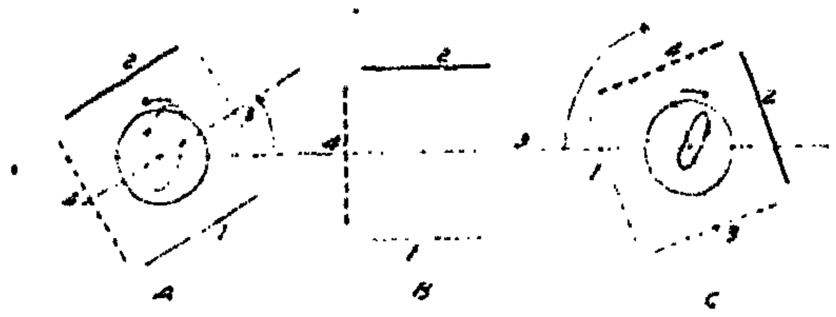

FIG. 3

The strongest evidence, however, that the "atom" was functioning asymmetrically, came when the above experiments were repeated with the "atom" inverted. The "atom" still transmitted preferentially the counterclockwise waves. Furthermore the relative resistances for the two kinds of waves was the same, within the accuracy of measurement. The data are summarized by Fig. 3 in which A, B, and C have interpretations corresponding with Fig. 2. The numbers identify the same springs.

It might be added that since the asymmetry of the "atom" was a function of the relative spring tensions, the effects upon incident waves could be increaed or decreased in magnitude, or reversed in direction merely by changing the tensions of the springs, or reversing their relative order.

Summary

Based upon the postulate that electrodynamical asymmetry of the four valence "bonds" of the carbon atom is the fundamental cause of the optical activity of the chemically asymmetric carbon atom, a mechanically analogous model has been constructed. This mechanical "atom" rotated the plane of "plane" polarized mechanical waves, and transmitted preferentially one of the two species of circularly polarized waves.

*Department of Chemistry,
University of Oregon,
Eugene, Oregon.*

THE APPLICATION OF THE LOGISTIC FUNCTION TO EXPERIMENTAL DATA[*]

BY LOWELL J. REED AND JOSEPH BERKSON

An extensive use has been made of this function for the elucidation of research problems in many fields. Yet in almost all cases, the mathematical phases of the treatment have been faulty, with consequent cost to the precision and validity of the conclusions drawn. Indeed, in numerous instances that have come under our notice, erroneous inferences were drawn as a result of a misconception of certain mathematical characters of the function. We deem it important, for these reasons, that a review of the basic properties of the equation be made, and some methods for its analysis indicated, towards which end this paper is contributed.

The curve has been frequently referred to as that of an autocatalytic reaction, from the fact that Ostwald applied it to a class of chemical reactions subsumed by him under that term. As will be illustrated below, however, it is descriptive of processes, even in the field of chemistry, in situations where the concept of autocatalysis has no place. We would recommend, therefore, that the more general term "logistic," which does not commit it to any specific mechanism, be retained in its stead.

The equation expressing the function is as follows:

$$y - d = \frac{K}{1 + Ce^{rt}} \qquad (1)$$

Logarithmically expressed it is

$$\ln \frac{K - (y - d)}{y - d} = \ln C + rt \qquad (2)$$

The differential form is

$$\frac{dy}{dt} = \frac{r}{K}[y - d][K - (y - d)] \qquad (3)$$

y is the dependent variable

t is the independent variable

K, d, r, and C are parameters

ln signifies the logarithm to the base e

K is the distance between two asymptotic values of y, and so demarks the range of the limiting values of y.

The quantity d is a constant which must be algebraically subtracted from y; it is this difference which varies logistically with t. In an experimental

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[*] This paper is issued jointly from the Department of Biometry and Vital Statistics and the Institute for Biological Research of the Johns Hopkins University. It constitutes No. 148 in the numbered series of publications of the Department of Biometry and Vital Statistics.

situation, one may think of d as an element incorporated gratuitously with each observational determination of y, itself not subject to the changes taking place during the course of the experiment. In many experiments, there is no such element, and $d = 0$.

r is a parameter associated with the intrinsic rate of the reaction; it is in fact K times the rate at which y is changing, expressed as a fraction of the product of $(y - d)$ by the difference between K and $(y - d)$.*

C is a constant of integration, depending mathematically on the choice of origin for the axis, and varying in any experiment with the value of the initial observation. It will simplify the presentation that follows, to assume its value as unity, and to discuss the significance of a departure from this value when we consider the experimental applications.

Description of the Function

The appearance of the function will change as the parameters assume different values. We shall consider the various possibilities seriatim.

*Case 1*** Figure 1.

$d = 0 \qquad C = +1 \qquad r = \pm$

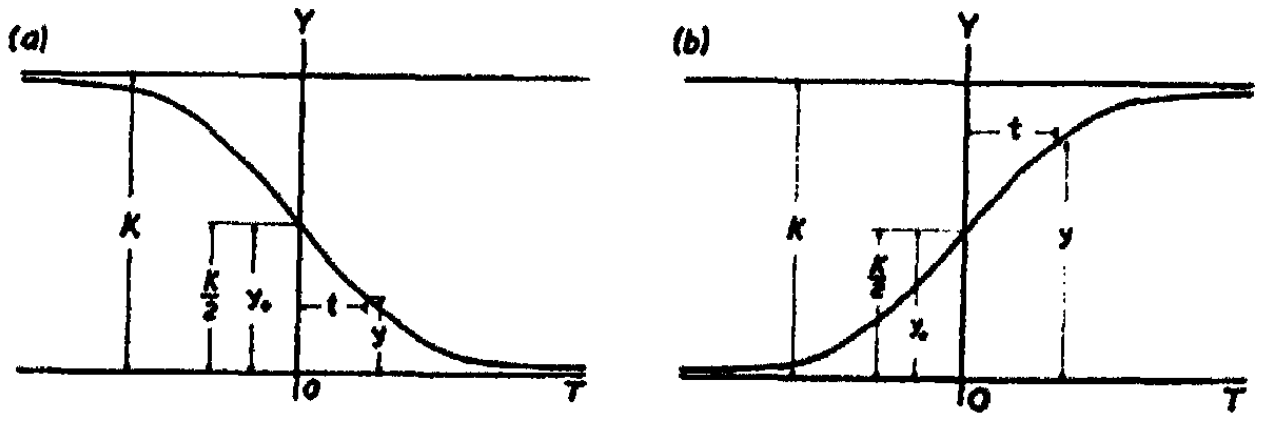

FIG. 1
Logistic for Case 1

$$y = \frac{K}{1 + e^{rt}} \qquad (4a) \qquad\qquad y = \frac{K}{1 + e^{-rt}} \qquad (4b)$$

$$\ln \frac{K - y}{y} = rt \qquad (5a) \qquad\qquad \ln \frac{K - y}{y} = -rt \qquad (5b)$$

$$\frac{dy}{dt} = -\frac{r}{K}(y)(K - y) \qquad (6a) \qquad\qquad \frac{dy}{dt} = +\frac{r}{K}(y)(K - y) \qquad (6b)$$

The following characters are notable:

(1) There are two asymptotes parallel to T axis, a lower at $y = 0$, and an upper at $y = K$.

(2) At the point where $t = 0, y = y_0 = K/2$; (7)

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* Vide equation (3).

** K will be assumed positive in all the cases to be considered. Where it is negative, the equation may be transformed by suitable rotation of the axis of reference to one of the forms with K positive, and is omitted from the discussion here.

At this point the curve has a point of inflection and the slope dy/dt is a maximum.

(3) For (a) $y_{-\infty} = +K$, and $y_{+\infty} = +0$ (8)
For (b) $y_{-\infty} = 0$, and $y_{+\infty} = K$ (9)

(4) The form (b) is the form (a) rotated about the Y axis. At any point t, the distance from the upper asymptote to (a), is equal to the distance from the lower asymptote to (b).

(5) The slope of the curve is at any point proportional to the product of the distances of the point from the lower and upper asymptotes.

(6) The curve has a point of symmetry at $t = 0, y = K/2$; if one-half of the curve is rotated about this point through an angle of 180°, it will coincide with the other half.

Case 2. Figure 2.

$d = +$ $C = +1$ $r = \pm$

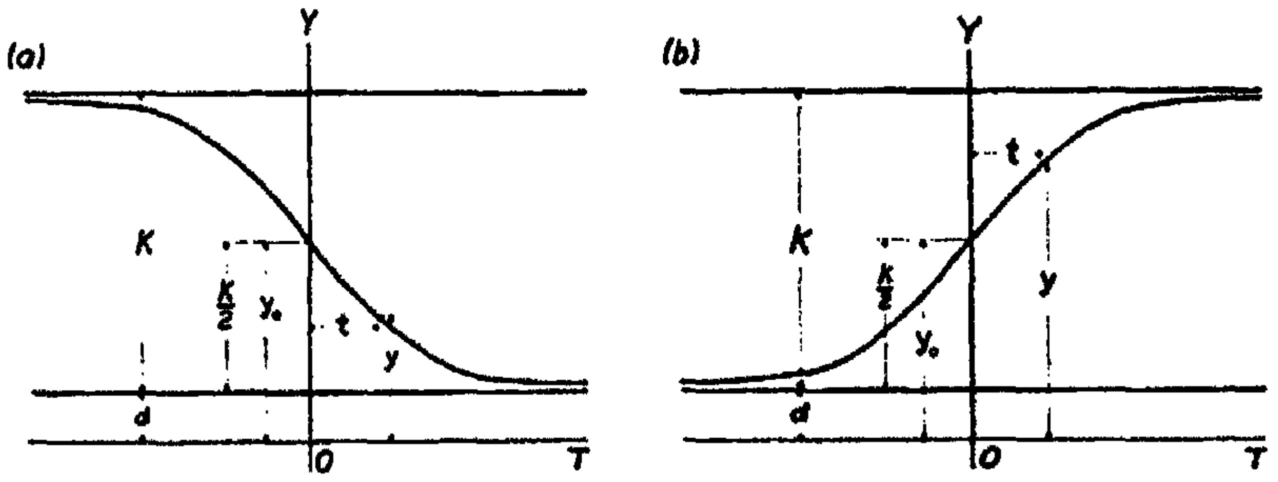

FIG. 2
Logistic for Case 2

$$y - d = \frac{K}{1 + e^{rt}} \qquad (10a) \qquad\qquad y - d = \frac{K}{1 + e^{-rt}} \qquad (10b)$$

$$\ln \frac{[K - (y - d)]}{y - d} = rt \qquad (11a) \qquad\qquad \ln \frac{[K - (y - d)]}{y - d} = -rt \qquad (11b)$$

$$\frac{d(y-d)}{dt} = \frac{dy}{dt} = -\frac{r}{K}[y - d][K - (y - d)] \qquad (12a)$$

$$\frac{d(y-d)}{dt} = \frac{dy}{dt} = +\frac{r}{K}[y - d][K - (y - d)] \qquad (12b)$$

Here we note;

(1) That forms (10a) and (10b) result respectively from (4a) and (4b), when the T axis is moved in the Y direction, a distance equal to minus d. Hence, they are exactly these equations with the quantity $(y - d)$ substituted for y.

(2) Where $t = 0, y = y_0 = K/2 + d$ (13)
(3) For form (a) $y_{+\infty} = +d$, $y_{-\infty} = K + d$ (14)
For form (b) $y_{+\infty} = K + d$, $y_{-\infty} = d$ (15)

(4) There are two asymptotes K distance apart as before, but the lower one is at $y = d$, not zero.

(5) The movement of the T axis has been represented as in the minus direction, and this corresponds experimentally to the addition of a constant element d to each observation. An analogous situation exists, if in a logistic process, each observation excludes a fixed quantity d. This corresponds geometrically to the movement of the T axis in a plus direction, and the relations given in this section would then hold with the sign of d changed from minus to plus.

Case 3.

Figure 3.

$d = 0 \qquad C = -1 \qquad r = \pm$

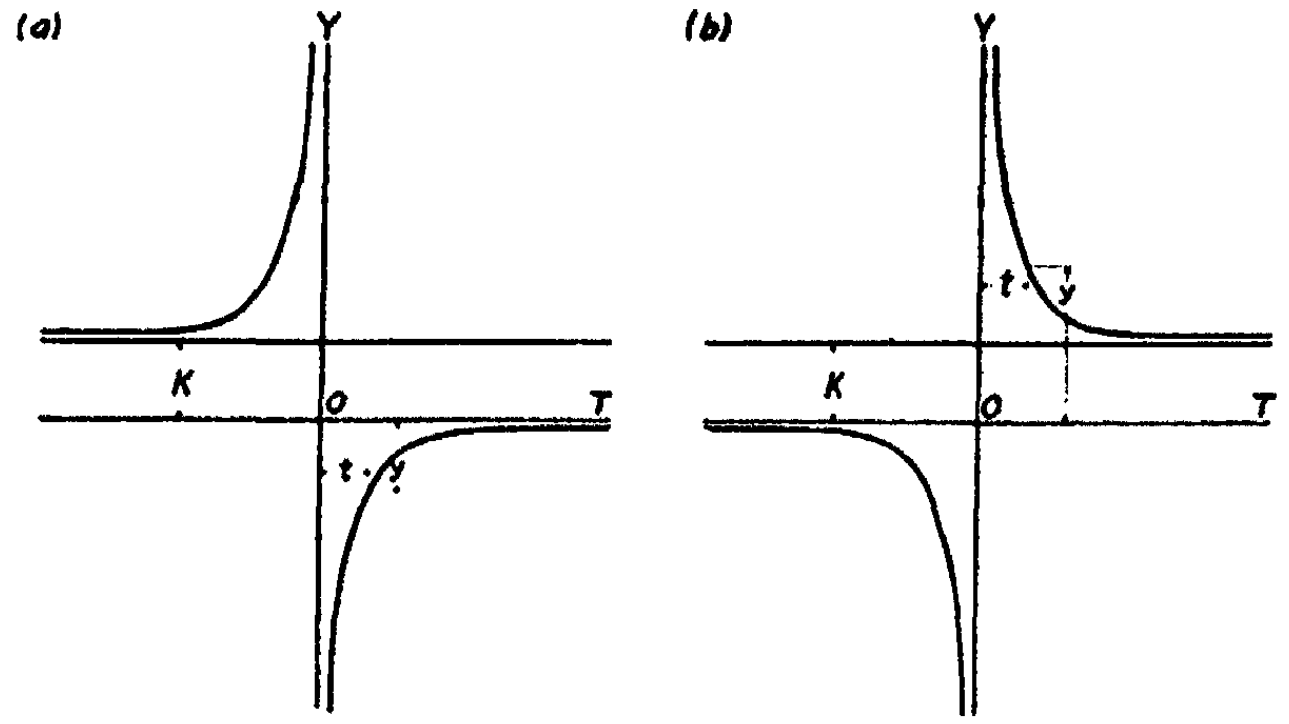

Fig. 3
Logistic for Case 3

$$y = \frac{K}{1 - e^{rt}} \qquad (16a) \qquad\qquad y = \frac{K}{1 - e^{-rt}} \qquad (16b)$$

$$\ln \frac{y - K}{y} = rt \qquad (17a) \qquad\qquad \ln \frac{y - K}{y} = -rt \qquad (17b)$$

$$\frac{dy}{dt} = \frac{r}{K}(y - K)y \qquad (18a) \qquad\qquad \frac{dy}{dt} = -\frac{r}{K}(y - K)y \qquad (18b)$$

We note here that:

(1) The two forms (16a) and (16b), though very different in geometric appearance from (4a) and (4b), bear a close resemblance to them analytically. They result from the latter, in fact, if the sign in the denominator be changed to minus.

(2) There are three asymptotes, two in a direction parallel to the abscissa, and one to the ordinate. The abscissal asymptotes are at a distance K apart, the lower at a position $y = 0$. The vertical asymptote is approached by both branches of the curve, one in the plus and the other in the minus direction.

(3) When $t = 0$, $y = y_0 = \pm\infty$ (19)

(4) For form (a) $y_{+\infty} = 0$, $y_{-\infty} = +K$ (20)

For form (b) $y_{+\infty} = +K$, $y_{-\infty} = 0$ (21)

(5) The point of inflection is at no real finite value of y. One cannot pass from minus to plus values of t without attaining infinite values of y. For $y = K/2$, as for all values of y between zero and K, t is imaginary.

(6) As in the corresponding form of (4), (b) may be obtained from (a) by rotation about the Y axis.

(7) The slope is proportional to $(y - K)$ instead of $(K - y)$ as in the previously considered forms. The quantity y is greater than K for all real values of y, an important distinguishing character of this form, and $y - K$ must, therefore, be a positive value.

Case 4. Figure 4.

$d = +$ $C = -1$ $r = \pm$

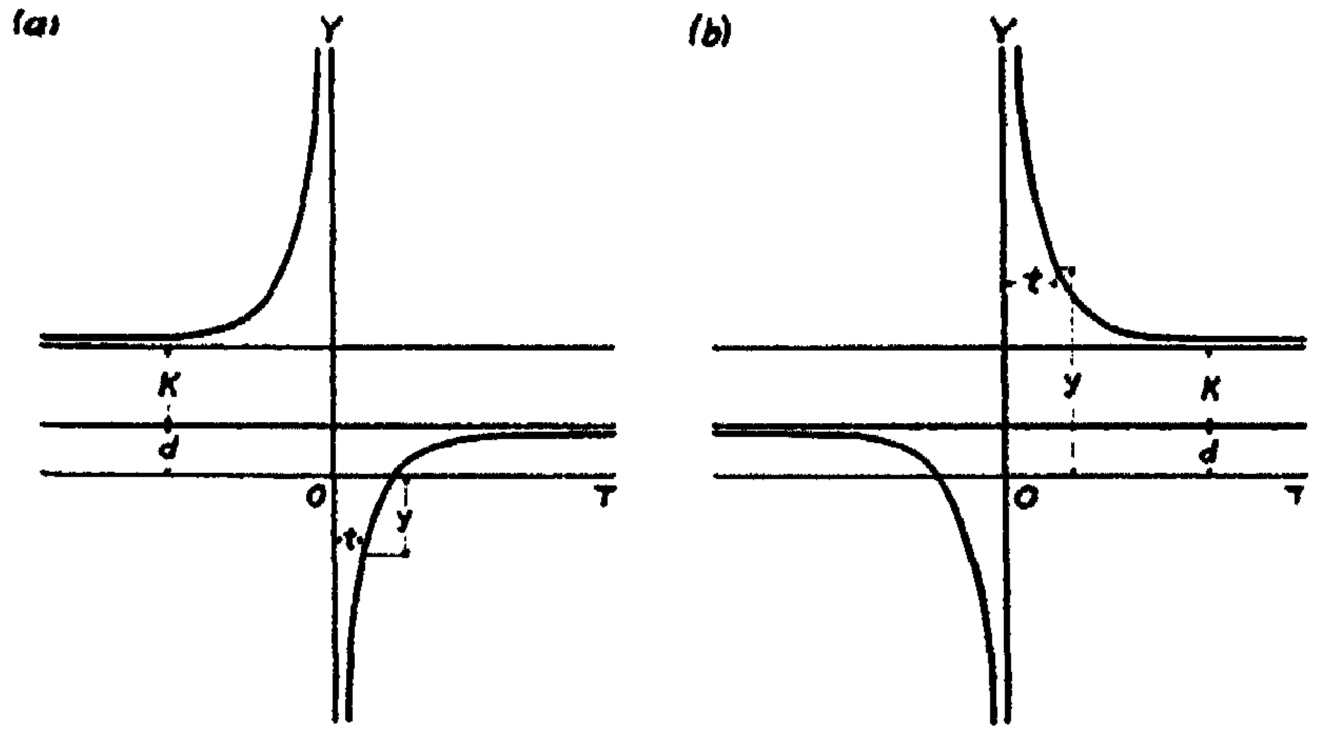

Fig. 4
Logistic for Case 4

$$y - d = \frac{K}{1 - e^{rt}} \qquad (22a) \qquad\qquad y - d = \frac{K}{1 - e^{-rt}} \qquad (22b)$$

$$\ln \frac{y - d - K}{y - d} = rt \qquad (23a) \qquad\qquad \ln \frac{y - d - K}{y - d} = -rt \qquad (23b)$$

$$\frac{d(y - d)}{dt} = \frac{dy}{dt} = \frac{r}{K}(y - d)(y - d - K) \qquad (24a)$$

$$\frac{dy}{dt} = -\frac{r}{K}(y - d)(y - d - K) \qquad (24b)$$

For these forms we note:

(1) That they bear the same relation to (16) that (10) does to (4).

(2) For form (a) $y_{+\infty} = d, \quad y_{-\infty} = d + K$ (25)

For form (b) $y_{+\infty} = d + K, \quad y_{-\infty} = +d$ (26)

Case 5. **Figure 5.**

$$d = 0 \qquad C = -1 \qquad r/K = \pm b \qquad K \doteq 0$$

If, in form (4) of the logistic function *r/K* be kept equal to a constant *b*, and *K* the distance between the abscissal asymptotes becomes smaller, approaching zero, the logistic approaches an hyperbola. The equation for this may be easily obtained by integration of form (6), setting $r/K = b$, and $K = 0$.

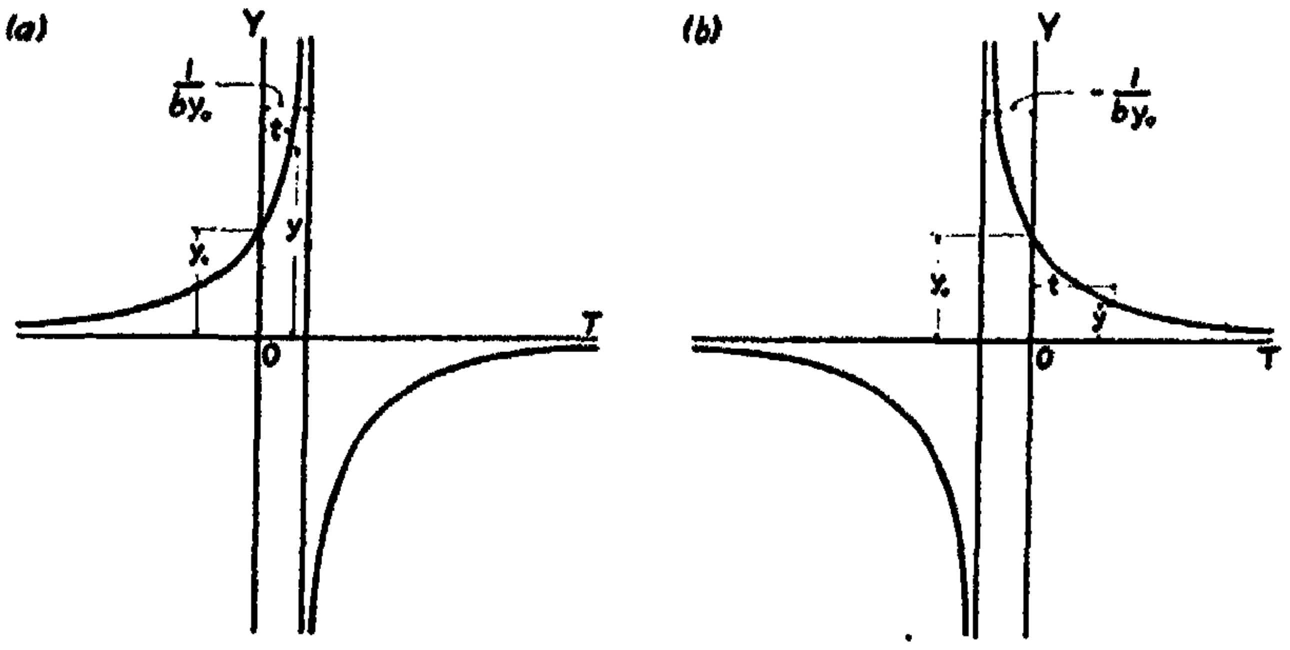

FIG. 5
Logistic for Case 5

$$-\frac{1}{y} = C_2 + bt \qquad (27a) \qquad\qquad -\frac{1}{y} = C_2 - bt \qquad (27b)$$

$$y = -\frac{1}{C_2 + bt} \qquad (28a) \qquad\qquad y = -\frac{1}{C_2 - bt} \qquad (28b)$$

$$\frac{dy}{dt} = by^2 \qquad (29a) \qquad\qquad \frac{dy}{dt} = -by^2 \qquad (29b)$$

b is a parameter that gives the rate at which *y* changes with *t* expressed as a fraction of y^2.

C_2 is a constant of integration which depends on the initial value of *y*. Here we note that:

(1) When $t = 0, y = y_0 = -1/C_2;\ C_2 = -1/y_0$ (30)

(2) When $t = \pm\infty, y = y_{\pm\infty} = 0$ (31)

(3) The curve has two asymptotes, one identical with the *T* axis, the other parallel to the *Y* axis; the latter intercepts the *T* axis at $t = +1/by_0$ for (a) and at $t = -1/by_0$ for (b).

Case 6. Figure 6

$d = +$ $C = -1$ $r/K = \pm b$

$$\frac{1}{d-y} = C_2 + bt \quad (32a) \qquad \frac{1}{d-y} = C_2 - bt \quad (32b)$$

$$y = d - \frac{1}{C_2 \pm bt} \quad (33a) \qquad y = d - \frac{1}{C_2 - bt} \quad (33b)$$

$$\frac{dy}{dt} = b\,(y-d)^2 \quad (34a) \qquad \frac{dy}{dt} = -\,b\,(y-d)^2 \quad (34b)$$

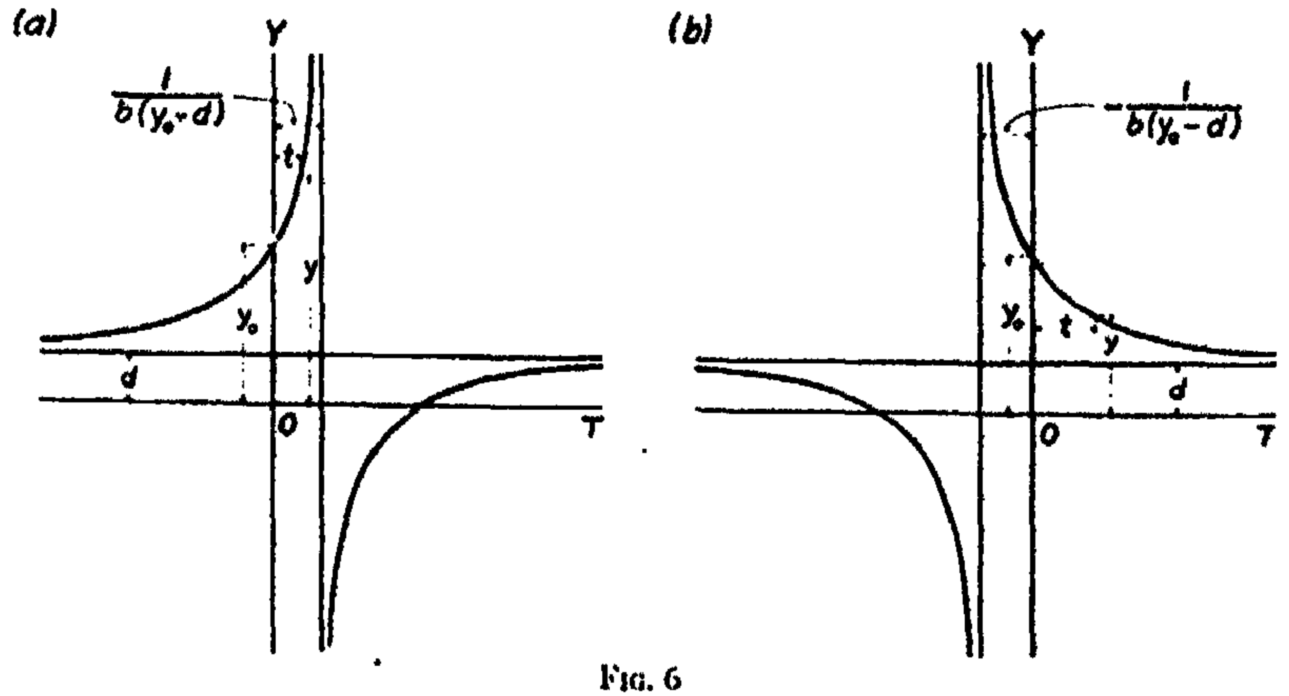

Fig. 6
Logistic for Case 6

C_2 and b are parameters of the same meaning as given for form (27). These forms are obtained from those given in 5 by movements of the T axis, similar to those discussed for cases 2 and 4.

Here we note:

(1) When $t = 0$, $y = y_0 = d - 1/C_2$ (35)

(2) When $t = \pm\infty$, $y = y^{\pm}_{\infty} = d$ (36)

(3) The curve has two asymptotes, one parallel to the T axis at $y = d$, the other parallel to the Y axis at $t = \frac{1}{(y_0 - d)b}$ for (a) and $t = -\frac{1}{(y_0 - d)b}$ for (b).

Determination of the Parameters

The method of least squares, when certain assumptions regarding the distribution of errors can be made, is mathematically the most proper. Against its use in practical problems involving the logistic curve, however, are the considerations, first that it is extremely difficult, and second that the basic conditions for its justification are seldom realized. For these reasons, we shall leave this method to one side and consider such technics as are readily applicable practically and which are fundamentally sound in methodology. In the following, we shall take up seriatim a number of such general methods, and then by application to concrete problems, indicate the mode of choice among them.

I—Logarithmic Graphic Method:

We assume $d = 0$, or its value known, y_∞ determinable with good approximation from experiment; we wish to determine K, r, and C.

The parameter K is determined from d, and observed or estimated values of y_∞. The relationship (9) (15) (21) or (26 is utilized according to the type of logistic function being fitted to the observations. With K thus fixed, a series of positive values, $K - y$, or $y - K$[*], depending on the relative sizes of K and y, are calculated, one for each observation of y, and from these in turn $\log \frac{K - y}{y}$ or $\log \frac{y - K}{y}$. The individual values in the resulting series are now plotted against corresponding values of t. Consideration of equation (2) will show that the relationship should be linear,[**] and the points will, except for experimental deviation, fall on a straight line. The "best" line is fitted by eye to the points.[***] From any two convenient points located on this line are determined the slope m, the intercept on the Y axis a, and from these the logistic parameters as follows:

$$r = 2.30259 \times m \tag{37}$$

$$C = \log^{-1} a \tag{38}$$

This method may be used advantageously also in many cases where K is not known, or any of the other parameters. An approximate value of K is assumed as the real value and $\log (K-y)/y$ vs. t plotted as explained. Generally a curvilinear relationship results. Changing K now, and plotting again, will give better linearity. By repeating this process, a value of K can be found that gives satisfactory linearity in the functional relationship (5), and this is taken as the value for K.

II—Function of (r, y, t) vs. y:

This method is available when r is known, and we are to determine K, C and d.

For the general logistic function (1) it may be shown that the following relationship obtains:

$$y = (1 + C)\,\frac{y_0 - ye^{rt}}{1 - e^{rt}} - d\,C \tag{39}$$

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[*] This assumes $d = 0$. When d is some value other than zero, substitute $(y-d)$ for y.

[**] If the logarithmic graph paper be available, the values of $\frac{K - y}{y}$ or $\frac{y - K}{y}$ may be plotted directly against t, a method equivalent to the one given in the text, but, practically, more rapid.

[***] One attempts in doing this to choose a line that minimizes the total deviations. The inexactness that might appear in such a method is not as serious as sometimes supposed. *A more rigid criterion, such as least squares, to be consistently rigid, requires an* analysis of the variable minimized, before its significance for a particular experiment is determined. Such an analysis would result generally in a weighting of the deviations, more or less complex, depending on the situation. Where such a weighing has not been evaluated, it seems supererogatory to overrefine the minimizing technic.

in which the symbols have the meanings given above.

It follows that the value $\frac{y_0 - ye^{rt}}{1 - e^{rt}}$ plotted against *y* is linear and from the resulting line the values of the logistic parameters determinable as follows:

Calculate the value of $\frac{y_0 - ye^{rt}}{1 - e^{rt}}$ for each observed value of *y*, and the corresponding *t*, and plot this vs. *y*. Fit the best line to the points by eye. Let the slope of this line be *m*, and its intercept on the *Y* axis *a*. The logistic parameters are evaluated from the following relations:

$$C = m - 1 \tag{40}$$

$$d = a/(1-m) \tag{41}$$

$$K = m\,(y_0 - d) \tag{42}$$

Where *r* is difficult to determine accurately, this method may be tried with several values of *r*, and that giving the best linearity in the function (39) used to fix the other parameters.

III—Slope of the Logarithmic Function vs. y.

We assume *d* = *0; K, r,* and *C* to be determined.

From (2) we have

$$\ln y = \ln (K - y) - rt - \ln C \tag{43}$$

and from this we may further prove

$$\frac{d(\log y)}{dt} = \pm \frac{r}{K} y - r \tag{44}$$

We may utilize this relationship for the evaluation of the parameters sought as follows:

Plot log *y* vs. *t*.* If the relationship between *y* and *t* be logistic, the points will fall curvilinearly according to (43). Draw the "best" curve to fit these points by eye. At particular values of *y*, over the entire range of the curve, determine the slope $= \frac{d(\log y)}{dt}$ graphically. Plot the values of the slope so determined vs. the corresponding values of *y*. This should result in the linear relation (44). Call the slope of this line *m*, and the intercept on the *Y* axis *a*. Then the parameters are determined as follows:

$$r = -a \tag{45}$$

$$K = a/m \tag{46}$$

$$C = (K - y_0)/y_0 \tag{47}$$

This method involves the graphical estimation of the slope of a curve drawn to a series of points by eye, and not very satisfactory for this reason. The linearity of the relationship (44) when plotted, depends on the judgment used in fitting the curve (43), and consequently so does the evaluation of the parameters.

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* or *y* vs. *t* on logarithmic graph paper.

An analytical form of this method of solution has been published by Hotelling.[1] It may be considered illustrative of many that may be worked out, by evaluating derivative functions of the logistic and treating these statistically. Of frequent occurrence in the literature, are cruder methods, involving analytically the same ideas, in which the weakness of the determinations are obscured by the more indirect calculations of the parameters.

IV—Parameters of the Hyperbola:

It was shown in Cases 5 and 6 that in certain situations where the logistic function held generally, special conditions would produce a degeneration of this to the hyperbolic form. In such instances, we may use relations (27) and (32) for the determination of the parameters, if d be 0 or known, as follows:

Plot $1/(d-y)$ vs. t. This should be linear. A line is fitted by eye, and from this the two unknown parameters b and C_2 determined as follows:

If m represents the slope of the fitted line and a the intercept on the Y axis

$$b = m \tag{48}$$

$$C_2 = a \tag{49}$$

Applications

We may now consider several problems to which the logistic function has been applied, for analysis from the point of view here presented.

1. Autocatalytic Reaction—Positive Autocatalysis

$$A \underset{\longleftarrow}{\overset{E}{\longrightarrow}} B + C$$

Substance A is transformed under the action of catalyst E into substance B and C; B itself acts catalytically for the same reaction, producing "autocatalysis."

Let A_o = original concentration of substance A
E_o = original concentration of catalyst E
y = concentration of B at time t
= also the concentration of C at time t.

Assuming that the reaction is practically unidirectional, and applying the mass rule, we have

$$dy/dt = c_1E_o(A_o-y) + c_2y(A_o-y) \tag{50}$$

where c_1 and c_2 are constants of proportionality in the reaction between catalyst and substrate. We have from this

$$\frac{dy}{dt} = c_2\,(A_o-y)\,(y + \frac{c_1}{c_2}E_o) = c_2\,[y + \frac{c_1}{c_2}E_o]\,[\,(A_o + \frac{c_1}{c_2}E_o) - (y + \frac{c_1}{c_2}E_o)\,] \tag{51}$$

(51) is recognized to be the differential form of the logistic (12b) in which

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[1] J. Am. Stat. Ass., 22, 283 (1927).

$$r = c_2K = c_2A_0 + c_1E_0 \qquad d = -\frac{c_1}{c_2}E_0 \tag{52}$$

$$K = A_0 + \frac{c_1}{c_2}E_0 = A_0 - d \tag{53}$$

We take the following example.[1] 1370 units of ethyl acetate are hydrolyzed, using acetic acid as catalyst, producing ethyl alcohol plus acetic acid; the latter product itself acts catalytically on the hydrolysis. Titrations of the concentration of acetic acid in excess of that originally present are made at successive intervals of t.

We have:

A_0 = units of ethyl acetate originally present = 1370
E_0 = units of acetic acid originally present = 1338
y = units of acetic acid at time t in excess of original

Since the catalyst and autocatalyst are the same, $c_1 = c_2$, and we have

From (52) $d = -E_0 = -1338$
From (53) $K = A_0 + E_0 = 2708$

$c_1 = c_2$ is unknown, and it remains to determine r and C. To this end we shall use Method I. (See Table I and Fig. 7).

$\log \dfrac{K+d-y}{y-d}$ is plotted vs. t; a line is fitted to the points by visual judgment (Fig 7) and from the slope and intercept

$r = -0.003716$ from (37)
$C = 0.9863$ from (38)

The equation now becomes

$$y = \frac{2708}{1 + .9863e^{-.003716t}} \tag{54}$$

The calculated and observed values are compared in Table I and Fig. 7.

TABLE I

t	y (observed)	$\log \dfrac{K-(y-d)}{y-d}$	y calculated from (54)
72	195	$\bar{1}.884$	205
144	377	$\bar{1}.763$	379
216	542	$\bar{1}.644$	540
288	687	$\bar{1}.528$	686
346	783	$\bar{1}.442$	787
432	911	$\bar{1}.310$	922

---

[1] W. Ostwald: J. prakt. Chem., 136, 481 (1883).

Supposing, in the same experiment, observations of the decreasing ester, instead of the increasing acid, were made; we then have

$$y' = A_0 - y$$

where y' is the concentration of ester at time t. Substituting in (51) we obtain

$$\frac{dy'}{dt} = -c_2\,[y']\left[\left(A_0 + \frac{c_1}{c_2}E_0\right) - y'\right] \tag{55}$$

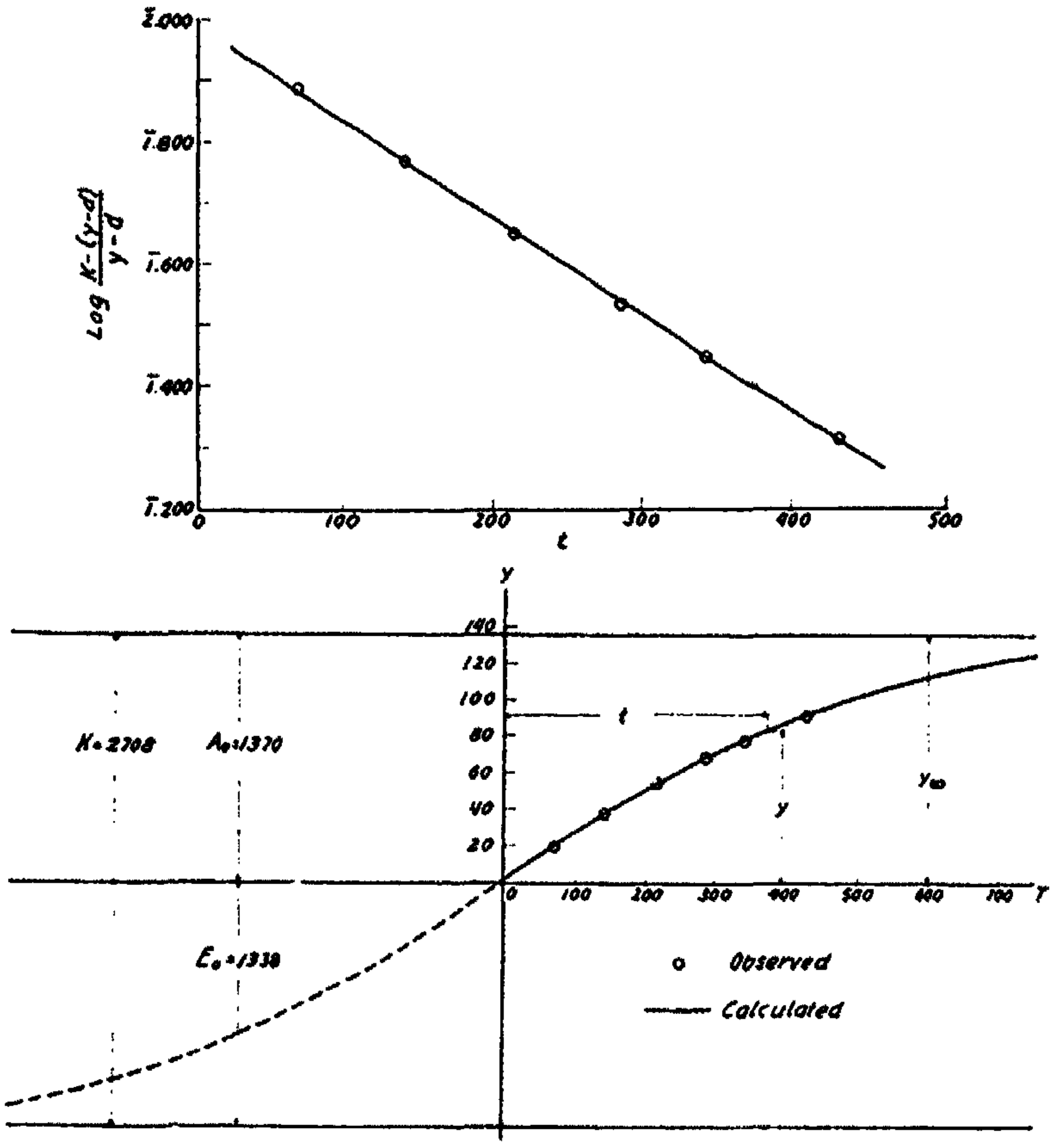

Fig. 7
Graphical Presentation, Example 1

Legend y = Units of acetic acid
t = time
A_0 = Ethyl acetate, original
E_0 = Acetic acid, original

which is form 6a. This is illustrative of the fact that forms (a) and (b) represent essentially the same changes; in one case a decreasing element is measured, in the other an accumulating one.

2. *Bimolecular Reaction*

$$A + B \rightleftarrows Y$$

Substances $A + B$ react bimolecularly to form Y. Let the initial concentration be A_0 and B_0, and y the concentration of Y at time t. Assuming $B_0 > A_0$, the mass law gives

$$dy/dt = C_1 (A_0 - y)(B_0 - y) \tag{56}$$

where C_1 is a constant of proportionality, depending on temperature, etc.

From (56) we may write

$$dy/dt = C_1 (y - A_0)[y - A_0 - (B_0 - A_0)] \tag{57}$$

(57) is seen to be the logistic of form (24) in which

$$K = B_0 - A_0 \quad d = A_0 \tag{58}$$

$$r = C_1(B_0 - A_0) \tag{59}$$

We take the following example.[1]

Methyl bromide and sodium thiosulphate were placed together for reaction and the following gives observations made of the quantities of the decreasing sodium thiosulphate.

A_0 = concentration of CH_3Br at the beginning of the experiment = 14.7 units

B_0 = concentration of $Na_2S_2O_3$ at the beginning of the experiment = 24.3 units

y = observed concentration of $Na_2S_2O_3$ at time t

$K = B_0 - A_0 = 9.6$ from (58)

Equation (22) applies and r is to be determined. We may utilize Method I with convenience since K is known. (See Table II, Fig. 8). Following the same procedure as that used for obtaining (54) we have

$$r = -.008455 \quad \text{from (37)}$$

$$C = .6047 \quad \text{from (38)}$$

The equation now becomes $y = \dfrac{9.6}{1 - .6047e^{-.008455t}}$ (60)

The calculated and observed values are compared in Table II and Fig. 8.

TABLE II

t	y (observed)	log (K-y)/y	y calculated from equation (60)
0	24.3	.7817	24.29
5	22.95	.7647	22.84
15	20.5	.7257	20.54
25	18.8	.6897	18.85
35	17.35	.6500	17.45
50	15.9	.5979	15.90
71	14.35	.5198	14.55
∞	9.6	.0000	9.60

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[1] Slator: J. Chem. Soc., 85, 1295 (1904).

3. Bimolecular Reaction with Equal Initial Concentration of Reactants. From (56), if $B_0 = A_0$ we have

$$dy/dt = c_1(A_0 - y)^2 \qquad (61$$

where c_1 is a constant of proportionality, from which by integration

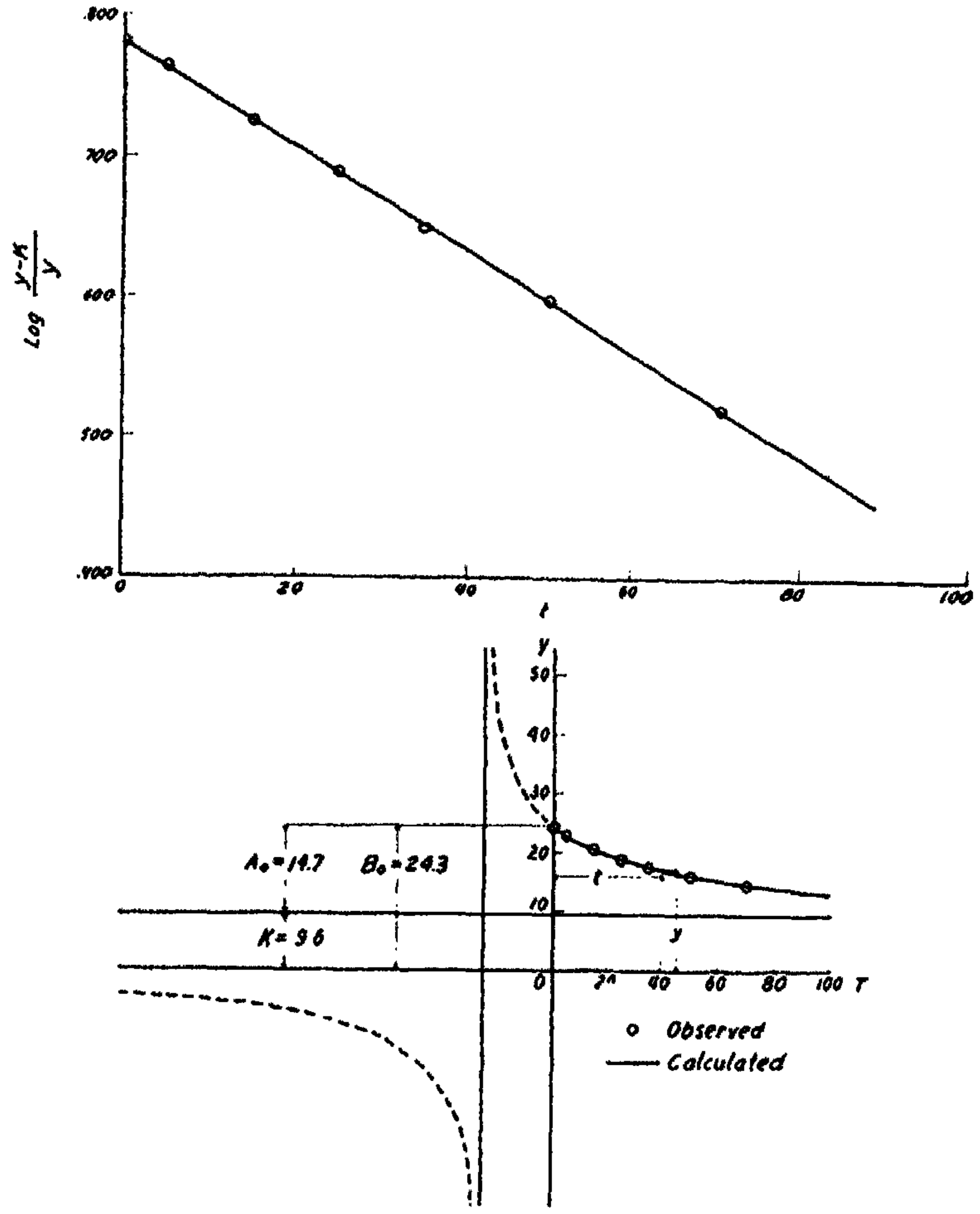

Fig. 8

Graphical Presentation, Example 2

Legend: y = Concentration $Na_2S_2O_3$
t = time
A_0 = Concentration CH_3Br, original
B_0 = Concentration $Na_2S_2O_3$, original

$$y = A_0 - \frac{1}{c_2 + c_1 t} \qquad (62)$$

where c_2 is a constant of integration that depends on the initial value of y. Form (62) is seen to be the hyperbolic form (33) in which

$$d = A_0 \qquad b = c_1 \qquad C_2 = c_2 \qquad (63)$$

We take the following example.[1]

Equivalent quantities of acetamide and hydrochloric acid in a water solution reacted to form ammonium chloride, and the progress of the reaction followed by observing at successive times t the amount of nitrogen produced as ammonium chloride.

$$A_0 = 26.80 \text{ (observed)}$$

We have now to determine b and C_2 and may conveniently use the method outlined under IV. (See Table III and Fig. 9).

$b = .000560$ From (48)

$C_2 = .035$ From (49)

The equation now becomes

$$y = 26.80 - \frac{1}{.035 + .000560t} \qquad (64)$$

The calculated and observed values are compared in Table III and Fig. 9.

TABLE III

t	y	$1/(A_0-y)$	y calculated from (64)
15	4.42	.044	3.54
30	7.53	.052	7.57
45	10.16	.060	10.13
60	12.13	.068	12.31
75	13.68	.076	13.81
90	14.97	.085	15.03
120	16.97	.102	17.00
150	18.40	.119	18.40
180	19.53	.138	19.45

4. Autocatalytic Reaction, Negative Autocatalysis.

If, in a catalytic reaction, one of the products acts as a "negative" catalyst, i.e., inhibits the main reaction, we have analogous to (50) the following

$$dy/dt = c_1E_0\,(A_0-y) - c_2y\,(A_0-y) = c_2\,(y - \frac{c_1}{c_2}E_0)\,(y-A_0) \qquad (65)$$

From which we may write

$$dy/dt = c_2\,(y - \frac{c_1}{c_2}E_0)\,[(y - \frac{c_1}{c_2}E_0) - (A_0 - \frac{c_1}{c_2}E_0)] \qquad (66)$$

This is seen to be form (24) in which

$$K = A_0 - \frac{c_1}{c_2}E_0 \qquad d = \frac{c_1}{c_2}E_0 \qquad r = c_2\,(A_0 - \frac{c_1}{c_1}E_0) \qquad (67)$$

An illustration is the following.[2]

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[1] W. Ostwald: J. prakt. Chem., 135, 14 (1883).

[2] J. Berkson and L. B. Flexner: J. Gen. Physiol., 9, 5, 433 (1928).

The proteolysis of gelatin by pancreatin was followed by measurements of the viscosity of the gelatin mixture. The time required for the flow of the mixture through a capillary was found to be a logistic function of the duration of the reaction, as follows:

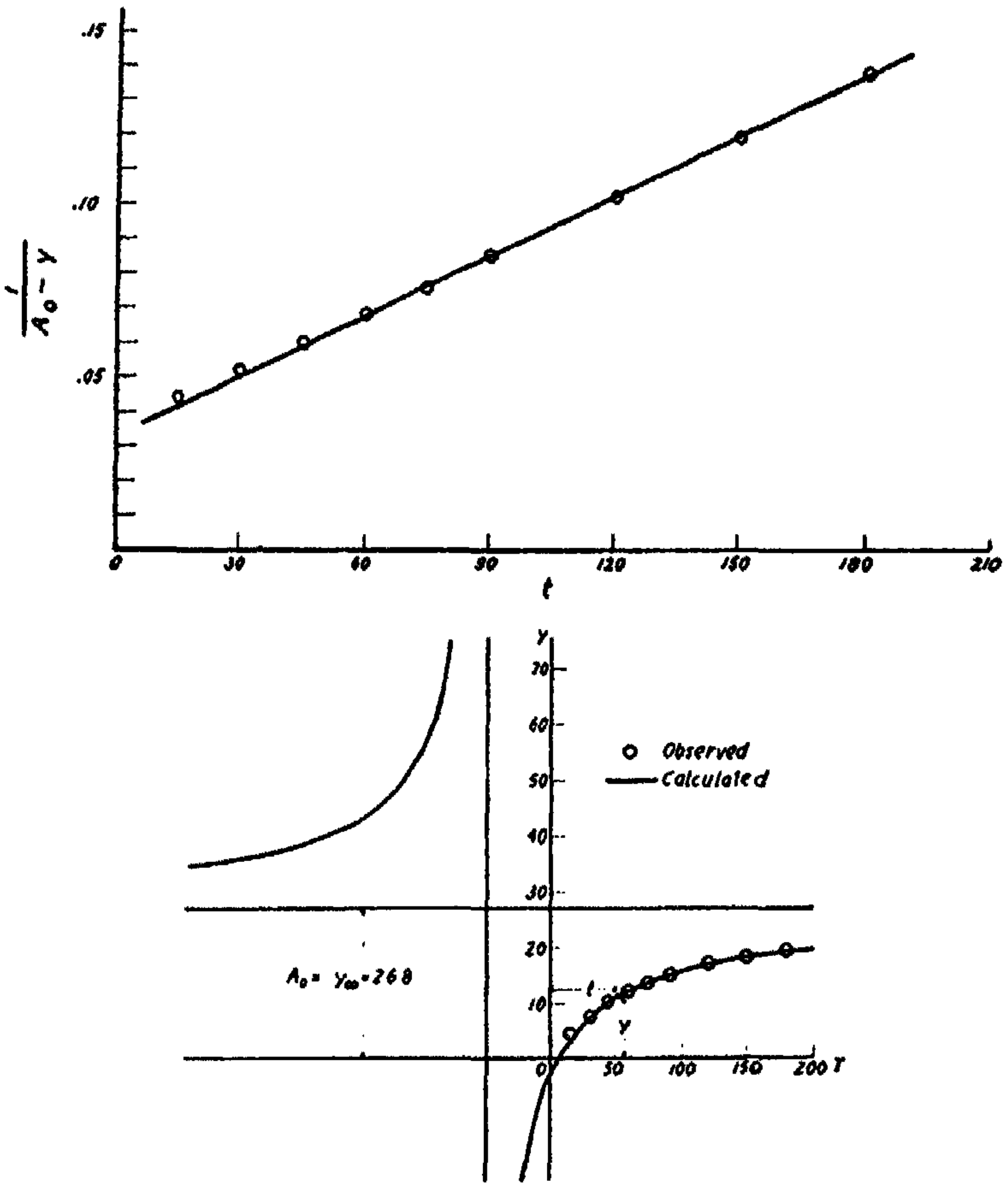

Fig. 9

Graphical Presentation, Example 3

Legend: y = N as NH_4Cl

t = time

A_0 = total N as NH_4Cl

$$y - y_w = \frac{y_f - y_w}{1 - \frac{y_0 - y_f}{y_0 - y_w} e^{-rt}} \qquad (68)$$

in which

y is the time of flow at time t

y_0 is the time of flow at $t = 0$

y_w is the time of flow of water

y_f is the time of flow when proteolysis is complete

This is seen to be the logistic of form (22) in which

$$K = y_t - y_w \qquad C = \frac{y_o - y_t}{y_o - y_w} \qquad d = y_w \tag{69}$$

From observation

$$y_t = 35.5 \qquad y_w = 29.5 \qquad y_o = 59.5$$

It remains to determine r. This is accomplished by use of Method I. (See Table IV and Fig. 10).

$$r = -0.006581 \qquad \text{from (37)}$$

$$K = 6 \qquad C = 0.800 \qquad \text{from (69)}$$

The equation now becomes

$$y = \frac{6}{1 - .800e^{-0.006581t}} + 29.5 \tag{70}$$

The calculated and observed values are compared in Table IV and Fig. 10.

TABLE IV

t	y (observed)	$\log \frac{y-d-K}{y-d}$	y calculated from equation (70)
0	59.5	$\bar{1}.9031$	59.5
4.5	56.3	$\bar{1}.8901$	56.4
10.0	53.2	$\bar{1}.8732$	53.4
14.5	51.3	$\underline{1}.8602$	51.5
19.5	49.6	$\bar{1}.8459$	49.8
24.25	48.4	$\bar{1}.8342$	48.4
29.5	47.2	$\bar{1}.8202$	47.1
34.25	46.0	$\bar{1}.8035$	46.1
40.75	45.0	$\bar{1}.7873$	45.0
46.5	44.4	$\bar{1}.7762$	44.1

5. *Oxidation and Reduction Potentials.*

The equation governing the electrode potentials in an oxidation-reduction reaction is given as follows:[1]

$$E_h = E_o' - \frac{RT}{nF} \ln \frac{S_r}{S_o} \tag{71}$$

in which

E_h = observed electrode potential measured against a hydrogen electrode
E_o' = a constant characteristic of the particular system
$R, T, F,$ = constants
n = the number of molecules involved
S_r = concentration of the reductant
S_o = concentration of the oxidant

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[1] W. Mansfield Clark: U. S. Pub. Health Rep., 38, 943 (1923).

If we denote by $K = S_o + S_r$, the total amount of substance involved in the reaction and by c the constant RT/nF, we may rewrite (71) as follows:

$$\ln \frac{K - S_r}{S_r} = -E_0'/c + 1/c\,E_h \qquad (72)$$

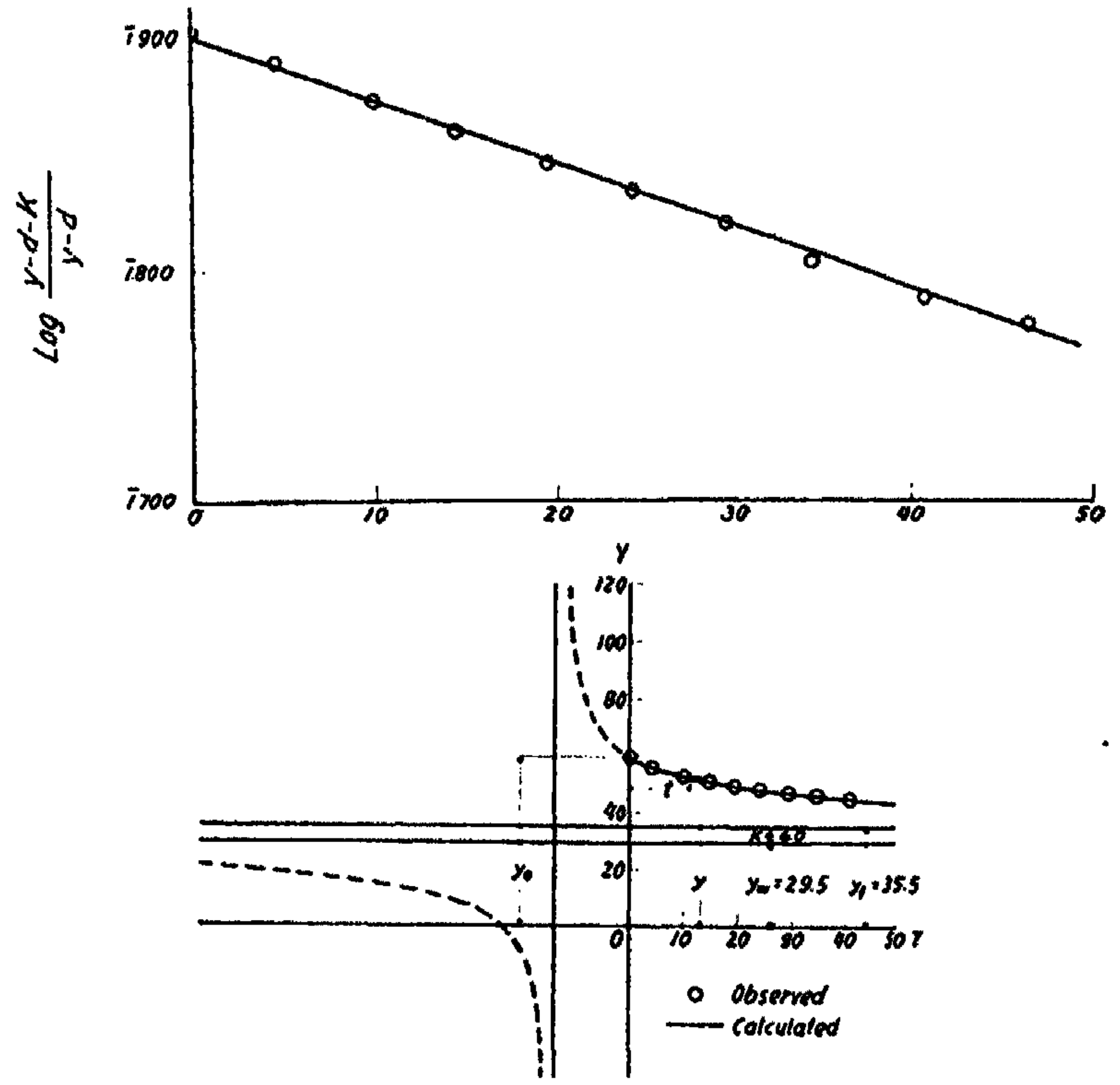

Fig. 10
Graphical Presentation, Example 4
Legend: y = viscosity, time of flow
t = time
$y_w = -d$ = viscosity for H_2O
y_f = viscosity, final

This is seen to be the logistic of the form (E_0') in which

$$y = S_r \qquad t = E_h \qquad r = 1/c \qquad \ln C = -E_0'/c \qquad (73)$$

We take the following example.[1]

1-napthol-2-sulphonate indophenol was reduced by addition of titanous chloride and the electrode potentials observed. The number of molecules involved, n, was independently determined as 2. It is desired to determine E_0'. Since $r = nF/RT$ is known, Method II can be conveniently used. It will be necessary to assume some single observation as y_o, and we choose one in the middle of the series at $y = 16$.

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[1] W. Mansfield Clark: U. S. Pub. Health Rep., 38, 946 (1923).

$r = 76.57889$ — constant

$\frac{y_0 - ye^{rt}}{1 - e^{rt}}$ vs. y is plotted (see Table V and Fig. 11) and from the slope m, K and C are determined as follows:

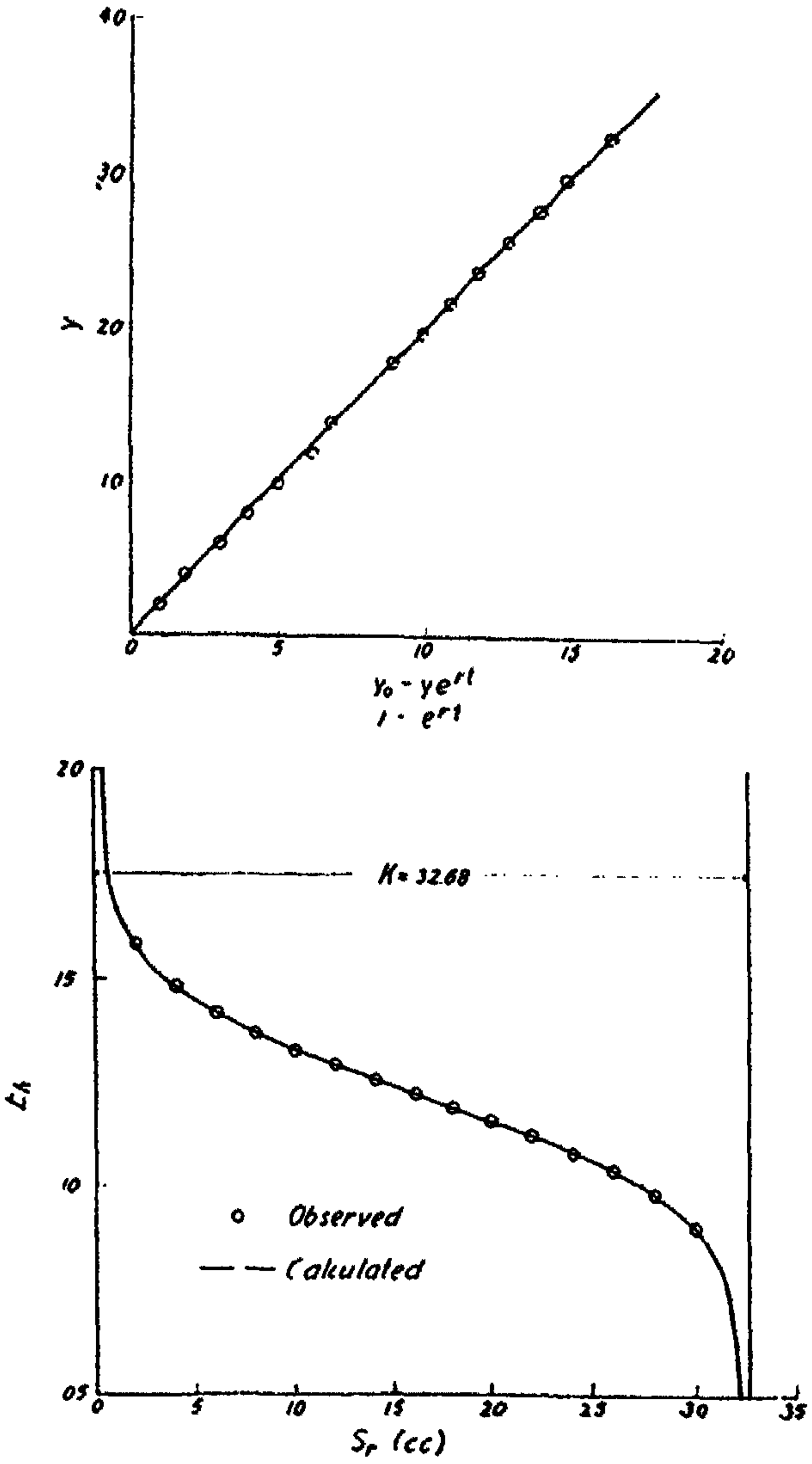

Fig. 11
Graphical Presentation, Example 5

Legend: y = Sr = Ti^{+++} cc.
t = E_h − .1224 = Potential against H electrode − 1224

$K = my_0 = 32.68$ from (42)

$C = m - 1 = 1.04225$ from (40)

$E'_a = -c \ln C = -.0005$ from (73)

$= -.0005 + .1224 = .1219$ in original units.

The equation now becomes

$$E_h = .1219 - .0130584 \ln \frac{S_r}{32.68 - S_r} \tag{74}$$

The calculated and observed values are compared in Table V and Fig. 11.

TABLE V

y Ti^{+++}cc.	E_h Observed	t $E_h - .1224$	$\frac{y_0 - ye^{rt}}{1 - e^{rt}}$	E_h Calculated from (74)
0	.287	.1646		
2	.1581	.0357	1.0272	.1575
4	.1479	.0246	1.8489	.1476
6	.1415	.0191	2.985	.1414
8	.1368	.0144	4.025	.1367
10	.1327	.0103	5.002	.1326
12	.1292	.0068	6.145	.1290
14	.1256	.0032	6.795	.1257
16	.1224	.00	00	.1224
18	.1192	.0032	8.797	.1193
20	.1159	.0065	9.801	.1159
22	.1124	.0100	10.786	.1125
24	.1085	.0139	11.771	.1086
26	.1041	.0183	12.730	.1042
28	.0985	.0239	13.707	.0985
30	.0905	.0319	14.667	.0904
32.8	.036	.0864	16.116	——

OBSERVATIONS ON THE CORROSION OF IRON

BY J. F. G. HICKS

Object of the Investigation:

From time to time carbon dioxide[1] oxygen[2] and electrochemical action[3] have been regarded as the cause of the corrosion of iron. The "differential oxygenation" principle of Evans[4] is perhaps the broadest generalization, having been shown to apply to the corrosion of other metals. While Evans' principle is essentially electrochemical in nature and involves the behavior of oxygen in the corrosion-process, it apparently does not take into consideration the underlying cause of corrosion in terms of preliminary dissolving of metal in water, nor the actual mechanism of the process with respect to oxygen and carbon dioxide. It is the object of this paper to attempt an answer to these questions.

Résumé of Previous Investigations:

Whitney,[5] also Cushman and Gardner,[6] showed that iron would dissolve without corrosion in water free from dissolved air and carbon dioxide, later confirmed by Shipley, McHaffie and Clare,[7] who showed that iron would dissolve in pure, carbon-dioxide-free water until the pH value reached 9.4, after which dissolving ceased. Walker, Cederholm and Bent[8] observed the depolarizing effect of oxygen, thus improving upon Whitney's conception of the process[5] now more fully developed by Evans.[9] Dunstan and associates[10] also Seligman and Williams[11] showed that a film of liquid water in contact with a metallic surface is pre-requisite to corrosion of that surface, and that water-vapor is much less active, perhaps quite inactive, in the process, which apparently points out the solvent action of the water as the real cause of corrosion.

Necessity of a Film of Liquid Water as a Solvent for Iron:

A series of test-flasks were set up as per Fig. 1. Test-pieces were spirals of Malin's #10 "Music Wire." Each set of tests at 25° and 0° was made upon the same set of flasks, first at the higher, then at the lower temperature, to insure condensation of moisture upon the metallic surfaces; weighings were made at 24-hour intervals. Due to the possibility of occlusion of gases by

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[1] Crum Brown: J. Iron Steel Inst. (London), 39, 129 (1888); Friend: 79, 5 (1908).

[2] Whitney: J. Am. Chem. Soc., 25, 394 (1903).

[3] See (2) above; also Walker, et. al.: J. Am. Chem. Soc., 29, 1251 (1907); Walker: J. Iron Steel Inst., 1, 70 (1909).

[4] Evans: "The Corrosion of Metals," 24, (1924).

[5] See (2).

[6] Cushman and Gardner: "Corrosion and Preservation of Iron and Steel," pp. 41-48, (1925).

[7] Shipley, McHaffie and Clare: Ind. Eng. Chem., 17, 4, 381 (1925).

[8] See (3).

[9] See (4).

[10] J. Chem. Soc., 87, 1548 (1905); 99, 1835 (1911).

[11] J. Inst. Metals, 23, 159 (1920).

the iron, all differences in weight less than 0.0005 gram were not considered as due to corrosion; "none," in the following table, therefore means "less than 0.0005 gram." Results follow:

TABLE I

Gas in Flask:	Days to reach constant weight		Increase in weight milligrams/sq. cm.		Remarks:
	25°	0°	25°	0°	
Dried O_2	5	5	none	none	From tanks; dried by concentrated H_2SO_4.
Dried CO_2	5	5	none	none	From tanks; dried by concentrated H_2SO_4.
Dried O_2 and CO_2	5	5	none	none	Mixed equal volumes, dried as above.
Dried air, CO_2-free	5	5	none	none	CO_2 removed by soda-lime; dried as above.
Dried air	5	5	none	none	Dried as above.
Water-vapor	6	6	none	none	Test-piece hung over H_2O; air removed by H_2.
Moist O_2	10	7	0.3	2.0	Hung over H_2O saturated with O_2; air swept out by O_2.
Moist CO_2	12	9	1.1	5.6	Same arrangements, CO_2 in place of O_2.
Moist O_2 and CO_2	10	8	2.7	13.2	Same arrangements. Gas-flow-rates equal.
Moist air.	15	13	1.2	1.1	Same arrangements; air bubbled thru water.

These tests involve the deposition of a film of liquid water upon the surface of the test-piece, by reason of a decrease in temperature in the same system. More water will be deposited at lower temperatures than higher, hence the greater corrosive effect is to be expected. This is in accordance with the findings of those who hold that a film of liquid water is pre-requisite to corrosion (foot-notes 10, 11) and points out as the cause of corrosion the initial dissolving of iron by water. The work of Shipley, McHaffie and Clare (foot-note 7) also serves to confirm this view. They showed that metallic iron would dissolve in water (pure, and free from dissolved air and carbon dioxide) without corrosion until the pH value 9.4 was attained,—in short, at that pH value, the concentration of H^+ is too low to permit any iron being dissolved. From the equilibrium

$$HOH \rightleftarrows H^+ + (OH)^-,$$

it follows that, since the initial value is 7.0, all that is necessary to produce a pH value of 9.4 is to add sufficient $(OH)^-$ to do this by "common ion effect," i.e., add $(OH)^-$ equal to $10^{-4.6}$ mols per litre. This is almost exactly the concentration of $(OH)^-$ which will turn phenolphthalein red (10^{-5}; see Washburn-Salm Indicator-table), and agrees quite well with the data furnished by the "ferroxyl-test" (see footnote 6) of Cushman and Davis, who showed that corrosion did not take place in solutions sufficiently alkaline to turn phenolphthalein red. It is also in agreement with the findings of Hall[12] in his study of the non-corrosive action of alkaline boiler-waters.

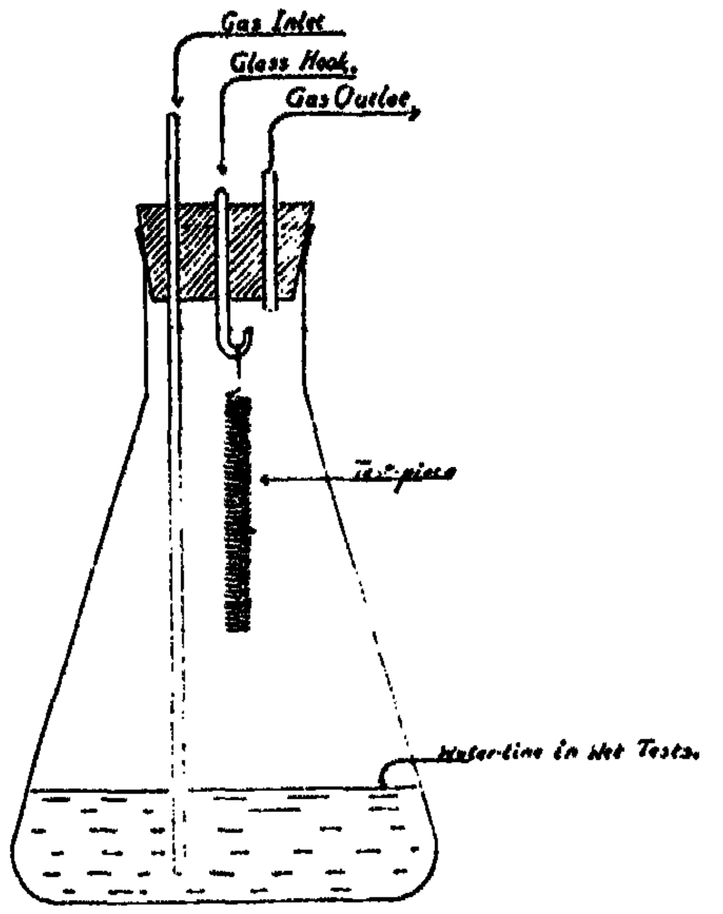

FIG. 1

From the above, then, we should assume the following system of equilibria as representing the dissolving of iron in water at room-temperatures:

$$Fe(solid) \rightleftharpoons Fe\ (dissolved) + 2HOH \rightleftharpoons Fe(OH)_2 + H_2.$$

TABLE II

Solute*	Solubility, 18°, grams per liter	Dissolved solute equivalent to g/L of: Fe	H_2	O_2	CO_2
$Fe(OH)_2$	9.6×10^{-4}	6×10^{-4}	1.3×10^{-5}	9×10^{-5}	4.7×10^{-4}
$Fe(OH)_3$	2.9×10^{-7}	1.7×10^{-7}	9×10^{-9}		
$FeCO_3$**	5.6×10^{-6}	2.77×10^{-6}	1.30×10^{-6}	1.73×10^{-6}	2.16×10^{-6}
O_2	0.070	0.16	0.009		
CO_2	1.872	2.376	0.178		
H_2	0.002	0.056			

* Values from Landolt-Börnstein-Roth, Physikalische-Chemische Tabellen; values in other columns calculated from these.

**Smith: J. Am. Soc., 40, 883 (1918).

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[12] R. E. Hall: Mechanical Engineering, 48, 4, 323.

The corrosion-process is usually continuous, altho Aston[13] showed that films of corrosion-products adherent to metallic surfaces may or may not be protective. It would therefore appear logical to conclude that the evolution of hydrogen displaced the above system of equilibria to the right, causing this continuity. The incorrectness of such a conclusion will be apparent from a consideration of the following table of solubilities and equivalents:

From comparisons of equivalents and solubilities in this table one may conclude that:

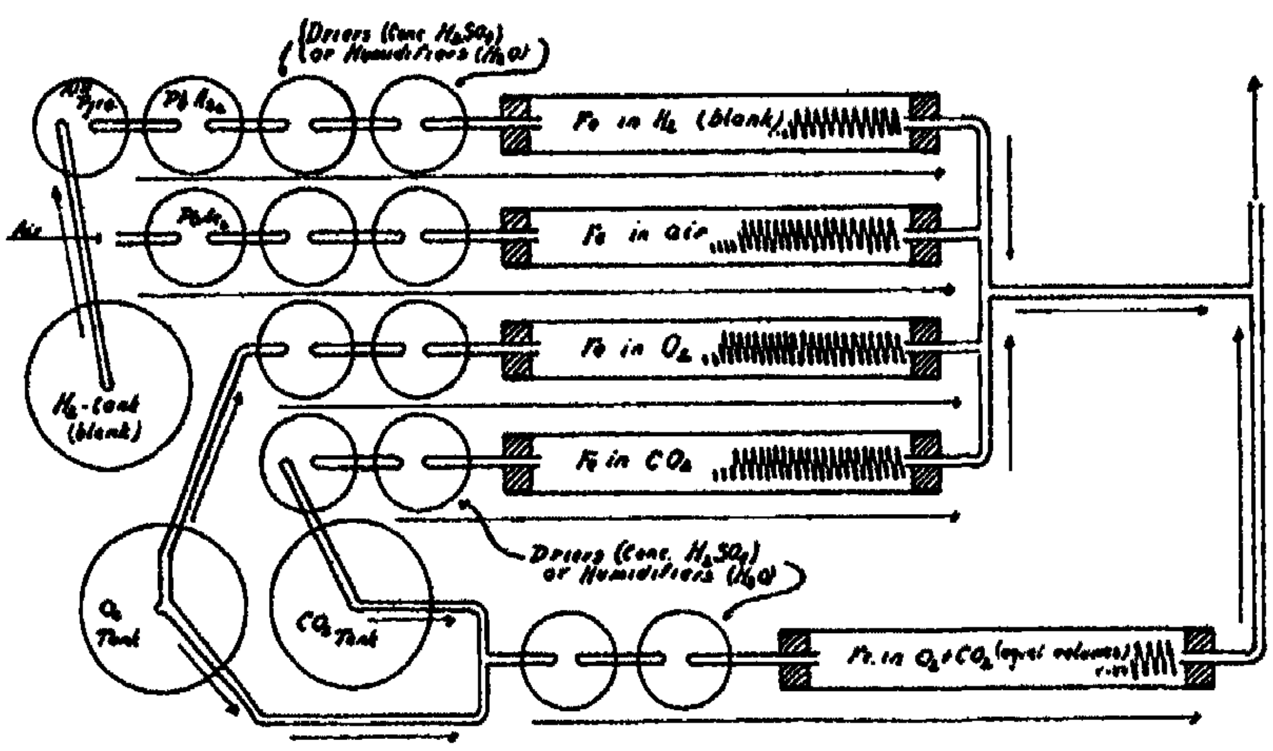

Fig. 2

I. Assuming a liter of water saturated with ferrous hydroxide at 18°, the hydrogen evolved by dissolving the equivalent quantity of iron in water is only 0.65% of the hydrogen which would saturate a liter of water at 18°, whence it follows that:

1. Evolution of hydrogen is not the cause of continuity of corrosion by displacement of the above equilibria, because the actual hydrogen evolved would remain in solution; it may also act as a polarizer of what might be called a "corrosion-cell."

2. Corrosion should be terminated by the saturation of water by dissolved ferrous hydroxide, hence the continuity of corrosion is explainable in terms of removal of this ferrous hydroxide (and also polarizing hydrogen) at a rate sufficient to prevent saturation (and complete polarization).

Rôle of Oxygen and of Carbon Dioxide:

Further consideration of Table II will lead to the conclusion that

II. The quantity of dissolved oxygen in a liter of water saturated with respect to oxygen at 18° is 800 times the quantity of oxygen required to

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[13] Aston: Trans. Am. Electrochem. Soc., 29, 449 (1916).

oxidize to ferric hydroxide all of the ferrous hydroxide present in a liter of water saturated with respect to ferrous hydroxide at 18°, whence it follows that one may be safe in assuming the possibility of:

1. Complete oxidation as above, accompanied by precipitation of ferric hydroxide, which is only 0.0003 as soluble as ferrous hydroxide at 18°;

2. Complete depolarization of the "corrosion-cell" by dissolved oxygen, for the excess of oxygen in a solution saturated with respect to it above that quantity of oxygen required to oxidize ferrous hydroxide as above is 662 times as much as will be required to oxidize the evolved hydrogen equivalent to the iron dissolved;

3. The function of oxygen in the corrosion-process as that of a "maintenance-factor," by reason of its oxidizing and depolarizing properties, is clearly indicated. Depending upon the concentration of dissolved oxygen, an accelerating effect should be noticed, which is another way of stating Evans' "differential oxygenation" principle.

III. The quantity of carbon dioxide present in a liter of water saturated with respect to that gas at 18° is 4000 times the quantity required to convert to ferrous carbonate the ferrous hydroxide present in a liter of solution saturated with ferrous hydroxide at 18°, hence one may be safe in assuming the possibility of:

1. Removal of ferrous hydroxide from the system by conversion to ferrous carbonate, which is less soluble than ferrous hydroxide;

2. Increase in concentration of H^+ (as dissolved H_2CO_3), thus bringing about increase in the quantity of iron dissolved and also in the rate of dissolving it;

3. Increase in concentration of H^+ means increase in quantity of hydrogen evolved, which in addition to polarizing the "corrosion-cell" may also act as:

(a) A loosening-agent for the corrosion-film, by reason of the fact that bubbles of hydrogen form between the film and the surface of the corroding iron;

(b) Preventive agent with respect to adherence of films, because of layer of adherent hydrogen upon the metallic surface.

4. The maintenance- and accelerator-effect of carbon dioxide (as dissolved H_2CO_3) is pointed out. While oxygen has these same effects, it operates in a different manner, as has been previously mentioned.

The following series of experiments was carried out for the purpose of confirming these predicted functions of oxygen and carbon dioxide:

The apparatus shown in Fig. 2 was used for a fifteen-day test; test-pieces consisted of spirals from the same sample of wire as used in the first series. Inter-diffusion of gases was prevented by keeping the gases constantly flowing in the same direction; this was accomplished by the actual pressure of the gases issuing from the container and by attaching a suction-pump to the other end of the system. The bubbling-bottles served a threefold purpose: counting bubbles for determining gas-flow-rates, dryers (filled with concentrated H_2SO_4) and humidifiers (filled with water). Results are shown in the graphs (Fig. 3, 3a) in which "moist carbon dioxide" is represented by "H_2CO_3":

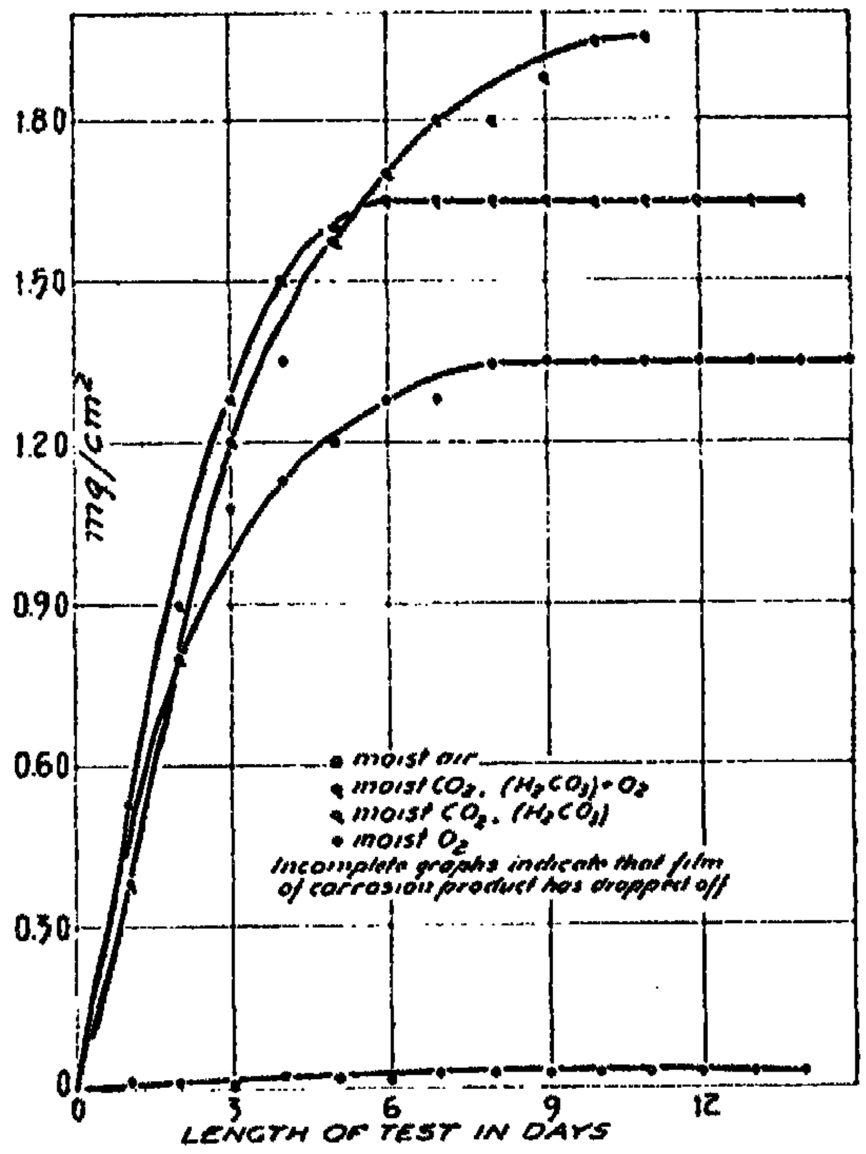

Fig. 3

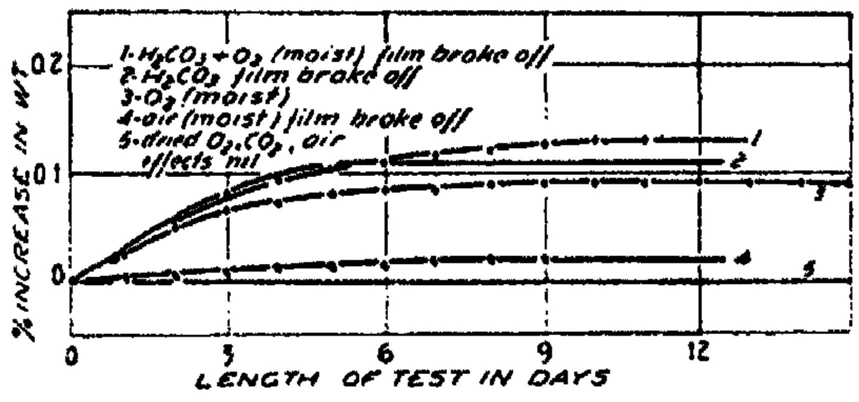

Fig. 3a

Inspection of these graphs leads to the following conclusions:

1. Water is necessary in the corrosion-process. The results of the previous series of tests seems to confirm the view that this "water" is an adherent liquid film. As there was no temperature-control for these tests, such a film could readily deposit when the laboratory cooled off during the night.

2. The intensifying and accelerating effect of oxygen is demonstrated, from which the "differential concentration" effect follows.

3. The intensifying and accelerating effect of increased concentration of H^+ is also demonstrated, and agrees with the fact that H_2CO_3 is a stronger acid than HOH.

4. The removal of adherent film by bubbles of hydrogen, as predicted above, is demonstrated by the fact that films did not drop off when the concentration of H^+ was at its lower lever; when it was increased by the formation of carbonic acid, the films always dropped off.

Possible Removal of Films by Hydrogen:

In discussing experimental data, Fujihara[11] states that "carbon dioxide evidently plays an important part in the corrosion-process. . . . The true action of the CO_2 probably lies in the removal of the protection-film, thus:

$$Fe(OH)_2 + H_2CO_3 \longrightarrow FeCO_3 + 2H_2O.$$

The main action is that of H_2CO_3 on alkaline ferrous hydroxide, consequently corrosion will again start by the electrolytic process as before." In another portion of his paper Fujihara concludes:

(1) "Iron with a clean surface will not continue* to corrode in water and in air free from CO_2, after a film has formed as a result of rusting sufficient to protect the iron from further corrosion. This is, however, true only when a definite amount of water** is used, as continued application of fresh water would remove the protective film and again induce rusting.

(2) "Pure water and pure oxygen alone cannot attack iron on which a protective film previously is produced, but the additional action of CO_2 is necessary to remove rust.",

The tests were carried out in the apparatus shown in *Fig. 1*. No fresh water was added, and the CO_2 was bubbled thru at the rate of 5 cc. per minute. The CO_2-inlet-tube was kept as far away as possible from the rusted iron test-pieces, to preclude removal of rust-coat by stirring of the liquid or actual abrasive action of the gas-stream, which was purposely slow and in small quantity. The following test-samples were prepared:

1. Naturally-rusted iron turnings, rust-coat strongly adherent.
2. Freshly-prepared $Fe(OH)_3$ washed free from $(NH_4)^+$, $(OH)^-$, Cl^-.
3. Freshly-prepared $Fe(OH)_2$, washed free from $(NH_4)^+$, $(OH)^-$, $(SO_4)^{--}$. Washings of $Fe(OH)_2$ were made with boiled distilled water in stoppered flasks.

Results of this series of tests are given in the table below:

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[11] Fujihara: Chem. Met. Eng., 32, 16, 810 (1925).

* The "maintenance-factor" role of CO_2 is clearly indicated here.

** More fresh water would also dissolve additional iron as well as adherent corrosion-film. This apparently implies the solvent action of water on iron as well.

TABLE III

Test-piece or Sample consists of	Visible Effect in:	Solvent Effect in:	Tests for Iron in Filtered Liquid:
I. Naturally-rusted iron: 1. Completely submerged:	Rust partly removed, exposing bright metal, 6 days.	A few gas-bubbles adhering to bright metal, 8 days.	Fe^{++} distinct; Fe^{+++} in faint traces only, probably admixed or by slight oxidation.
2. Partially submerged: (a) Submerged portion:	Same as I, 1, 5 days.	Same as I, 1, 7 days.	Same as I, 1.
(b) Unsubmerged portion:	None.	None.	
II. Freshly prepared $Fe(OH)_3$, washed:	None.	None.	Negative.
III. Freshly prepared $Fe(OH)_2$, washed:	Dark green ppt. turns nearly white, 10 days.	Doubtful. Conversion to $FeCO_3$ complete.	Fe^{++} very faint; Fe^{+++} negative.

From which one may conclude that:

(1) The positive test for Fe^{+++} in I, 1 is most likely due to air-oxidation of Fe^{++} during filtration, or to minute suspended particles of $Fe(OH)_3$ which had passed thru the filter;

(2) Carbonic acid attacks metallic iron appreciably and completely converts $Fe(OH)_2$ to $FeCO_3$. Its action upon $FeCO_3$ is quite doubtful (not being under increased pressure, as in mineralization), and it has no effect upon $Fe(OH)_3$.

(3) Carbonic acid acts as a maintenance-factor in the corrosion-process, in two ways:

(a) It penetrates an adherent film of corrosion-product, attacks the iron beneath, liberating hydrogen, bubbles of which force off particles of the film, removing them from the sphere of action, and in time exposing the cleaned metallic surface to further action.

(b) Direct acidic effect, due to increased concentration of H^+, before the formation of a film of corrosion-product. The direct acidic effect and the acidic effect after penetration of the film are, of course, identical chemical reactions,—the interaction of carbonic acid and metallic iron.

(4) Fujihara's conclusions are confirmed.

The conclusions of (3) above include the generalizations of Aston (see footnote 13) and Evans (see footnote 4) because:

(a) Polarity of adherent film and metallic iron with respect to each other (Aston) can bring about the electrolysis of the carbonic acid solution which has penetrated the film or else come in contact with a broken film, and therefore with film and metal simultaneously.

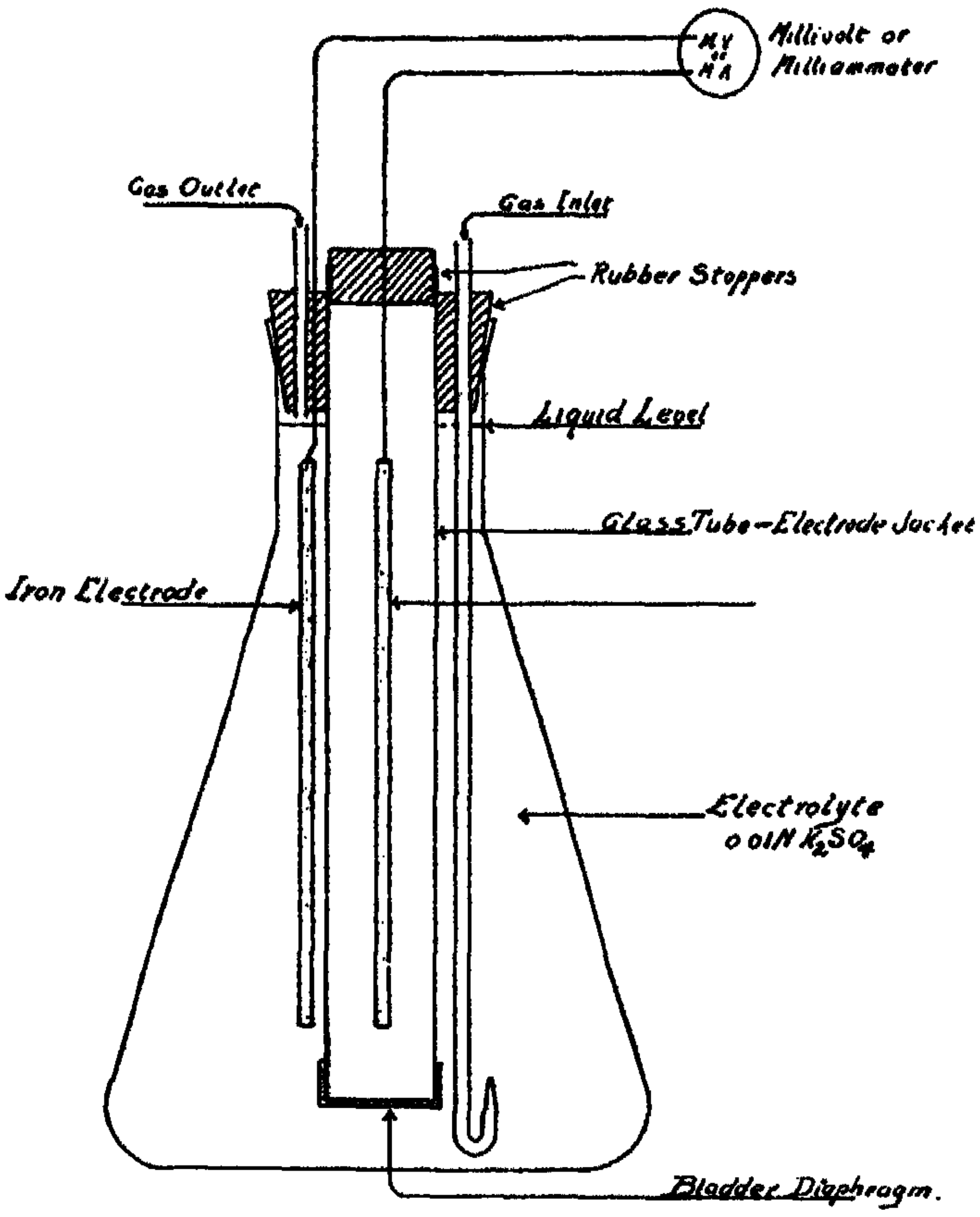

FIG. 4
Eight Cells in Series for E. M. F. readings
Eight Cells in Parallel for Current readings

(b) When carbonic acid comes in contact with a broken adherent film of corrosion-product, regardless of how the break may have been formed, we have a condition of differential concentration of H^+ with respect to two different portions of the same piece of metallic iron, and therefore corrosion can take place because of the resulting E.M.F. set up between the exposed (direct contact, higher H^+ concentration) and unexposed (penetration-contact, lower H^+ concentration) portions of the iron (Evans).

Electrochemical Effects:

There now remains only to check the conclusions from the graphs of Fig. 3 in terms of E.M.F. produced by differential concentration of the H^+ of H_2CO_3, and of O_2 upon the same piece of iron. The apparatus shown in Fig. 4 was used, and is obviously based upon the principle of differential concentration. It is essentially the same as the cells of Hall (see footnote 12) and of Evans (see footnote 4), with the added features of excluding air (to prevent oxidation) and an inlet and outlet for CO_2. The electrolyte was a solution of K_2SO_4 (0.01 N) in boiled distilled water. All electrodes were cut from the same piece of iron. Cells were allowed to stand until the millivoltmeter registered equilibrium at 25°, after which the gases used were bubbled thru until equilibrium was again recorded. Eight of these cells, representing an electrode-area of 370 sq. cm., were used,—in series for the E.M.F.-readings and in parallel of the current-readings. Results are shown in Table IV:

TABLE IV

Gas passed	Millivolts:	Milliamperes:
O_2	4.00	0.55
CO_2	0.85	0.15
$CO_2 + O_2$, equal volumes	2.15	0.25
Air	0.75	0.15

It will be noted that the maximum E.M.F., and therefore the maximum current productive of corrosive effect, is due to oxygen. From this and preceding results, it would appear that the function of oxygen in the corrosion-process was that of an accelerator, and that its depolarizing- and oxidizing-effects were maintenance-factors, and therefore of secondary importance. This state of affairs no doubt explains the fact that so many observers have considered oxygen as the cause of corrosion.

Mechanism of the Corrosion Process:

1. Metallic iron dissolves in water in an adherent film of liquid water as ferrous hydroxide until pH = 9.4.
2. The presence of oxygen insures maximum E.M.F., and therefore acts as an accelerator.
3. The system of equilibria

$$\text{Fe(solid)} \rightleftarrows \text{Fe (dissolved)} + 2\text{HOH} \rightleftarrows \text{Fe(OH)}_2 + \text{H}_2$$

is *shifted to the right, and corrosion maintained* by O_2 and CO_2 as follows:

(a) O_2 removes $Fe(OH)_2$ by oxidation to less soluble $Fe(OH)_3$, also H_2 by oxidation (depolarization);

(b) CO_2 removes $Fe(OH)_2$ by conversion to less soluble $FeCO_3$, also forms H_2CO_3, the H^+ of which dissolves metallic iron and favors corrosion.

4. Therefore, from the generalizations above, so long as there is present in the system any agent capable of removing ferrous hydroxide and hydrogen (depolarizing-agent) with sufficient rapidity to preclude saturation of adherent water with respect to ferrous hydroxide and hydrogen, this will take place while either exists in solution, and either will be dissolved so long as iron is in contact with liquid water and a depolarizer. This is a general statement for continuous corrosion of any metal above hydrogen in the electromotive series.

Summary:

1. The primary cause of the corrosion of iron is the actual dissolving of iron in water. This takes place before any other chemical action starts.

2. A film of liquid water adhering to the metallic surface undergoing corrosion is necessary to this dissolving process.

3. Oxygen produces the maximum E.M.F. with respect to dissolving iron, hence acts as an accelerator; its oxidizing action removes both ferrous hydroxide and hydrogen, this latter being a depolarizing effect. The oxidizing action of oxygen is therefore a maintenance-factor in the corrosion-process.

4. Carbon dioxide (as dissolved carbonic acid) furnishes additional H^+, thereby acting as an accelerator. By converting ferrous hydroxide into less soluble ferrous carbonate, it removes the former and acts as a maintenance-factor also.

5. A generalization concerning the corrosion of metals above hydrogen in the electromotive series has been derived from the results of the experiments recorded. It is not at variance with the accepted views of the corrosion-process, but agrees with them.

North Pacific College
Portland, Oregon.

OPTICAL PROPERTIES OF SOME SALTS OF GLUCONIC ACID[*]

GEORGE L. KEENAN AND SAMUEL M. WEISBERG

Introduction

During the course of experimentation with a new fermentation process for the production of gluconic acid carried out by the Color and Farm Waste Division, United States Department of Agriculture[1],[2], quantities of gluconic acid were accumulated. As at present no satisfactory qualitative methods exist for the identification of gluconic acid, it was thought advisable to prepare several of its pure salts and to determine their optical properties.

This paper presents certain optical properties of those gluconates which seemed to lend themselves to optical measurement, namely, the ammonium, potassium, sodium, barium, and lead salts, and also gluconic-γ-lactone.

Experimental

The ammonium, potassium, and sodium gluconates were prepared by treating a weighed quantity of chemically pure barium gluconate in solution with an equivalent amount of the pure sulphate of the metal desired. The sulphate was added drop by drop to a hot solution of the barium gluconate, stirring constantly. The barium sulphate formed was filtered off. The filtrate was concentrated by evaporation and then approximately 10 volumes of alcohol were added. The salt soon crystallized. Crystallization was repeated twice.

All of the salts were analyzed for hydrogen and the metal. The hydrogen determinations were made with the new Phillips-Hellbach combustion apparatus.[3] Nitrogen determinations were made by the Kjeldahl-Gunning-Arnold method.

Ammonium Gluconate

The well-crystallized ammonium salt was dried over night at 60°C in the constant temperature oven. It readily became anhydrous and on analysis showed: 6.48 per cent, 6.48 per cent N; 7.08 per cent H. Theory for $NH_4C_6H_{11}O_7$: 6.57 per cent N; 7.23 per cent H.

Optical Properties: The anhydrous salt occurs as irregular grains. The indices of refraction are: $n_\alpha = 1.510$, $n_\beta = 1.555$, $n_\gamma = 1.577$, all ± 0.003. The double refraction is very strong ($n_\gamma - n_\alpha = 0.067$). In convergent

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[*] From the Microanalytical Laboratory, Food, Drug, and Insecticide Administration, and the Color and Farm Waste Division, Bureau of Chemistry and Soils, United States Department of Agriculture.

[1] O. E. May, H. T. Herrick, C. Thom, and M. B. Church: "The Production of Gluconic Acid by the Penicillium Luteum-Purpurogenum Group," J. Biol. Chem., **75**, 417 (1927).

[2] H. T. Herrick and O. E. May: "The Production of Gluconic Acid by the Penicillium Luteum-Purpurogenum Group. II. Some Optimal Conditions for Acid Formation," J., Biol. Chem., **77**, 185 (1928).

[3] M. Phillips and R. Hellbach: "An Electrically Heated Furnace for Organic Combustion," J. Assoc. Official Agr. Chemists, **11**, 393 (1928).

polarized light, biaxial interference figures are common, many grains showing sections perpendicular to the acute bisectrix; the axial angle is approximately $2E_D = 65 \pm 5°$. Sign −. $2E_r < 2E_v$.

Potassium Gluconate

The potassium salt was dried at 90°C. for about two days in the vacuum oven over calcium chloride. The salt became anhydrous under these conditions. Potassium was determined as the sulphate by heating with concentrated sulphuric acid. Analysis for the anhydrous salt ($KC_6H_{11}O_7$): 4.74 per cent H; 16.63 per cent, 16.65 per cent K. Theory: 4.80 per cent H; 16.69 per cent K.

Optical Properties: The anhydrous compound consists of irregular grains and rods, Fig. 1.* The indices of refraction are: $n_\alpha = 1.523$, $n_\beta = 1.548$, $n_\gamma = 1.565$, all ± 0.003. The double refraction is strong ($n_\gamma = n_\alpha = 0.042$); sign of elongation +; extinction is parallel. In convergent polarized light, biaxial interference figures are common, although 2E is much too large for measurement under the microscope.

FIG. 1
Potassium gluconate (× 37)

Sodium Gluconate

The sodium salt was dried and analyzed like the potassium salt. Analysis (anhydrous salt, $NaC_6H_{11}O_7$): 5.00 per cent H; 10.44 per cent, 10.42 per cent Na. Theory: 5.08 per cent H; 10.54 per cent Na.

Optical Properties: The anhydrous compound consists of irregular fragments without definite habit. The indices of refraction are: $n_\alpha = 1.523$, $n_\beta = 1.569$, $n_\gamma = 1.589$, all ± 0.003. The double refraction is very strong ($n_\gamma - n_\alpha = 0.066$). In convergent polarized light, biaxial interference figures are common, grains frequently lying perpendicular to an optic axis; the axial angle is large; and the sign − .

Barium Gluconate Monohydrate

The barium gluconate was prepared by directly neutralizing gluconic acid with a slight excess of the metal carbonate and heating the solution to boiling for approximately an hour. The solution was filtered to remove excess carbonate and then four volumes of alcohol were added. A monohydrate of barium gluconate was obtained by drying for two hours at 65°C. Analysis

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* The crystal forms illustrated in the figures do not remain intact in obtaining the optical constants. In many instances it is necessary to crush the material, thereby obtaining irregular fragments.

($Ba(C_6H_{11}O_7)_2 . H_2O$): 4.46 per cent H; 25.33 per cent, 25.30 per cent Ba. Theory: 4.44 per cent H; 25.20 per cent Ba.

Optical Properties: In ordinary light the monohydrate consists of irregular fragments, some of which are roughly six-sided, Fig. 2. The indices of refraction are: $n_\alpha = 1.570$ and $n_\gamma = 1.613$, both ± 0.003, n_β being indeterminate. The double refraction is strong ($n_\gamma - n_\alpha = 0.043$). Only partial biaxial interference figures were obtainable in convergent polarized light.

FIG. 2
Barium gluconate (× 75)

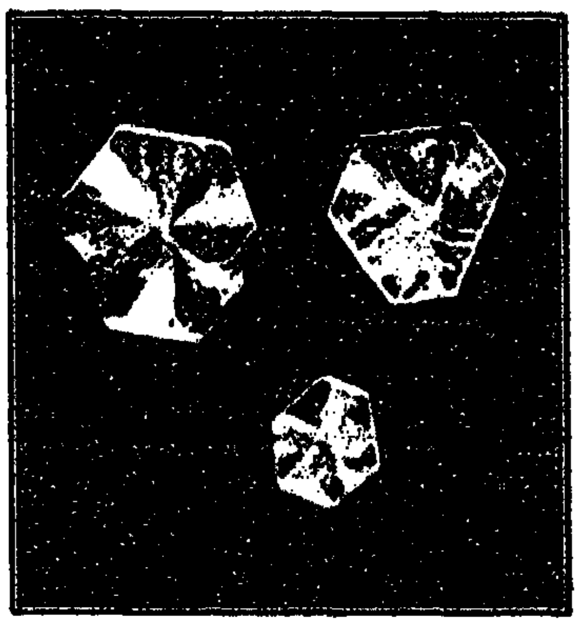

FIG. 3
Lead gluconate (× 2)

Lead Gluconate

The lead gluconate was prepared exactly as the barium gluconate. It readily became anhydrous on drying overnight at 65°C. It was analyzed for hydrogen and lead, the lead being determined as the chromate. Analysis ($Pb(C_6H_{11}O_7)_2$: 3.64 per cent H; 34.61 per cent, 34.77 per cent Pb. Theory 3.71 per cent H; 34.70 per cent Pb.

Optical Properties: The large crystals before being crushed for optical study consist of six-sided plates, Fig. 3. In ordinary light the anhydrous salt shows, after crushing, irregular grains without significant habit. The indices of refraction are: $n_\alpha = 1.624$, $n_\beta = 1.633$, $n_\gamma = 1.635$, all ± 0.003. The double refraction is moderate ($n_\gamma - n_\alpha = 0.011$), mostly first order colors being shown. In convergent polarized light, interference figures occasionally seen perpendicular to acute bisectrix; axial angle 10 ± 2°; optic sign −.

Gluconic-γ-Lactone

The γ lactone of gluconic acid was prepared in a pure state from gluconic acid. The gluconic acid was liberated from its barium salt with dilute sulphuric acid. The gluconic acid was then evaporated down to a higher concentration on the steam bath. It was next placed in a vacuum oven over calcium chloride at 50°C. for several days. The gluconic acid went over into a white solid. This solid was recrystallized several times from hot ethyl alcohol. It gave a melting point of 131–134°C. Analysis: 5.71 per cent H. Theory: 5.66 per cent H.

Optical Properties: The material occurs as irregular grains. The indices of refraction are: $n_\alpha = 1.517$, $n_\beta = 1.544$, $n_\gamma = 1.577$, all ± 0.003. The double refraction is very strong ($n_\gamma - n_\alpha = 0.060$). In convergent polarized light, biaxial interference figures are common; optic sign+; axial angle too large to measure under the microscope.

Microscopical Identification of Compounds

Table I was prepared to aid in the rapid identification of the salts described. The index given in the left-hand column is the minimum refractive index for each compound. In order to use the table the crystalline material is immersed successively in the liquids indicated in the left-hand column. With polarizer in place and diaphragm partially closed, the material is examined under the microscope, trying one liquid after another, until the outlines of the fragment have disappeared when its refractive index has been matched in one position of the field. The identity of the substance is confirmed by the data in the central column and the name of the compound is given in the right-hand column.

TABLE I

Determinative Table

Index	Confirmatory Data	Compound
1.510	Confirm by immersing in liquid 1.577 which matches γ....................	$NH_4\ C_6H_{11}O_7$
1.517	Confirm by immersing in liquid 1.577 which matches γ..................	Gluconic-γ-lactone
1.523	Confirm by immersing in liquid 1.565 which matches γ..................	$K\ C_6H_{11}O_7$
1.523	Confirm by immersing in liquid 1.589 which matches γ..................	$Na\ C_6H_{11}O_7$
1.570	Confirm by immersing in liquid 1.613 which matches γ..................	$Ba\ (C_6H_{11}O_7)_2$
1.624	Confirm by immersing in liquid 1.635 which matches γ..................	$Pb\ (C_6H_{11}O_7)_2$

TABLE II

Summary of Optical Data

	$NH_4C_6H_{11}O_7$	$KC_6H_{11}O_7$	$NaC_6H_{11}O_7$	$Ba(C_6H_{11}O_7)_2\ H_2O$	$Pb(C_6H_{11}O_7)_2$	Gluconic-γ-lactone
Habit	*grains*	*rods*	*grains*	*grains*	*grains*	*grains*
Indices						
n_α	1.510	1.523	1.523	1.570	1.624	1.517
n_β	1.555	1.548	1.569	indet.	1.633	1.544
n_γ	1.577	1.565	1.589	1.613	1.635	1.577
$n_\gamma - n_\alpha$:	0.067	0.042	0.066	0.043	0.011	0.060
Figures:	frequent	frequent	frequent	occasional	occasional	frequent
2E	65 ± 5°	large	large	indet.	10 ± 2°	large

NEW BOOKS

Soluble Silicates in Industry. *By James G. Vail. 23 × 15 cm; pp. 443. New York: Chemical Catalog Company, 1928. Price: $9.50.* The chapters are entitled: introduction; the constitution of silicate solutions; definite soluble silicates; reactions; preparation; commercial forms and properties; silicate cements; adhesives; sizes and coatings; deflocculation and detergency; gelatinous films and gels; additional uses.

The author has covered the ground pretty well in the chapter on the constitution of silicate solutions and it is not his fault that so little comes out of it. The people who experiment with silicate solutions seem to be singularly unsuccessful in drawing definite conclusions from their work. The reviewer has read most of this literature fairly carefully and about all that one can swear to is that the amount of hydrolysis is much less than one had originally supposed.

There is one bad slip on p. 55. "When sodium has been adsorbed on colloidal silica, it reduces but does not entirely destroy the tendency of the particles to coalesce." Since colloidal silica is negatively charged, the adsorption of sodium ions would decrease the stability and not increase it. The author is really talking about the adsorption of hydroxyl ions.

"On an industrial scale, soluble silicates are made by melting soda ash and silica or salt cake (Na_2SO_4), carbon, and silica in furnaces built of clay refractories. As in the glass industry, the open hearth regenerative type of furnace is most widely used, although satisfactory results are also obtained from reverberatory furnaces in which coal is burned on a grate and from furnaces heated with mineral oil. The temperatures in vogue range from 1300°-1500°C., sufficient to drive out sodium chloride which is always present in the raw materials. In soda ash produced by the ammonia process, the amount is usually very small, but some of the natural sodas may contain 5 or 6 per cent. This, except from the point of view of loss, is not objectionable because it is completely expelled with the furnace gases. In the regenerative system in which the gas is cooled to temperatures below the condensation point of sodium chloride there is a tendency for this salt to accumulate, but it is found after the furnace has been shut down, as sodium sulfate, the sulfur in the fuel having been sufficient to produce enough sulfuric acid to decompose the condensed chloride.

"It has been proposed to prepare soluble silicates in arc furnaces and this is entirely possible, the question being one of cost of units of heat supplied by electricity as compared with those supplied by coal, petroleum or gas. The problem of refractories, however, becomes very serious at higher temperatures for the melt contains so much silica that it readily attacks any basic refractory, and the equilibrium between silica and soda is such that highly silicious refractories fail almost equally rapidly. It would therefore appear that future developments, if they involve high temperatures, will also have to take into account the necessity of enclosing the fusion in a mass which is little reactive because it is cooled, and the economic aspect of this is likely to be discouraging," p. 103.

"There is no point at which a solution of $Na_2O, 3SiO_2$ may be said to be saturated, as homogeneous systems of the solid and water may exist in all proportions at ordinary temperatures. A lump of the glass which has been exposed to an atmosphere of steam will, if broken across, exhibit a sharply defined outer layer which, though it retains the appearance of glass, has lost its original hardness and becomes more resilient. This outer layer contains water and may easily be dissolved in hot water, though the portion which has not been hydrated is brought into solution very slowly and incompletely by similar treatment.

"Morey has pointed out that these solutions are very different from the systems in which definite equilibria between true solutions and crystalline phases exist, and has called attention to the fact that silicate of potash appearing as a viscous liquid at ordinary temperatures may be prepared which would not be stable as a true solution below 450° to 500°. Silica must, from this point of view, be regarded as present in a colloidal condition but this does not explain the mechanism of its behavior. Whether the solution of silicates of soda and potash, like that of a high-grade animal glue, necessarily goes on in two stages, the first of which is hydration and the second dispersion, has not been proven, but some hydration can be brought about and leads to the most satisfactory solutions. Industrial methods for bringing such materials into solution must provide conditions which suppress hydrolysis and favor hydration. Glasses of the composition of the disilicate or mixture of metasilicate and disilicate dissolve without decomposition," p. 104.

"Glasses produced by the sulfate process are never equal in quality to the carbonate glasses. Sodium sulfate dissolves to about 1 per cent in the glass and can always be found in the solutions. Sodium sulfide formed by the action of some form of carbon on the sulfate is subject to serious loss by volatilization at the temperature necessary to produce the silicate, and it attacks the refractories of the furnace with much more vigor than the carbonate batch. The composition is, therefore, difficult to control. Sulfate glasses are most successfully made in continuous furnaces permitting a slow reaction. All sulfides must be oxidized in the final glass or the solutions will be black from sulfides of iron. Sulfate glasses are usually ultramarine blue, irregular from one batch to the next and unsatisfactory for the more refined uses of the solution," p. 111.

"Sodium oxide is best determined by titration with N/5 hydrochloric acid and methyl orange, which gives a much sharper end point in silicate than in carbonate solutions. Phenolphthalein always gives low results. The error is greatest with the solutions of high silica ratio. Stericker found the fractional amounts of the total titratable with this indicator [running down to 85%].

"This may be due to adsorption of sodium oxide on colloidal silica or to the formation of acid silicates. The end point is difficult to fix and this indicator should not be used. Methyl red and brom-phenol blue are satisfactory, but phenol red, attractive on account of its resistance to hydrogen peroxide, only gives part of the total sodium oxide in silicate solutions," p. 157.

"Wheeler prepared a structural material by preparing a stiff dough from short asbestos fiber with or without any mineral matter. This was pressed into form and baked at 200° to 270°C. to form a hard substance, called Alignum, which could be used for doors and trim but which could at the same time be worked with wood-cutting tools. $Na_2O, 3.3SiO_2$ was used and satisfactory fire doors were made, though at somewhat greater cost than steel doors, which were commercially perfected at a later time," p. 191.

"Setting caused by chemical reaction is usually accompanied by loss of ultimate strength and by increase of resistance to water, for silica gels are insoluble. Their strength is greatest when they are formed in the presence of little water. They are solids, while the soluble silicate is liquid even when so viscous as to appear perfectly rigid. A quality of toughness inheres in cements in which soluble silicate remains as such so long as any water is present. Rock-like masses of hydrated silicate show a resilience suggestive of rubber. The rebound of a sledge or cutting tool driven into them will amaze the uninitiated," p. 194.

"The advent of the fiber shipping container made from corrugated or solidly laminated sheets of paper has opened a wide field for silicate adhesives. The heavier laminated paper products such as wall board, cloth board, and paper tubes, have also assumed an important place in industry. Each presents its own problems of adaptation of adhesive to machine and papers. On this account, and because growth is still active, the processes will be separately treated in some detail but always from the point of view of the function of the silicate adhesives. The transition from wood, which is used once and burned, to paper, which can be reclaimed many times is of primary economic significance in a country whose forest reserves are being rapidly depleted in the face of an expanding industrial life and an inadequate program of reforestration," p. 223.

"Casein-lime-silicate glues make joints on wood which are stronger than the wood fiber. They will stand prolonged immersion in water or even boiling. They have somewhat greater tendency than animal glues to dull knife edges of woodworking tools, but can be easily sawed. Among the many combinations possible it appears that casein glues free from lime and containing silicate can be produced with a high degree of water-resistance, but the technic of their manufacture has not been divulged. They are said to have no more effect on cutting tools than the wood itself," p. 247.

"Ceramic colors painted upon surfaces to be decorated with the aid of a silicate binder which sets in the air and permits of easy handling have been found convenient and economical, and zinc silicate glazes applied in this manner have yielded some of the most beautiful crystalline effects. Kraner found that step in the preparation of these glazes could be omitted by using a silicate solution as binder for the glaze materials and calculating the soda and silica of the silicate as part of the final composition. In this way the alternative of frit, weakly attached with an organic binder which had to be burned out at a low temperature prior to the final firing, was avoided and decorative effects of rare beauty were obtained. Zinc silicate crystals are able to absorb certain coloring materials, such as the oxides of cobalt, manganese, copper, uranium, nickel, and iron in such a way that bright colored crystal masses appear upon a background of contrasting color. It is not possible to present this adequately in monochrome, but the author possesses two vases similar to the one shown in the cut. Their surfaces are strewn with delicate blue crystal tracery on a background of brownish buff, most pleasing to the eye. Many color combinations are possible," p. 275.

"The process of sizing paper consists in depositing upon or among the fibers which form the sheet colloidal substances so chosen as to modify the finished product to fit it for specific uses. Rosin is the material mostly used, and its primary contribution is to impart a resistance to water. It does not give to paper all the desirable qualities, and as forest reserves are depleted its cost increases. These two considerations have led to the use of several other colloids which serve in some instances by themselves and in other cases in an accessory capacity.

"The soluble silicates fall into this group. To understand their place in the industry it is necessary to have clearly in mind their relation to the process of sizing with rosin. Both are alkaline colloidal materials, for rosin is always dispersed by making a soap which contains more or less free rosin. In their alkaline condition they are not retained by cellulose fiber and would be lost in the process of making paper unless a precipitant were used. Various salts and acids have been tried, but the one in almost universal use is aluminum sulfate, known as papermaker's alum. The theory of rosin sizing has not been set forth in such a way as to be completely satisfying, but it is evident that both aluminum hydroxide and colloidal rosin play a part in giving the paper the ability to resist the penetration of water or aqueous inks. It has been assumed that rosin sizing and soluble silicates are incompatible. This is an error. It is necessary to add a sufficient amount of alum to precipitate both silicate and rosin when they are used together, just as they must be precipitated when they are used separately. Pulp which has been treated with rosin size and just enough alum will not be properly sized if made alkaline with silicate. When the silicate is precipitated with alum both are in condition to be retained and to affect the finished paper," p. 278.

"McDowell believes that the better color of dyed goods which have been treated with silicate solutions is due to the deposition of a protective film. He found indanthrene and other vat colors after kier treatment in the presence of silicate became insensitive to chlorine bleach to such an extent that goods with designs in color could be bleached by the methods ordinarily used for 'gray' goods without the ned of any after treatment to restore an altered color," p. 344.

"Of the many uses of silicate solutions, the practice of employing them for the preservation of eggs is, perhaps, the most familiar. Under the name 'waterglass,' silicates of varying composition, concentration, and fitness for the work are sold and regularly used by great numbers of householders. The process is essentially one of gelatinous film formation. The shell of the egg must be protected against the entrance of bacteria which cause decay. For this reason it is necessary to start with fresh, preferably sterile eggs. They should not be washed, as this removes a natural mucilaginous film and increases the danger of infection before the silicious gel has formed an effective seal. It is probable that both the albuminous constituents of the shell and the calcium compounds reduce the stability of the silica and thus aid the formation of gel. A silicate near the composition $Na_2O,3.3SiO_2$ is best. It should be diluted just enough to allow the eggs to sink (about 4° Baumé) and put into a stone crock or other tight container. One U.S. gallon of specific gravity 1.38 will suffice for 50 to 80 dozen eggs, according to size of eggs and shape of container. The eggs are laid in the solution and kept covered by two inches of liquid till ready for use.

"More dilute solutions can be used, but comparative tests indicate that when this is done the quality of the eggs after storage of six months or longer is inferior. Sometimes, especially if the container has not been tightly covered and the silicate has concentrated or absorbed much carbon dioxide, the whole of the liquid will gel. This does not affect the quality of the eggs; but because it is unpleasant to some people to put their hands into the soft gel to remove the eggs for use, a more stable silicate has been proposed. $Na_2O,2SiO_2$ under ordinary conditions of storage remains clear and liquid in contact with the eggs, but the preservation is not so good as that secured with the solutions containing more silica. This is manifest in an earlier thinning of the egg albumin and a depreciation of flavor due to the entrance, by dialysis, of trifling amounts of Na_2O," p. 385.

"Rayon formed by extruding viscous solutions of cellulose into a bath which coagulates the liquids to produce threads for a wide variety of textile uses, has of later years assumed great technical importance. The viscous process, which depends upon the formation of xanthogenate by the action of sodium hydroxide and carbon disulfide upon cellulose, is one of the most important. The coagulating bath first used for this process was made from acid salts, notably bisulfites; but it was found that the threads after leaving such a bath could be passed through a silicate bath with the result that they had less tendency to stick together. It has also been proposed to add silicate solutions to the sodium hydroxide used in preparing the viscose colloid, the purpose being to obtain a stiffer fiber adapted to the imitation of horsehair and other special uses, such as fabric for Welsbach mantles," p. 409.

Wilder D. Bancroft

The Annual Survey of American Chemistry. *Edited by Clarence J. West. Vol. III. 21 × 14 cm; pp. 395. New York: The Chemical Catalog Company, 1928. Price: $3.00.* The evil that one does in chemistry apparently lives after one. Because one chairman of the Division of Chemistry and Chemical Technology thought that it would be a good thing to review American Chemistry only, his successors have to follow in his footsteps. The justification now is that the product sells well, which is also an argument in favor of bootlegging as a profession.

The increase in production of lead due to selective flotation is estimated to be about 440,000 tons, p. 113. "The enormous existing tonnage of low grade lead-zinc sulfide ores is beginning to be tapped just as the richer deposits of galena are showing some signs of depletion. In order to utilize these low grade ores economically, it was necessary to secure a better separation of lead and zinc minerals than had heretofore been possible. Results have now been obtained which establish good separation into marketable concentrates. It is true that there has been some further improvement in equipment represented by the new type of pneumatic flotation machines, using from 2 to 3 pounds air pressure, but the salient factor in flotation progress has been the development of chemical 'addition agents,' the reagents which cause a selective wetting of sulfide particles in the froth. The oils formerly used as frothing agents are still used but in greatly reduced quantities.

"A number of special selective agents have come into use during the last few years, such as potassium xanthate. Xanthate was considered the best reagent a year ago and is still widely used in conjunction with the older reagents, especially since the litigation which formerly tied up its use has now been favorably settled. More recently, however, several newly discovered agents, which show signs of great promise in the lead-zinc field, have been coming to the fore.

"Thiocarbanilide is said to have a greater selective action and less tendency to promote bulk flotation of all sulfides. Phosphocresylic acid, originally devised for the selective flotation of copper minerals from pyrite, is finding use in separating lead and zinc minerals. Still others, which it is unnecessary to name, show signs of promise in selective work."

"Zinc oxide holds a unique position in outside paints which is being more clearly recognized all the time. Due to its opacity to ultraviolet light and its ability to chemically stabilize the film, it is coming to be regarded as an essential ingredient in all high-grade paints which must stand exposure to the weather no matter what other pigments are used." p. 117.

"In the pigment field this trend toward process improvement and better plant control is even more noticeable. Modern lithopone is quite a different product from that of even two or three years ago, and the end is not yet in sight. Much of this development has been in the direction of designing the pigment for specific purposes and is the result of careful laboratory study of each step followed by strict plant control. In zinc oxide manufacture the practice of producing both paint and rubber oxide on the same furnace at the same time is waning. The modern practice is rather to so control the charge and the furnace that the product will be specially suited to either paint or rubber manufacture as the case may be. Even further specialization is probable in the future," p. 118.

"The aromatic halogen compounds have received particular attention during the last year. A series of papers by Nicolet and his students dealing with positive halogen in the benzene ring have appeared. The halogens in *o*-and *p*- halogenated amines, phenols and naphthols and in iodimesitylene are easily removed from the ring by the action of boiling hydrochloric acid. The rate of removal of halogens from halogenated phenols and naphthols increases with increase in hydrogen ion concentration. No similar production of positive halogen could be obtained by *m*-substitution with such groups as the nitro group. This has led to the view that a quinoid form of the molecule may be the active form," p. 141.

"A curious explosion is described by van Brunt. A carboy containing ammonia liquor was used as an egg to elevate ammonia liquor. To avoid excess pressure an iron U-tube containing mercury was attached as a safety valve. This device has been in use daily for ten years, when a violent explosion occurred, limited to a small area on the ammonia side of the U-tube, opening the iron pipe for about four inches. The explosion may have been due to a mercuri-ammonium oxide, formed at room termperatures by the long exposure of mercury oxide to ammonia gas," p. 330.

"McLaughlin, Highberger and Moore have demonstrated that the action of lime solutions upon skin is purely chemical in nature and have shown that at the point of hair slippage (regardless of time required for slippage) a definite minimum amount of sulfur is found dissolved in the lime solution. This dissolved sulfur is derived mainly from the keratin of the skin epidermis, which holds the hair in the follicle. They show, also, thet the heightened unhairing power of a re-used lime solution is not due—as has been variously held—to the presence of accumulated bacteria, enzymes, ammonia, or sulfur; but to the presence of small quantities of primary amines, formed largely through the action of proteolytic bacteria upon the skin during the processes preceding liming," p. 371.

Wilder D. Bancroft

Heat and Thermodynamics. *By J. K. Roberts. 23 × 15 cm; pp. xvi + 454. London: Blackie and Son, Ltd., 1928. Price: 30 shillings.* "There shall be heard in many parts of Europe instruments of various sizes making divers melodies, causing great weariness to those who hear them most closely" (Leonardo da Vinci).

In the fifteenth century this was said of the bells worn by mules. Perhaps it could be applied now as aptly to the knowledge which students have to acquire out of the concert of modern physics. Books, then, that collect together recent work and present the outcome clearly are welcome.

Mr. Roberts' book on "Heat and Thermodynamics" should be a most useful one to the Honour student. With sufficient detail and yet with clarity it presents to him in chapters of the right length the present position of the subject, and describes briefly the experimental work which has led to advance.

Reference to work of recent date and suppression of unnecessary detail about older experiments which survive in many books on Heat, is a noteworthy feature of this book.

Temperature, quantity of heat, behavior of gases, change of state, conductivity and kinetic theory, etc., are conveniently dealt with before the generalisation of thermodynamics are discussed. The chief applications of thermodynamics to engineering are briefly, but satisfactorily, described in a chapter on Power Cycle. The consequences of the two laws as expressed by $ds - \frac{dv - dw}{T} \geqslant 0$ are then followed up in two chapters on Equilibria; the subject is very clearly presented. This leads to an account of the Nernst Theorem and the outcome of Eucken's examination of its validity. The small departures found are of particular importance theoretically. The book contains a chapter on the Thermodynamics of Radiation and then ends with three chapters introducing the Quantum Theory,—Planck's radiation formula, Debye's Theory of the Specific Heat of Solids and the Equation of State for solids as first presented by Grüneisen. A short account of Callendar's work on the properties of steam and a useful account of Thermodynamic relations is appended. A large scale I Φ chart is affixed to the cover.

The author is to be congratulated on the selection of material for inclusion in the book, such as Knudsen's investigations on the properties of gases at low pressures, Eucken's work on conductivity and other interesting points which have been accessible up to the present, only in the original papers. On some matters, such as the equipartition of energy in the discussion on the specific heat of gases, a fuller treatment could have been given, but in such cases it is noted that the author has always referred to the pages of other treatises, e.g. Jeans' Dynamical Theory of Gases, in which the matter is dealt with fully.

Apart from the useful scope and clear arrangement of the book, it is most of all the lucidity of presentation that commends it. *Alfred Egerton*

Physikalisch-chemische Praktikumsaufgaben. *By Arnold Eucken and Rudolf Suhrmann. 22 × 15 cm; pp. xii + 240. Leipzig: Akademische Verlagsgesellschaft, 1928. Price: paper, 13 marks; bound, 14 marks.* In the introduction the authors say: "The training in physical chemistry is done, as in most other branches of the natural sciences, through lectures, seminars (quizes), and laboratory practice. The main features of the physical chemistry lectures and of the quizes are pretty well standardized by now and therefore do not give rise to much discussion; but it is quite different with the laboratory course because this serves several quite different purposes simultaneously. In the first place it makes the student really familiar, by concrete illustration, with the fundamental laws of physical chemistry discussed in the lectures. Secondly, it gives him manipulative skill. Lastly it should bring out more completely than any lecture or text-book can do, the numerous connections between the physical-chemical theories and the fields in which they are applied."

It is not clear how a laboratory course can do this last better than a text-book can; but that is not important. The outcome is that each head of a laboratory wishes to write his own laboratory manual and that Professor Eucken is no exception to this rule.

The experiments are grouped under three main heads with many subdivisions under each. First, we have fundamental physical methods of measurements, grouped in the imposing subdivisions: mechanics; optics; heat; electricity. This is followed by physical-chemical analysis with the same subdivisions as in the first part. The bulk of the manual is devoted to the determination of physical-chemical constants. Under thermal constants we find: homogeneous substances and solutions; homogeneous chemical equilibrium; heterogeneous systems. Next come caloric constants and then reaction velocity. Under constants from the field of electrolysis we find: electrochemical equivalent; migration velocities; galvanic polarization. Under surface phenomena we find surface tension; adsorption; colloidal solutions. Under the constitution of matter the sub-heads are: molecules; atoms; electrons.

The reviewer is no judge because he has never tried to run a laboratory course in physical chemistry; but this seems rather like a good book. The reviewer would have been better pleased if some reference had been made, p. 205, to the errors in the titrimetric determination of adsorption. *Wilder D. Bancroft*

THE ANODE REACTIONS OF FLUORINE*

BY NEWTON C. JONES

Fluorine is the most electronegative of all known chemical agents. It possesses an even higher oxidation potential than ozone, since ozone is produced when fluorine acts on water.[1] The potential of the normal fluorine electrode is usually given as 1.9 volts but this cannot be right as fluorine decomposes water and sulfuric acid. Latimer[2] calculated this potential from thermochemical data and found a value of 2.85 volts, which is probably very nearly right. With fluorine, then, we should be able to duplicate by purely chemical means any electrochemical anode process or, in short, any oxidation process using any other oxidizing agent.

Fichter, in a lecture before the Société de Chimie physique,[3] formulated the idea as follows: "I would like to take from inorganic chemistry two examples, the preparation of persulfates and of simple salts of trivalent cobalt. I am taking but these two cases because current opinion, as is found at any time in the literature, is that these two oxidations can be effected only in aqueous solution at a platinum anode; there still survives a remnant of the electrochemical mysticism which attributes to electrodes and to ions forces inaccessible to the ordinary chemist. Modern chemical thought which interprets all chemical phenomena as a transfer of electrons obliges us on the contrary to postulate that we should be able to imitate all purely chemical reactions at the anode and that inversely we should be able to carry out all electrochemical reactions by purely chemical means; it is simply a question of finding the oxidation potential. Ozonized anodic oxygen with its potential of 1.9 volts with respect to the normal hydrogen electrode is found in the table of potentials near the head of the non-metals, immediately below fluorine; if we wish to equal or surpass the reactivity of anodic oxygen, fluorine alone is to be considered."

There is yet another way of stating the idea, namely, that fluorine will displace the negative portion of any other substance. The actual product obtained will be either the negative portion of the molecule acted on, or a decomposition product of the negative portion, or a product of a reaction of the radical freed with fluorine or some other substance present at the time. For example, we know that chlorine is more electronegative than bromine and displaces the latter from its salts. This thought is the opposite of the well-known fact that zinc, being more electropositive than copper, will displace the latter from a solution of one of its salts.

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* This work is part of the programme now being carried out at Cornell University under a grant to Professor Bancroft from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] Moissan: Compt. rend., 119, 570 (1899).

[2] J. Am. Chem. Soc., 48, 2868 (1926).

[3] J. Chim. phys., 23, 490 (1926).

Furthermore, we can say that if a mixture of substances is treated with fluorine, the least electronegative constituent will be liberated first, because it comes off at the lowest voltage. For example, if chlorine is run into a mixture of bromide and iodide, no displacement of the bromine will take place until all the iodine has been displaced, providing there is no impoverishment of iodide. This concept is made use of in the electrolytic separation of copper and zinc from an acid solution. All the copper is plated out before hydrogen comes off and further all the hydrogen must be plated out before any zinc can appear on the cathode.

Fichter and his co-workers have shown that gaseous fluorine will oxidize many substances, some of which had previously been oxidized only at the anode. They obtained persulfate from cold saturated solutions of acid sulfate, and dry acid sulfate but none from dry normal sulfate,[1] cobaltic sulfate from cobaltous sulfate,[2] ozone and ozonates from water and alkali,[3] persulfate and sulfur tetroxide from sulfuric acid,[4] perphosphate, percarbonate and perborate from the corresponding phosphates, carbonates and borates,[5] and finally chromate and permanganate from trivalent chromium and divalent manganese.[6]

The explanations offered by Fichter as to how and why these reactions proceed the way they do may be summed up as follows:—

1. In solutions where there is but little or no sulfuric acid present, ozone seems to be the true oxidizing agent.

2. In solutions containing much sulfuric acid, the labile peroxide of sulfur, SO_4, is the true oxidizing agent. High acid concentration also retards the formation of hydrogen peroxide which would reduce with evolution of oxygen the oxidized compound formed.

3. The oxidation always takes place by means of some intermediate oxidizing agent resulting from the action of fluorine on the solvent, never directly except where the cation of a metal fluoride is oxidized to the fluoride of the metal in a more oxidized condition.

After a moment's reflection, however, it will be evident that an intermediate oxidizing agent cannot be formed, as the formation of such an agent requires a higher potential than that necessary to cause the oxidation reaction that takes place. One does not say that when caustic soda solution is electrolyzed, sodium ion is discharged first and that then the free sodium reacts with the water present to give hydrogen; one says that as hydrogen ion is discharged at a lower voltage than sodium ion, the former will be discharged directly without disturbing the sodium ions at all. The modern theory postulates that that reaction takes place which does so at the lowest voltage,

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[1] Brunner: Helv. Chim. Acta, 3, 818 (1920); Fichter and Humpert: 6, 640 (1923); 9, 467, 521, 602 (1926).

[2] Fichter and Wolfmann: Helv. Chim. Acta, 9, 1093 (1926).

[3] Fichter and Bladergroen: Helv. Chim. Acta, 10, 549 (1927).

[4] Fichter and Bladergroen: Helv. Chim. Acta, 10, 553 (1927).

[5] Fichter and Bladergroen: Helv. Chim. Acta, 10, 559, 566 (1927).

[6] Fichter and Brunner: J. Chem. Soc., 133, 1862 (1928).

that is, with the least expenditure of energy. It is proposed to show that this theory holds for oxidations by means of fluorine in the same way that it holds for electrolytic oxidations at an anode. The chemical and electrochemical cases are strictly parallel.

The Production of Persulfates

Fichter has shown that when fluorine acts on cold saturated solutions of potassium or ammonium acid sulfates the corresponding persulfates are formed, along with some ozone and other products. This has been confirmed by us. The same result was obtained by passing fluorine over dry acid sulfates, but no persulfate was formed from dry potassium sulfate (no acid present). Potassium fluorsulfonate was formed as well as persulfate when fluorine and hydrofluoric acid were allowed to act on dry potassium sulfate. The reactions were formulated by Fichter as follows:

$$KHSO_4 + F_2 = K_2S_2O_8 + 2HF,$$
$$3K_2SO_4 + F_2 + 2HF = K_2S_2O_8 + KFSO_3 + H_2O + 3KF.$$

A complete study of the action of fluorine on potassium and ammonium sulfates[1] showed that a highly oxidizing solution containing permonosulfuric acid (Caro's acid, H_2SO_5), persulfuric acid, fluorsulfonic acid, ozone and another "vergängliches Oxidationsmittel, V.O." (transient oxidizing agent) was formed. The conclusions found may be quoted:

"(a) the yield of oxidizing agents is greater the more concentrated the solution chosen;

(b) the yield of oxidizing agents is greater the lower the temperature. These two conditions contradict themselves in so far as at the low temperature the solubility of the salts is diminished. Therefore the most soluble of the salts worked with, ammonium acid sulfate, gives the best yields of oxidizing agents;

(c) the yield of the most efficient oxidizing agents (O_3 + V.O.) is relatively higher the shorter the duration of the action, as they partly decompose, partly change over into persulfate;

(d) the relative yield of O_3 and V.O. is greater in dilute solutions of the neutral sulfate than in concentrated solutions of the acid sulfate;

(e) the relative yield of permonosulfuric acid (assuming it to be a question of this acid) is greater the more dilute the solution;

(f) the quantity of the fluorsulfonic acid on the other hand rises with the concentration of the solution. We have not found a relation between the fluorsulfonic acid and the per-acids."

It was found later[2] that the transient oxidizing agent referred to as "V.O." is really identical with the sulfur tetroxide, SO_4, first prepared by Berthelot[3] by passing sulfur dioxide and an excess of oxygen together through an ozon-

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[1] Fichter and Humpert: Helv. Chim. Acta, 9, 602 (1926).

[2] Fichter and Bladergroen: Helv. Chim. Acta, 10, 553 (1927).

[3] Compt. rend., 86, 20, 288 (1878).

izer. The tetroxide exists only in solution and decomposes in a short time with the formation of ozone. Its actual existence mixed with sulfur trioxide has been since confirmed.[1]

Since the yield of persulfate is a maximum when a saturated solution of an acid sulfate (e.g. $KHSO_4$) is electrolyzed[2] and when fluorine acts on an acid sulfate, but no persulfate is obtained when fluorine acts on a dry normal sulfate, the primary reaction must be the discharge not of sulfate ions but of the acid sulfate ions

$$2HSO_4' = H_2S_2O_8$$

to form persulfuric acid. This is substantiated by the fact that in concentrated solution the ionization of sulfuric acid is primarily as follows:[3]

$$H_2SO_4 = H^{\cdot} + HSO_4',$$

and no persulfate is ever formed from a dilute solution where the ionization to $2H^{\cdot} + SO_4''$ is predominant. No sulfur tetroxide is formed in the electrolytic preparation of persulfate, so the oxidation potential of the latter must be less then that of the sulfur tetroxide. That some was actually formed when fluorine acts on acid sulfate solutions must therefore be due to impoverishment of the HSO_4' ions and not to the sulfur tetroxide being formed first and then oxidizing the sulfate to persulfate. At higher temperatures, the persulfate is less stable, hydrolyzing to acid sulfate and ozonized oxygen. Hence raising the temperature diminishes the yield of persulfate, as was found.

In a concentrated solution, another reaction is possible, the formation of fluorsulfonate. Salts of fluorsulfonic acid are formed by treating a fluoride with fuming sulfuric acid.[4] In dilute acid or dilute alkali solutions the fluorsulfonates are completely hydrolyzed to acid sulfate and hydrofluoric acid, but are stable in very strong sulfuric acid solution and at low temperature.[5] When concentrated sulfuric acid is electrolyzed, oxygen and hydrogen are given off; in other words, water is removed. In time then the sulfuric acid will contain an excess of sulfur trioxide, and if hydrofluoric acid is present, fluorsulfonic acid will be formed. Platinum anodes corrode under these conditions,[6] however, so it is cheaper to devise and run another experiment that will show the same thing. If on passing fluorine free from hydrofluoric acid into pure 100% sulfuric acid or fuming sulfuric acid, oxygen is liberated and fluorsulfonic acid is formed, then our explanation of the mechanism of the formation of fluorsulfonate is substantiated. This is actually the case, the reactions being

$$2H_2SO_4 + F_2 = 2HF + H_2SO_4.SO_3 + O = HF + HFSO_3 + H_2SO_4 + O,$$
$$H_2SO_4 . SO_3 + F_2 = 2HFSO_3 + O.$$

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[1] Meyer, Bailleul and Henkel: Ber., 55, 2953 (1922).

[2] Elbs and Schönherr: Z. Elektrochemie, 2, 245 (1895).

[3] Treadwell-Hall: "Analytical Chemistry," 1, 8 (1921).

[4] Traube: Ber., 46, 2525 (1913).

[5] Traube, Hoerenz and Wunderlich: Ber., 52, 1272 (1919).

[6] Tommasi: "Traité d'Electrochimie," 585 (1889).

Therefore, when fluorine is passed into an acid solution of sulfate, fuming sulfuric acid is formed, which is converted into fluorsulfonate by the hydrofluoric acid produced at the same time. More of the fluorsulfonate will appear the more concentrated the solution. In dilute solutions, fluorsulfonate cannot be formed as no sulfur trioxide can be produced (except by running in fluorine for a long time) and as the hydrolysis reaction of fluorsulfonate is the more rapid one.

It must be emphasized that the formation of fluorsulfonate is not the result of oxidation but is merely a side reaction that is more prominent the more concentrated the solution. No relation should exist between the amounts of persulfate and fluorsulfonate produced.

In a dilute solution of acid sulfate, one gets more of the Caro's acid, H_2SO_5. The reason for this is apparent from the work of Müller and Schellhaas.[1] They found that the reaction

$$H_2S_2O_8 + H_2O = H_2SO_4 + H_2SO_5$$

takes place. In very strong acid solution, permonosulfuric acid is not stable while the persulfuric acid is stable; in a more dilute solution, the permonosulfuric acid is stable while the persulfuric acid is not, hydrolyzing according to the above equation. It was also found that the hydrolysis of persulfuric acid is catalyzed by $H^{\cdot}$ ion. It can be readily seen that the reaction must be necessarily slow in very strong potassium acid sulfate solution as the ionization is chiefly as follows:

$$KHSO_4 = K^{\cdot} + HSO_4{}'$$

while in more dilute solution there are more $H^{\cdot}$ ions:

$$KHSO_4 = K^{\cdot} + H^{\cdot} + SO_4{}''$$

and the hydrolysis reaction is rapid. Also there are relatively less $HSO_4{}'$ ions in a dilute solution and simple oxidation of sulfuric acid is favored. For a dilute solution then the reaction for the oxidation of potassium acid sulfate by fluorine must be written:

$$KHSO_4 + F_2 + H_2O = KF + HF + H_2SO_5.$$

The latter compound is obtained in dilute solution in preference to persulfate or fluorsulfonate.

Of course, all the products were obtained by simply bubbling fluorine through an acid solution of sulfate as there were no precautions taken to prevent impoverishment. However, in more concentrated solutions the relative yield of persulfate and fluorsulfonate must be higher, while in more dilute solutions the relative yield of permonosulfuric acid must be higher. This is in perfect accord with the experimental facts.

Electrolysis of saturated, cold, acid sulfate solutions yields persulfate at the anode. The yields of persulfate are increased and the salt may be obtained at a lower concentration of either acid sulfate or acidified normal sulfate if fluoride ion (usually added as hydrofluoric acid) is present in the

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[1] Z. Elektrochemie, 13, 257 (1907).

bath used. Skirrow[1] explained the effect of fluoride ion as due to oxygen liberated at a higher potential but obtained no persulfuric acid on electrolyzing dilute sulfuric acid in the presence of hydrofluoric acid. Müller,[2] however, obtained persulfuric acid by using a more concentrated solution of sulfuric acid and a higher current density. The yield was much smaller than when potassium or sodium sulfate was used. He argued that the presence of fluoride ion increased the potential of the platinum anode so that oxidation is favored over evolution of oxygen. Curves were given to show that the potential rises from a value of 1.9 volts to one of 2.2 volts on adding hydrofluoric acid.

Isgarischew and Stepanow[3] studied the influence of fluoride ion on the overvoltage at platinum anodes in sulfuric acid and caustic potash, and found maxima in the potential curves for certain concentrations of fluoride added. "The raising of the overvoltage in presence of fluorides was explained by the formation of oxyfluorides that covered the anode with a stable layer. The decrease in polarization resulting from elevation of the concentration of sodium fluoride and ammonium fluoride was due to the solvent action of the salts on the fluorides and on the platinum oxides." Their theory will not, however, explain the action of chloride, sulfate, chlorate[4] and nitrate[5] ions in raising the potential of the anode, as these ions do not form complex salts with oxides.

When sulfates are electrolyzed, the case is complicated by two factors which do not appear in the purely chemical oxidation, namely, the specific effect of the anode at which the oxidation takes place and the oxygen overvoltage at that anode. Bennett and Thompson[6] postulate that during electrolysis unstable intermediate products above the equilibrium concentration are formed, giving rise to overvoltage. The unstable products are the monatomic forms in the case of gases, e.g. O_1, H_1, Cl_1, etc., which are more reactive than the final products O_2, H_2, Cl_2, etc. At metals with high oxygen overvoltages the reaction

$$2O_1 = O_2$$

is slow; when the overvoltage is low, the reaction is rapid.

Since all the electrolytic oxidations cited in the first part of this paper were done at platinum anodes, the specific effect of the electrode metal drops out and can be ignored in the following discussion. The other factor, the oxygen overvoltage, is the deciding one. This idea is not new. Müller[7] found that the presence of chloride, sulfate, chlorate or fluoride in the electrolytic bath favored the formation of periodate from iodate, the fluoride having the greatest effect. "The fact that the presence of fluoride ion presents the possi-

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[1] Z. anorg. Chem., 33, 25 (1902).
[2] Z. Elektrochemie, 10, 776 (1904).
[3] Z. Elektrochemie, 30, 138 (1924).
[4] Müller: Z. Elektrochemie, 10, 753 (1904).
[5] Schellhaas: Z. Elektrochemie, 14, 121 (1908).
[6] J. Phys. Chem., 20, 296 (1926).
[7] Z. Elektrochemie, 10, 753 (1904).

bility of raising the anode potential to abnormal values depends in any case . . . on the fact that thereby the evolution of oxygen at the platinum is decreased. We can also express it: The fluoride ion raises the anodic overvoltage of the platinum. Whence it follows that the overvoltage is dependent in evident measure on the nature of the electrolyte."

With the help of Bennett's conclusions it is now possible to present an explanation as to *how* the overvoltage is raised by the fluoride ion. The reaction

$$2O_1 = O_2$$

is retarded by the fluoride ion, the overvoltage rises or the oxidation potential of the electrode is increased and oxidation is favored over oxygen evolution. This can happen only in case the fluoride ion is adsorbed on the anode. It must be emphasized, however, that an indifferent ion cannot raise the potential of the electrode all the way up to, or above, the potential at which the indifferent ion itself is discharged, otherwise one would be lifting oneself by one's own bootstraps. In no case is the indifferent ion itself discharged.

If an ion which is not itself discharged is adsorbed on a platinum anode the active surface of the metal is decreased, and further, if the platinum is the agent that catalyzes the reaction

$$2O_1 = O_2$$

and not the adsorbed ion then the speed of this reaction will evidently diminish and the overvoltage of oxygen will rise. We do know that the electrode metal has a catalytic action but we do not know that the adsorbed ion does not. Hence all we can say at present is that, for certain cases, this appears to be the mechanism by which the overvoltage is raised. No case has yet been found where the opposite is true.

The Production of Perphosphates

When cold fluorine is led into a cold phosphoric acid solution, a mixture of permonophosphoric acid (H_3PO_5) and perphosphoric acid ($H_4P_2O_8$) is obtained.[1] The best yield is produced from a 5M solution. Alkali phosphates and pyrophosphates give salts of perphosphoric acid, provided a slight alkalinity is maintained throughout the run. Permonophosphoric acid is practically the sole product in strongly acid solutions; perphosphate is the chief product in alkaline solutions.

Electrolysis of solutions of phosphates to which fluoride has been added between platinum electrodes gives solutions which contain active oxygen in the form of unstable salts of permonophosphoric acid and stable salts of perphosphoric acid.[2] The best yields are obtained from practically neutral solutions of mixtures of the acid and normal phosphates. Ozone alone is the product from phosphoric acid.

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[1] Fichter and Bladergroen: Helv. Chim. Acta, 10, 559 (1927).

[2] Fichter and Müller: Helv. Chim. Acta, 1, 297 (1918); Fichter and Gutzwiller: 11, 323 (1928).

A really quantitative study of the electrolysis of phosphates was carried out by Fichter and Rius y Miró.[1] It appears advantageous to summarize the results:

(1) Phosphates of potassium, ammonium and rubidium on electrolytic oxidation at a platinum anode yield salts of perphosphoric acid. Good yields are obtained only when the solution is kept slightly alkaline.

(2) Unstable salts of permonophosphoric acid are also formed. These, on standing in alkaline solution, decompose with evolution of oxygen.

(3) The relative amount of the permonophosphoric acid increases with increasing current density, with decreased concentration of phosphate present, and with increased acidity.

Recently[2] more work was done on the favorable effect of fluoride ion on the electrolysis of phosphates to give perphosphates. The theory assumes that the fluoride ion is primarily discharged, then acts in a roundabout way through a platinum peroxide or directly on the substance in the solution and on the water. He then contradicts himself when he says that since the decomposition potential of fluorine is high, it is not discharged, the anode being depolarized by the oxidizable substances. The latter statement is the right one.

Fichter and Rius y Miró explain the purely chemical and electrochemical formation of peracids of phosphorus from the same viewpoint by assuming that the electrolytic oxidation of perphosphate proceeds after a previous dehydration to pyrophosphate:

$$2H_3PO_4 = H_4P_2O_7 + H_2O.$$

Oxidation then carries the pyrophosphate to perphosphate:

$$H_4P_2O_7 + O = H_4P_2O_8$$

To support this theory they electrolyzed a mixture of "tetra- and dipotassium pyrophosphates" and got perphosphate. The formation of permonophosphoric acid was conceived as a further oxidation of perphosphate:

$$H_4P_2O_8 + O + H_2O = 2H_3PO_5.$$

According to this, then, one should get more permonophosphoric acid from a concentrated solution where the anode potential is higher and relatively more perphosphoric acid from a more dilute solution where the anode potential is necessarily lower. More oxygen comes off at the lower potential; oxidation is favored at the higher potential. Therefore the highest form of oxidation product should be obtained at the higher potential. This is the direct opposite of the theory of Fichter, and is not in accord with the experimental results.

We must fall back on the theory that that reaction will take place which does so with the least expenditure of energy. The electrolytic results and the results upon fluorination can be explained on the same basis and so for the sake of simplicity and clarity, the results will be discussed as though fluorine were the oxidizing agent employed.

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[1] Helv. Chim. Acta, 2, 3 (1919).

[2] Rius y Miró: Añales soc. españ. fís. quím., 20, 644 (1922); Centrallblatt, III, 1249 (1923).

The best yields of perphosphate are obtained when a slightly alkaline solution of KH_2PO_4 is treated with fluorine. The ionization of this salt in concentrated solution may be written:

$$KH_2PO_4 = K^{\cdot} + H_2PO_4{}';$$

the ionization of concentrated phosphoric acid is chiefly as follows:[1]

$$H_3PO_4 = H^{\cdot} + H_2PO_4{}'.$$

The primary reaction must then be the discharge of the $H_2PO_4{}'$ ions to give perphosphoric acid:

$$2H_2PO_4{}' + H_4P_2O_8.$$

The slight excess of alkali serves to convert this into stable potassium perphosphate.

In a more acid solution, the oxidation to permonophosphoric acid takes place directly

$$H_3PO_4 + H_2O + F_2 = 2HF + H_3PO_5,$$

it being easier to oxidize phosphoric acid than it is to discharge the now much less concentrated $H_2PO_4{}'$ ions.

We have also the fact that in acid solution, permonophosphoric acid is more stable, while perphosphoric acid is unstable, spontaneously changing over into permonophosphoric acid and orthophosphoric acid

$$H_4P_2O_8 + H_2O = H_3PO_5 + H_3PO_4$$

in the course of two days.[2]

In alkaline solution the reverse is true. Perphosphoric acid is the stable compound (now present as a metallic salt); permonophosphoric acid is unstable, breaking down to form orthophosphoric acid and ozone. Hence one would expect perphosphoric acid to be the chief product in alkaline solution, while permonophosphoric acid would be the chief product in acid solution (both solutions concentrated). The actual experimental results are as outlined.

The action of fluorine on pyrophosphates is evidently the simple oxidation to perphosphate or permonophosphoric acid depending on whether the solution is alkaline or acid. These reactions take place in dilute or concentrated solutions.

In a dilute solution of phosphoric acid or of a phosphate, the oxidation to permonophosphoric acid can take place directly, but no perphosphate can be formed at all. In alkaline solution one will get only oxygen as the permonophosphoric acid is unstable under these conditions, breaking down to give orthophosphoric acid and oxygen. Perphosphate can be formed only when the solution is alkaline and the concentration is as high as possible.

The Production of Percarbonates and Perborates

Fluorine oxidizes carbonates and borates to the corresponding percarbonates and perborates.[3] Electrolysis of alkali carbonates yields percarbonates;[4] in the presence of much carbonate alkali borate yields perborate.[5]

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[1] Cf. Treadwell-Hall: "Analytical Chemistry," 1, 10 (1921).
[2] Fichter and Rius y Miró: Helv. Chim. Acta, 2, 3 (1919).
[3] Fichter and Bladergroen: Helv. Chim. Acta, 10, 566 (1927).
[4] Constam and von Hansen: Z. Elektrochemie, 3, 137 (1896).
[5] Salzer: Z. Elektrochemie, 8, 900 (1902).

The electrolysis of carbonate for percarbonate works best when a neutral saturated solution of carbonate is electrolyzed; too much alkali or acid (more acid than bicarbonate) cuts the yield down to almost nothing.

The formation of percarbonate from a concentrated solution of acid carbonate must take place according to the following scheme:

$$2HCO_3' = H_2C_2O_6,$$

or

$$2KHCO_3 + F_2 = 2HF + K_2C_2O_6,$$

as the ions present in such a solution are chiefly $K^{\cdot}$ and HCO_3'.

Too much acid is deleterious, as percarbonates hydrolyze[1] very readily in acid solution to give hydrogen peroxide:

$$K_2C_2O_6 + H_2SO_4 = H_2O_2 + K_2SO_4 + 2CO_2.$$

Hydrogen peroxide or its decomposition product ozone is therefore the chief product in acid solution. Too much alkali inhibits the formation of percarbonate, as the latter reacts with dilute alkali[2] with the evolution of ozone:

$$K_2C_2O_6 + 2KOH = 2K_2CO_3 + H_2O + O.$$

Favorable yields of perborate are obtained only when a considerable excess of carbonate is present and the solution is kept slightly alkaline. Since the accepted formula for the perborate[3] is $NaBO_2.H_2O_2$ and carbon dioxide is evolved on electrolyzing[4] we are obliged to concur with Fichter and Bladergroen as to the reactions involved. They do not say whether carbon dioxide is evolved when fluorine acts on the alkaline solution of carbonate and borate, nor were they able to isolate the perborate formed. Metaborate is formed first when carbonate or alkali acts on borax:

$$Na_2B_4O_7 + Na_2CO_3 = 4NaBO_2 + CO_2,$$

$$Na_2B_4O_7 + 2NaOH = 4NaBO_2 + H_2O.$$

These reactions are reversible and proceed toward the right as the metaborate is used up in the oxidation.[5] Percarbonate formed primarily by the oxidizing agent used on alkaline hydrolysis yields hydrogen peroxide, which then combines with the metaborate to give the perborate. That no product could be isolated and that the yield decreased with the time of fluorination must be due to the interaction between ozonate from the action of fluorine on alkali[6] and the perborate

$$NaBO_2.H_2O_2 + NaOH.O = NaBO_2 + H_2O + NaOH + O_2.$$

Oxygen is evolved but it has not been shown that this is the reaction which produces it.

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[1] Friend: "Textbook of Inorganic Chemistry," 5, 137 (1917).

[2] Mellor: "Comprehensive Treatise on Inorganic and Theoretical Chemistry," 6, 83 (1925).

[3] LeBlanc and Zellman: Z. Elektrochemie, 29, 192 (1923).

[4] Arndt and Hantge: Z. Elektrochemie, 28, 263 (1922).

[5] Mellor: "Modern Inorganic Chemistry," 627 (1922).

[6] Fichter and Bladergroen: Helv. Chim. Acta, 10, 549 (1927).

The Preparation of Fluorine

Gaseous fluorine was prepared by the electrolysis of fused potassium hydrogen fluoride, according to the method first worked out by Argo, Mathers, Humiston and Anderson,[1] later modified by Meyer and Sandow,[2] and by Simons.[3] The cell proper (Fig. 1) consists of a magnesium pot, which serves as cathode, heated electrically by a nichrome element wound around the outside, and a magnesium diaphragm, to prevent mixing of the hydrogen and fluorine generated at the respective electrodes, through the top of which passes a heavy copper lead threaded to a graphite rod which serves as anode. The wire is insulated from the diaphragm by a portland cement seal, as recom-

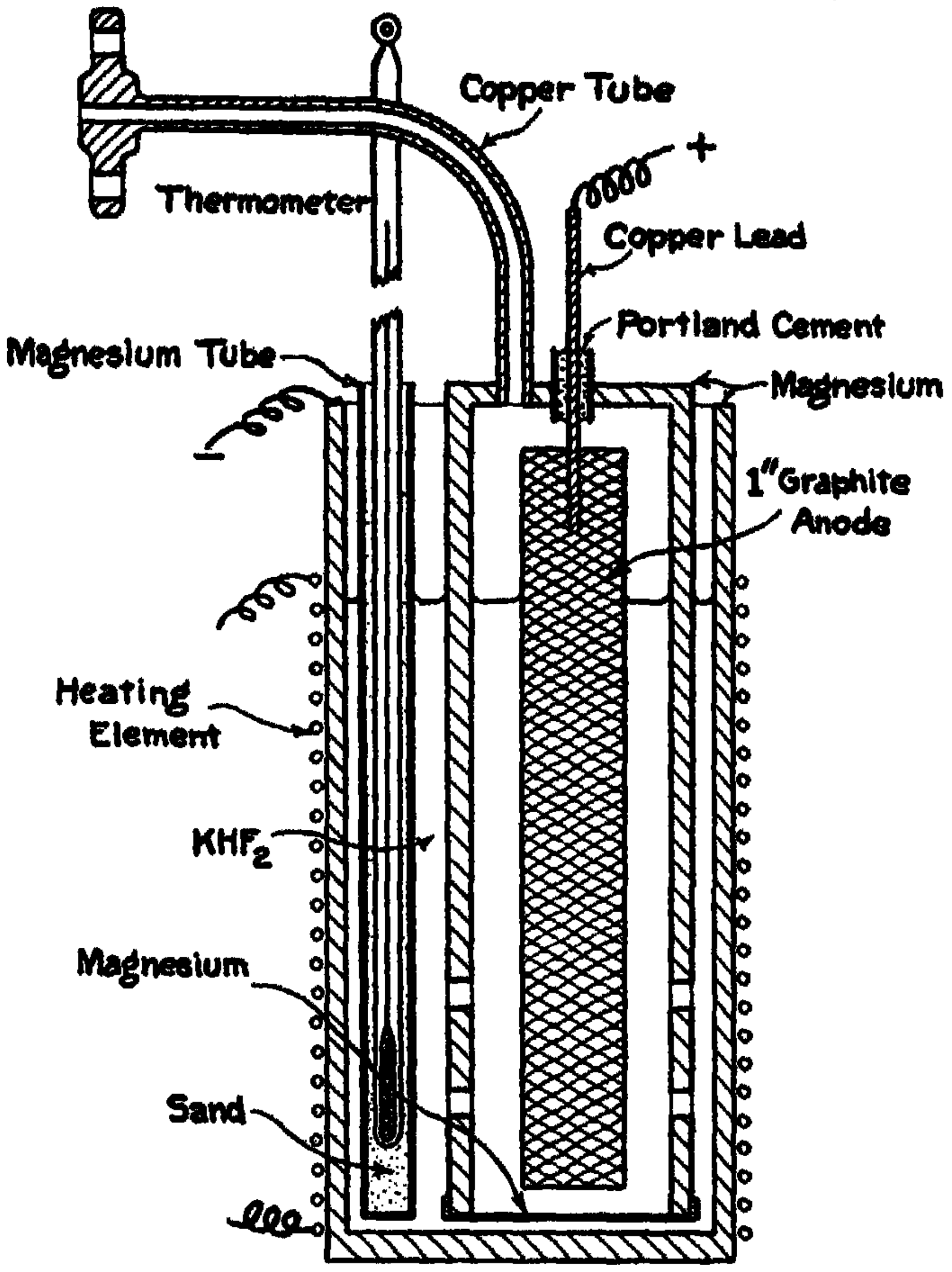

Fig. 1

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[1] Trans. Am. Electrochem. Soc., 35, 335 (1919).

[2] Ber., 54, 759 (1921).

[3] J. Am. Chem. Soc., 46, 2175 (1924).

mended by Simons. The bottom of the diaphragm is covered with a thin magnesium sheet which prevents the cathodic hydrogen from entering from below. The diaphragm is pierced near the bottom with a number of holes to permit circulation of the electrolyte and is suspended in the electrolyte in such a way that the bottom just fails to touch the bottom of the cathode pot. The heating element on the cathode pot is insulated from the latter by one layer of asbestos paper. Several layers of asbestos paper outside of this prevent excessive loss of heat. The temperature of the bath is determined by a thermometer inside a magnesium well which is immersed in the electrolyte. Copper has been used on previous cells but is somewhat corroded by the electrolyte. Magnesium resists perfectly the action of hydrofluoric acid[1] by forming on its surface a thin adherent coating of magnesium fluoride which is insoluble even in the hot electrolyte. For this reason all parts coming directly in contact with the hot electrolyte were made of magnesium. No corrosion of the cell is apparent after more than a year's use.

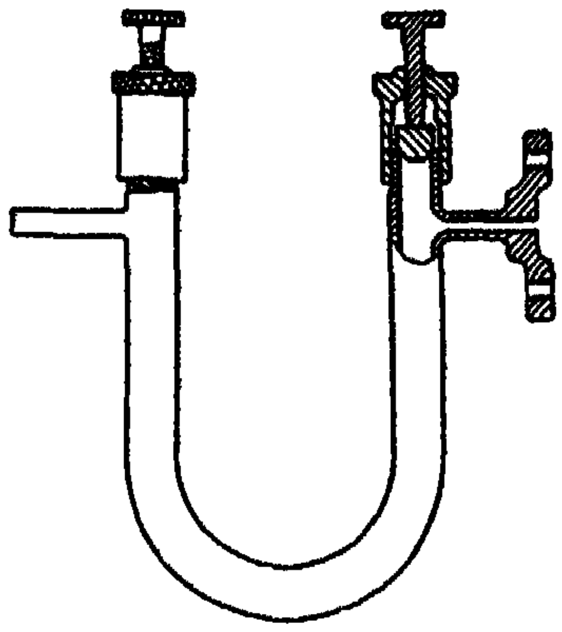

Fig. 2

The original cell was kindly loaned us by Professor Frank C. Mathers of Indiana University. The cathode pot was too large, however, requiring too much electrolyte. One of a smaller diameter was kindly made and given us by the Magnesium Corporation of America.

The cathode pot stands 8½ inches high and is 3¾ inches internal diameter; the diaphragm is 7 inches high by 2 inches internal diameter. Both pieces are ¼ inch in wall thickness. The anode is a one-inch graphite rod 6½ inches high. The thermometer well was made by drilling a 5/16 inch hole almost through a ½ inch magnesium rod 9 inches long.

A ¼ inch copper tube leads off from the top of the anode compartment and connects to a double U-tube made of copper (Fig. 2) by means of a copper flange union. The figure shows but one of the U-tubes as the second is an exact duplicate of the first. The U-tubes contain lumps of sintered sodium fluoride which remove hydrofluoric acid gas from the fluorine. No other attempt at purification of the fluorine was made as other impurities[2] are present in but small amount and are not harmful. The caps on the U-tubes consist of a copper plug around which a screw cap fits, and a set screw. The plug is set on the top of the tube and the casing is screwed down fairly tightly on the tube; the set screw is then turned down until the plug is tight. This arrangement prevents corrosion of the threads. It was first used in this laboratory on Professor Dennis' fluorine cell. A platinum tube screws onto the outlet

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[1] Chem. Met. Eng., 31, 383 (1924).

[2] See Meyer and Sandow: Ber., 54, 759 (1921).

of the last U-tube and carries the fluorine under the surface of any solution one has to work with. Platinum is the only substance that resists mineral acids and alkali as well as hydrofluoric acid.

The potassium hydrogen fluoride used as electrolyte was Kahlbaum's purest and was found to be especially good for this purpose. About 1500 grams are used for each charge and may be used for a considerable length of time before replacement is necessary. The cell is heated by an element connected through an ammeter and rheostat to the 110-volt alternating-current line. Four to five amperes are sufficient to keep the electrolyte just above the melting temperature during a run, although more current is necessary when originally heating the bath. Professor Mathers recommends that the temperature be kept as low as possible and not have the electrolyte solidify, as too high a temperature causes excessive loss of hydrofluoric acid, 'anode effect' and no fluorine. The anode effect was got around by putting 110 volts direct current on the electrolyzing circuit, in which an ammeter, a voltmeter, and a rheostat were also suitably connected.

On starting the electrolysis, the anode covers itself with a film of oxygen, because the water in the bath electrolyzes out first before any fluorine will appear. This film is not pierced appreciably by 40 volts, but 110 volts breaks through with ease. Electrolysis is carried out at 2-3 amperes until fluorine comes off, when the voltage across the cell decreases and the current may be stepped up to 6-8 amperes without polarization of the anode.

If the cell is allowed to stand hot, the outlet tube from the diaphragm plugs up with sublimed electrolyte. This trouble is avoided by heating the outlet tube from time to time to melt the acid fluoride out of it, as recommended by Simons.

As electrolysis proceeds, hydrofluoric acid is used up and the bath becomes richer in potassium fluoride, increasing the melting point. The electrolyte when cold is then deliquescent but no precautions are taken to keep the electrolyte out of contact with atmospheric moisture. Not much water gets in the bath and this is soon boiled and electrolyzed out when the cell is again used. Potassium acid fluoride melts at about 220° but the electrolyte may be used until the melting point is over 300°.

The cell delivers about 250 cc. fluorine per ampere per hour and may be used for at least thirty to forty hours at 5-6 amperes before it is necessary to replenish the electrolyte. The current efficiency of the cell is about 30%.

The Production of Hydrogen Peroxide

The electrolysis of cold, concentrated solutions of alkali yields primarily hydrogen peroxide at the anode.[1] Ozonate is also formed but comes from a secondary reaction. The maximum yield of hydrogen peroxide is obtained from a 33% solution of potassium hydroxide at −40° using platinum electrodes. The ozonate yield increases continuously as the temperature is lowered down to −60°.

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[1] Riesenfeld and Reinhold: Ber., **42**, 2977 (1909).

Fichter and Bladergroen[1] passed fluorine into 10N (about 40%) potassium hydroxide solution at 0° and obtained hydrogen peroxide at first and then relatively much more of the ozonate while explosions in the reaction vessel took place. This ozonate was considered to be partly transformed to potassium tetroxide and to partly decompose water to give hydrogen peroxide, oxygen, and alkali.

If our theory is right, the primary reaction should be the discharge of hydroxyl ions, which unite to form hydrogen peroxide. Ozonate and other products must be due to secondary reactions, depending on the temperature (stability of the compounds formed) and concentration of the alkali solution used.

The reaction

$$2H_2O_2 + 2KOH = (KOH)_2O_2 + 2H_2O$$

is evidently the low-temperature one, as greater yields of it are obtained the lower the temperature, while the reactions

$$2H_2O_2 + (KOH)_2O_2 = 2KOH + 2H_2O + 2O_2,$$
$$H_2O_2 = H_2O + O$$

are apparently the high-temperature reactions (0°). This means that we should get a maximum in the hydrogen peroxide formed at some temperature, more ozonate the lower the temperature, and more oxygen the higher the temperature. High concentrations of OH' ions should also favor hydrogen peroxide formation. This is actually the case.

The identity between the electrolytic and the purely chemical reactions was tested out by passing fluorine into a 33% potassium hydroxide solution (freed of carbonate by adding a few crystals of barium hydroxide) at −40° to −45°. The solution used is the one Riesenfeld and Reinhold employed. Hydrogen peroxide was formed abundantly from the very start; ozonate did not appear (tested by the darkening of the solution) until fluorine had been bubbled through the solution for some time. No explosions occurred at any time during the fluorination, but the fluorine bubbled quietly and steadily through the solution.

Oxidation of Divalent Cobalt

The oxidation of cobaltous salts to the cobaltic salts is the first case of direct oxidation of the cation that was done with fluorine.[2] It was found that in solution in 8N sulfuric acid cobaltous sulfate is oxidized to cobaltic sulfate. This experiment was confirmed by us. On the other hand, a solution of cobaltous carbonate in dilute sulfuric acid gives only small amounts of cobaltic salt. If the hydrofluoric acid concentration is allowed to rise a compound of the formula $CoF_2.5HF.6H_2O$ is the chief product. On the basis of these results Fichter assumes an intermediate oxidation product from the action of fluorine on sulfuric acid that "alone can effect the oxidation of bivalent cobalt to trivalent cobalt."

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[1] Helv. Chim. Acta, 10, 549 (1927).

[2] Fichter and Wolfmann: Helv. Chim. Acta, 9, 1093 (1926).

The last statement cannot be true. It is easier to oxidize cobaltous to cobaltic than it is to discharge sulfate ions, because ozone or a lead peroxide anode will cause the oxidation to take place[1] but will not liberate free sulfur tetroxide from any sulfate solution. The oxidation equation must be written thus:

$$2CoSO_4 + H_2SO_4 + F_2 = Co_2(SO_4)_3 + 2HF.$$

In a dilute acid solution, oxygen will come off in preference to oxidizing the cobaltous salt as the normal potential for the reaction $Co^{\cdot\cdot} \longrightarrow Co^{\cdot\cdot\cdot}$ is quite high, 1.8 volts. In the presence of much fluoride the insoluble cobaltic fluoride should be formed. Barbieri and Calzolari[2] electrolyzed between platinum electrodes a saturated solution of cobaltous fluoride in 40% hydrofluoric acid and obtained cobaltic fluoride as a green powder which did not redissolve on stopping the current. Hydrogen peroxide reduces the compound or solutions of it immediately to the cobaltous state. As high concentrations of acid do not permit the formation of hydrogen peroxide, one should get the cobaltic fluoride on treating Barbieri and Calzolari's solution with fluorine. The observation of Fichter that only cobaltous fluoride is formed must be a case of experimental error.

To test this out, 5 grams of cobaltous carbonate were dissolved in 25 cc. 48% hydrofluoric acid in a platinum crucible and fluorine was bubbled through for an hour. At the end of that time the solution was much darker in color and reacted with hydrogen peroxide energetically with the evolution of oxygen. Neither hydrofluoric acid itself nor a solution of cobaltous carbonate in hydrofluoric acid would give this reaction. It is evident then that cobaltic fluoride was formed, substantiating the analogous electrolytic oxidation.

The Oxidation of Manganese

In sulfuric acid solution, manganous sulfate is oxidized anodically to manganese dioxide and in hydrofluoric acid solution to manganese tetrafluoride, according to Skirrow.[3] No permanganate is formed until all the manganous manganese is oxidized. In sulfuric acid solution, no permanganate ever resulted, as *all* the manganous ion is not oxidized to manganese dioxide. This was substantiated by running two experiments showing that suspensions of manganese dioxide in sulfuric acid and in hydrofluoric acids are oxidized readily to permanganate.

Müller and Koppe,[4] however, found that, in the presence of hydrofluoric acid, the manganous salt reduces both permanganate and manganese dioxide to the manganic state, according to the following scheme:

$$MnO_4' + 4Mn^{\cdot\cdot} + 8H^{\cdot} = 5Mn^{\cdot\cdot\cdot} + 4H_2O,$$

$$MnO_2 + Mn^{\cdot\cdot} + 4H^{\cdot} = 2Mn^{\cdot\cdot\cdot} + 2H_2O.$$

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[1] Marshall: J. Chem. Soc., 59, 760 (1891).

[2] Atti Accad. Lincei, (5) 14I, 464; J. Chem. Soc., 88II, 393 (1905).

[3] Z. anorg. Chem., 33, 25 (1902).

[4] Z. anorg. Chem., 68, 160 (1910).

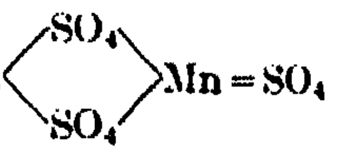
Manganese dioxide dissolved in hydrofluoric acid only when manganous salt was present.

It is probable that Skirrow jumped to the conclusion that he had obtained manganese tetrafluoride by anodic oxidation of manganous salt in hydrofluoric acid solution by reasoning from the analogous experiment in sulfuric acid which gives manganese dioxide. However, he got a rose-red precipitate on adding ammonium fluoride. Complex fluorides of trivalent manganese are red in color[1] while complex fluorides of tetravalent manganese are yellow.[2]

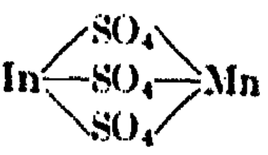
Evidently one gets trivalent manganese on electrolytic oxidation of manganous salt in hydrofluoric acid solution, while tetravalent manganese is formed when sulfuric acid is used. This must be due to the fluorides of trivalent manganese being more stable than the fluorides of tetravalent manganese, while manganese dioxide is the more stable form when other acids besides hydrofluoric are used. This was confirmed by adding hydrofluoric acid to a solution of manganese disulfate in sulfuric acid. Oxygen is evolved and the manganese is reduced to the manganic state. No oxidation to permanganate can take place as long as divalent manganese is present, as the latter reduces permanganate.[3]

The action of fluorine on solutions of manganese salts is strictly analogous to the anodic oxidation, as one should expect. Fichter and Brunner[4] could not make manganese tetrafluoride but easily obtained the trifluoride by passing fluorine through a suspension of manganous fluoride. The strong sulfuric acid solution of manganous sulfate gave the unstable sulfate of tetravalent manganese. Dilution of this solution yielded manganese dioxide. Permanganate was found only when a dilute solution of manganous sulfate in strong sulfuric acid was treated with fluorine. The obvious explanation is that *all* the divalent manganese must be oxidized to a valence of three or four before any further oxidation can take place.

Sem[5] has assumed that salts of trivalent manganese possess the structure, take manganic sulfate for example,



in which the manganese has a valence of two and four rather than the simpler structure



where the manganese appears only with a valence of three. In support of this view he cited the fact that manganic salts hydrolyze into manganese dioxide and a manganous salt:

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[1] Christensen: J. prakt. Chem., (2) 35, 57 (1887).

[2] Weinland and Lauenstein: Z. anorg. Chem., 20, 40 (1899).

[3] Compare Volhard method for determining manganese. Treadwell-Hall: "Analytical Chemistry," 2, 521 (1924).

[4] J. Chem. Soc., 133, 1862 (1928).

[5] Z. Elektrochemie, 21, 426 (1915).

$$Mn_2(SO_4)_3 + 2H_2O = MnSO_4 + 2H_2SO_4 + MnO_2.$$

Christensen[1] found that water decomposed the complex salt potassium manganifluoride with the formation of a "higher oxide of manganese." This was undoubtedly manganese dioxide as he obtained the potassium manganifluoride by heating manganese dioxide with acid potassium fluoride. This supports the view that the fluoride of tetravalent manganese is less stable than the fluoride of trivalent manganese and will therefore be formed when fluorine acts on manganous fluoride.

This, coupled with the work of Müller and Koppe, makes it a certainty that fluorine will oxidize manganous fluoride to manganic fluoride and as soon as all the divalent manganese has disappeared. oxidation to permanganate will take place.

We are now in a position to explain how manganous sulfate is oxidized by fluorine. The first stage is the oxidation of the manganous sulfate to the manganic state:

$$2MnSO_4 + H_2SO_4 + F_2 = Mn_2(SO_4)_3 + 2HF.$$

One cannot assume that free sulfate or persulfate does the oxidation as the latter proceeds at a lower voltage than either of the other two processes. No salt of tetravalent manganese can form because hydrofluoric acid is always present.

As soon as *all* the manganese ions are oxidized to manganic, then oxidation proceeds directly to the permanganate stage, since tetravalent manganese is not stable in the presence of fluoride and manganate is stable only in alkaline solution.[2] The reaction follows:

$$Mn_2(SO_4)_3 + 8H_2O + 4F_2 = 2HMnO_4 + 3H_2SO_4 + 8HF.$$

The concentration of the acid must be high in order to get permanganate, otherwise ozone or hydrogen peroxide is also formed from the action of fluorine on the water and permanganate is not stable in contact with either.

The Oxidation of Chromium Salts

Acid chromium sulfate solutions are oxidized anodically to chromate.[3] The chemical counterpart of this reation was worked on by Fichter and Brunner.[4] To quote from their paper: "A solution of chromium alum, acidified with very dilute sulfuric acid, is not altered by the passage of fluorine for several hours, but if the concentration of the acid is as high as 1.5N, a regular oxidation to chromic acid sets in, and is easily recognized by the change of color from violet to yellow. Higher concentrations of acid have the same effect. The oxidation is certainly indirect, for if the amount of chromic acid is determined by titration, the fresh solution, which evolves ozone, has about

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[1] J. prakt. Chem., (2) 35, 57 (1887).

[2] Mellor: "Modern Inorganic Chemistry," 478 (1922).

[3] Allmand and Ellingham: "Applied Electrochemistry," 472 (1924).

[4] J. Chem. Soc., 133, 1862 (1928).

1.5 times the possible oxidizing power. After standing overnight or heating on the water bath, the excess of oxidizing substances is destroyed, and the solution has an oxidizing power corresponding exactly to the theoretical amount of chromic acid. The oxidizing substance must be sulfur tetroxide, for it is effective at 0°, whereas persulfate oxidizes chromic salts only at higher temperatures."

When oxidation takes place in strongly acid solutions, the primary reaction must be the formation of chromate,

$$Cr_2(SO_4)_3 + 8H_2O + 3F_2 = 2H_2CrO_4 + 3H_2SO_4 + 6HF.$$

The oxidation of chromic salts is a relatively easy process compared with the formation of either persulfate or sulfur tetroxide; and therefore the latter can only be formed as a result of impoverishment of chromic ions. That no oxidation takes place in weak acid solutions is due to its being easier to form oxygen than it is to oxidize chromium.

Fluorine also acts *apparently* as a reducing agent. We will quote again from Fichter and Brunner's paper: "If a dilute solution of potassium dichromate is treated with fluorine, it becomes green and is reduced to chromic salt, most probably the fluoride. . . . This contradictory behaviour must be explained by the intermediate formation of hydrogen peroxide, thus:

$$2H_2O + F_2 = H_2O_2 + 2HF.$$

The formation of hydrogen peroxide can be detected by working with a small quantity of chromic acid and in the presence of dilute sulfuric acid; under these conditions and by proper cooling we obtain the blue perchromic acid soluble in ether. Perchromic acid is very unstable, losing oxygen and yielding chromic salts; in this manner the reduction of dichromate can be carried out quantitatively by prolonged treatment with fluorine. . . .

"Both reactions which chromium undergoes under the influence of gaseous fluorine must be explained by intermediate products formed by the action of fluorine upon water and upon sulfuric acid. Consequently, in oxidations with fluorine, an excess of this gas is often detrimental, for it destroys, by secondary reactions, the substances which it formed at first."

Since it is a well-known fact that hydrogen peroxide is the reagent used to get the blue perchromic acid test for chromium, the latter reaction must take place at a lower potential than that necessary to form hydrogen peroxide. Hence the primary reaction will be the oxidation to perchromic acid and *not* the formation of hydrogen peroxide:

$$H_2CrO_4 + H_2O + F_2 = 2HF + H_2CrO_5.$$

The secondary reaction is the catalytic decomposition of this acid in the presence of either sulfuric acid or hydrofluoric acid which are present in small amounts:

$$2H_2CrO_5 + 6HF = 2CrF_3 + 5H_2O + 5O,$$
$$2H_2CrO_5 + 3H_2SO_4 = Cr_2(SO_4)_3 + 5H_2O + 5O.$$

We see then that oxidation takes place first; but the chemistry of the substances formed is responsible for the reduction to chromic salts. Fichter showed that perchromic acid was actually formed, by obtaining a blue color upon shaking with ether a solution of chromate to which had been added a few bubbles of fluorine.

Chromium sulfate cannot be oxidized in weak acid or neutral solution, as the catalytic reduction is more rapid than the oxidation. The sum total effect is simply the evolution of ozonized oxygen.

Electrolytic and Chemical Oxidation of Lead Salts

When an acid solution of lead nitrate is electrolyzed between platinum electrodes, all the lead is deposited on the anode as lead dioxide.[1] Electrolysis of pure sulfuric acid (sp. gr. 1.7–1.8) between lead electrodes yields lead disulfate, which hydrolyzes to lead dioxide when the solution is diluted.[2] Electrolysis of a solution of lead sulfate in a more dilute sulfuric acid (sp. gr. 1.07–1.14) yields chiefly lead dioxide, although small quantities of lead disulfate are found in the bath.[3] Electrolysis of lead acetate solutions yields lead dioxide at the anode, which is supposed to result from the hydrolysis of lead tetra-acetate.[4]

The fundamental anode process involved in all these cases is the oxidation of the lead from the plumbous to the plumbic state. Whether the plumbic lead so formed remains as such in the solution, comes out as a salt of tetravalent lead, or hydrolyzes to lead dioxide will depend entirely on the properties of the solution. Very strongly acid solutions evidently stabilize salts of tetravalent lead, while, in slightly more dilute solutions, lead dioxide separates as a result of hydrolysis.

It has been said[5] that the only function of the current is to tend to set free ions at the electrodes; what happens afterwards is purely a matter of chemistry.

When fluorine is passed into acid solutions of a lead salt, no lead dioxide separates, neither does the solution darken, nor lead fluoride separate. However, the solution liberates iodine from potassium iodide and oxidizes manganous sulfate to permanganate. Addition of sodium hydroxide causes a reddish-brown precipitate to separate, soluble in excess on heating; ammonium hydroxide gives the same precipitate but it is insoluble in excess, hot or cold. This precipitate is partially soluble in concentrated nitric acid, a brown residue of lead dioxide remaining.

The oxidizing action of the solution may be due to any of four factors: (a) dissolved hydrogen peroxide, (b) dissolved ozone, (c) possible hypofluorite (HOF) comparable to hypochlorite (HOCl), (d) plumbic lead. The first is ruled out because a trace of permanganate is not decolorized, even on

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[1] Treadwell-Hall: "Analytical Chemistry," 2, 179 (1924).

[2] Elbs and Fischer: Z. Elektrochemie, 7, 343 (1900).

[3] Elbs and Rixon: Z. Elektrochemie, 9, 267 (1903).

[4] Elbs: Z. Elektrochemie, 3, 70 (1896).

[5] Bancroft, Trans. Am. Electrochem. Soc., 8, 33 (1905).

long standing; besides, the solution will oxidize manganous salt to permanganate. The second and third are ruled out because half an hour's boiling of the solution does not affect its oxidizing properties. The only tenable position therefore is that tetravalent lead is present in the solution. This is confirmed by the fact that ammonia precipitates lead dioxide.

If now fluorine is passed through an alkaline solution of a lead salt, say lead hydroxide, lead dioxide separates immediately. When fluorine is bubbled through a suspension of white lead in water, the color darkens immediately and lead dioxide may be detected in the precipitate by simply taking a sample and leaching out the soluble salts with nitric acid. But if fluorine is bubbled long enough to neutralize the basic constituents of the white lead and the suspension becomes acid, the precipitate again turns white. The solution after filtering and boiling, however, shows an oxidizing reaction and lead dioxide may be obtained by treating with ammonium hydroxide.

To confirm these experiments, fluorine was bubbled through neutral and alkaline suspensions of lead sulfate and lead fluoride. The solutions were respectively acid and alkaline at the end of half an hour, when fluorination was stopped. The acid solutions were colorless and the precipitates white but the former showed oxidizing properties and lead dioxide could be separated by making alkaline with ammonia. The alkaline suspensions, on the other hand, were dark-colored and the precipitates contained lead dioxide.

The foregoing experiments indicate that in the presence of fluoride and acid, plumbic lead is soluble. It is worth noting here that chlorine, hypochlorite, bromine, hydrogen peroxide and persulfate will oxidize lead to lead dioxide *only* in alkaline solution.[1] No mention is made as to whether plumbic lead is formed in acid solution.

If plumbic lead is soluble in acid solutions containing fluoride, one should be able to dissolve lead dioxide in an acid solution of fluoride. Mathers[2] states that freshly prepared lead dioxide is insoluble in 50% hydrofluoric acid but is readily soluble in the 96% acid. Dry lead dioxide is not soluble even in the anhydrous acid but is soluble on fusing with potassium hydrogen fluoride. If potassium or ammonium fluoride is first added, the solution of lead dioxide is more stable due to the formation of a double salt of lead tetrafluoride in solution. On the other hand, Zotier[3] found that lead dioxide is attacked very slowly by mineral acids and by alkali and that the rate of solution is accelerated greatly by warming the reagents.

Mathers fails to state whether small amounts of lead dioxide did dissolve in more dilute acid. In order to show that this is actually the case some experiments were tried. Lead dioxide itself is not soluble at all in acid solutions of fluoride, hot or cold. Small amounts of red lead, Pb_3O_4, are insoluble in potassium fluoride or potassium sulfate but may be dissolved completely when the solutions are acidified with hydrofluoric acid and warmed. The

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[1] Treadwell-Hall: "Analytical Chemistry," 1, 219 (1921).

[2] J. Am. Chem. Soc., 42, 1309 (1920).

[3] Bull., (4) 21, 244 (1917).

solutions show the oxidizing reactions of tetravalent lead. Lead tetra-acetate dissolves completely in acid solutions of fluoride in the cold; but lead dioxide separates on diluting the solution excessively. However, the solution itself still exhibits oxidizing properties. Hutchinson and Pollard[1] say that the hydrofluoric acid solution of lead tetra-acetate may be evaporated to dryness without separation of lead dioxide if a little ammonium fluoride is added first. Neutralization of all the above solutions precipitates lead dioxide.

It has been shown that tetravalent lead can and does exist in solutions containing hydrofluoric acid in relatively low concentration, and that such solutions are obtained upon fluorinating suspensions or solutions of divalent lead salts. However, the fluorinations were all run in the presence of an excess of the divalent lead; none of the oxidations were run to completion. No appreciable amount of fluoride ion could be present in the solution even after fluorine had been passed in for some time as lead difluoride never precipitated though it is insoluble even in moderately acid solution. This meant one of two things, that the lead tetrafluoride is not dissociated in solution or that the fluorine has gone into a complex ion.

There are no data on lead tetrafluoride itself but the hydrofluoplumbic acid H_2PbF_6 has been prepared, in solution only.[2] An acid H_4PbF_8 has been mentioned.[3] The free acids have never been isolated but the salts of both are known.[4] The work of Furman on tin tetrafluoride[5] throws considerable light on the behavior of the lead tetrafluoride. Stannic tin in acid solution containing hydrofluoric acid does not hydrolyze on great solution or after long standing, is not reduced to the metal electrolytically, is not reduced to the stannous condition or to the metal on boiling with zinc or aluminum, gives no precipitate with hydrogen sulfide, and on neutralization does not precipitate all the tin, considerable remaining in solution. From this he concludes that solutions of stannic fluoride "give none of the characteristic reactions of the stannic ion." This behavior is characteristic of fluorides of antimony, tungsten and molybdenum in their highest states of oxidation.[6]

Furman summarizes the behavior of acid solutions of stannic fluoride as follows:[7] "The function of the hydrofluoric acid . . . is a double one—it represses the dissociation of certain fluorides to such an extent that . . . it is difficult or impossible to observe any of the reactions of the ions of these metals; further, the acid supplies a sufficient concentration of hydrogen ions to prevent the hydrolysis of the metal fluorides. There are at least two ways in which we might explain the apparent absence of the ions of these metals, when a suitable quantity of hydrofluoric acid is present. These different

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[1] J. Chem. Soc., 69, 212 (1896).

[2] Fischer and Thiele: Z. anorg. Chem., 67, 312 (1910).

[3] Brauner: Z. anorg. Chem., 7, 2, 9 (1894).

[4] "Gmelins Handbuch der anorganischen Chemie," 5, 64 (1926).

[5] J. Am. Chem. Soc., 40, 895 (1918).

[6] McCay and Furman: J. Am. Chem. Soc., 38, 640 (1916).

[7] J. Am. Chem. Soc., 40, 913 (1918).

view-points may be illustrated by the facts relating to stannic fluoride, as follows:

"(a) Stannic fluoride undergoes a slight initial dissociation into its ions, as indicated by its very slight conductivity. A suitable excess of hydrofluoric acid represses this dissociation to such an extent that none of the characteristic reactions of the stannic ion can be observed.

"(b) Stannic fluoride may form a complex with the excess of hydrofluoric acid, of the general type H_nSnF_{4+n}. Any tendency of the complex to dissociate and give rise to the formation of ions of stannic tin would be diminished or completely prevented by a sufficient excess of hydrofluoric acid."

Furman believes the first explanation to be the more tenable, giving three reasons why the complex acid cannot exist. Stannic fluoride can be made to hydrolyze completely, an electrometric titration with alkali shows no inflection for a complex acid, and hydrogen sulfide precipitates the tin practically completely from solutions containing much alkali fluoride where conditions are ideal for the formation of a complex.

Since silicon forms compounds of the type H_2SiF_6 readily and since stannic tin forms such complexes with difficulty, if at all, it appears very probable that lead tetrafluoride exists as the undissociated salt in the solutions resulting from the fluorination of solutions of plumbous salts. This belief must be modified somewhat, however.

We have found that a lead anode in hydrofluoric acid corrodes to give some tetravalent lead but no lead dioxide separates. A solution of lead difluoride in nitric acid, when electrolyzed, yields no lead dioxide at the anode but simply a solution of tetravalent lead. Lead dioxide dissolves much more readily in hydrofluoric acid solutions containing plumbous lead than it does in acid solutions alone or in acid solutions containing potassium fluoride. Some lead difluoride separates when the hydrofluoric acid is added but this goes back into solution almost immediately. Neutralization of the mixtures obtained on fluorination of solutions of lead salts precipitates in every case a plumbous-plumbic oxide and not lead dioxide alone. It appears therefore that the lead tetrafluoride is stabilized by plumbous ion more than it is by acid or by another metal ion. The acid serves merely to prevent hydrolysis by repressing the ionization of the tetravalent lead salt. Although the lead tetrafluoride has not been isolated for analysis, it is believed the compound is of the type $PbF_2.PbF_4$ and not of the type H_2PbF_6 or K_2PbF_6.

It is worth noting that the great difference between lead tetrafluoride on the one hand and lead tetrachloride or disulfate on the other hand is the low concentration of acid which is necessary to prevent hydrolysis of the tetrachloride.

The Kolbe Synthesis

Electrolysis of concentrated solutions of the alkali acetates yields chiefly ethane and carbon dioxide at the anode.[1] It should be possible to duplicate this reaction with flurine and further avoid the complication of the cathode

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[1] Kolbe: Ann., 69, 257 (1849).

reaction. This was found to be the case[1] and the reaction may be written as follows:

$$2CH_3COOK + F_2 = C_2H_6 + 2CO_2 + 2KF.$$

A number of theories have been advanced to account for the facts and the synthesis is by no means as simple as the above reaction indicates. Methane, ethylene, methyl alcohol, methyl acetate, carbon monoxide and other substances have all been obtained from acetate solutions. It is intended to make a more complete study of the Kolbe reaction.

Summary

1. The chemical action of fluorine on aqueous solutions is the same as the electrolytic anode reaction plus any disturbances due to the hydrofluoric acid formed.

2. Instead of reacting with the water of the aqueous solution, fluorine forms persulfate from acid sulfate solutions, perphosphate, percarbonate, and perborate from the corresponding phosphates, carbonates, and borates, hydrogen peroxide from alkali, ethane from potassium acetate solution, and oxidizes cobaltous, chromic, manganous and plumbous salts to salts containing the metal with a higher valence.

3. Electrolysis of pure sulfuric acid gives $H_2SO_4.SO_3$ at the anode. Fluorine gives fluorsulfonic acid because the hydrofluoric acid formed combines with the sulfur trioxide to give this acid.

4. Certain indifferent ions, when present in an electrolytic bath, raise the potential of the anode since they are adsorbed on the anode, cutting down the rate of the reaction $2O_1 = O_2$. It appears that those ions which are adsorbed on the anode and which are not themselves discharged raise the overvoltage of oxygen at that anode.

5. Fluorine was generated by the electrolysis of fused potassium acid fluoride in a modification of the magnesium cell devised by Professor Mathers.

6. The *primary* action which takes place when fluorine acts on cold, concentrated solutions of alkali is the discharge of hydroxyl ions to form hydrogen peroxide. Ozonate and ozone are the result of secondary reactions.

7. Contrary to what Fichter found, cobaltous fluoride in hydrofluoric acid solution is oxidized to cobaltic fluoride by fluorine.

8. Manganese dioxide is the final product when manganous salts are oxidized in presence of an excess of the latter, except when hydrofluoric acid is present, when the final product is manganic fluoride (MnF_3). Permanganate results in both cases only after *all* the manganous ions are oxidized to a higher intermediate stage of oxidation.

9. The fact that fluorine *apparently* reduces dichromate to a chromic salt is due to a catalytic reduction by small amounts of acid present in the solution of the perchromic acid first formed. In strongly acid solution oxidation of chromic salt to chromate proceeds regularly according to the scheme for electrolytic oxidation.

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[1] Fichter and Humpert: Helv. Chim. Acta, 9, 602 (1926).

10. Fluorine gives lead dioxide only from alkaline solutions or suspensions of plumbous salts. Fluorine does not give lead dioxide with acid lead nitrate or fluoride solutions because lead tetrafluoride is stable in acid solution. Lead dioxide precipitates when such solutions are neutralized. The tetravalent lead is not present in a complex anion but as undissociated lead tetrafluoride, stabilized by plumbous lead and by small amounts of acid.

Acknowledgments

This research was suggested by Professor Wilder D. Bancroft and was carried out under his direction. The author welcomes this opportunity to express his deep appreciation for the kindly criticism and help that were ever freely given.

The author also thanks Professor Frank C. Mathers of Indiana University and the Magnesium Corporation of America for their kindness in furnishing parts of the fluorine apparatus.

Cornell University.

ULTRAVIOLET LIGHT, INSULIN, AND AMINO ACID CATALYSIS

BY JOHN M. ORT

It has been found that certain of the common amino acids accelerate the action of small amounts of hydrogen peroxide on dextrose and levulose.[6,7] Insulin under the same conditions has some retarding influence in the absence of the amino acids and is without much effect when they are present. This paper is a report of further studies by the oxidation potential method on the first steps in the oxidation of these sugars. The additional effect of ultraviolet light is also considered.

The procedures were similar to those of the former experiments and when the solutions were irradiated with ultraviolet light they were essentially as follows: When the drifts of reduction potentials in the solutions became relatively steady following the removal of dissolved air by nitrogen gas, ultraviolet light was admitted. After the potentials had reached a chosen value, 0.5 c.c. of a 0.03 per cent solution of hydrogen peroxide was added. Then the course of the reaction was followed by observing the drift of potentials. Since it was found that ultraviolet light greatly hastened the development of a reducing intensity when the air was removed, it was not necessary in these experiments to allow the solutions to stand over night. An entire experiment could be completed within a few hours. If the solutions were allowed to stand over night, prior to irradiation, the results were not much different, if the hydrogen peroxide was added at about the same reducing intensity.

In order to transmit the ultraviolet light the electrode vessel was made of transparent fused silica. Temperature control was effected by hand, ice water in a casserole being placed intermittently around the bottom of the vessel. This, for short periods, cut off the light from the lower part of the solutions inside but maintained the temperature at 30°C. ± 1°.

The source of light was a standard Victor quartz mercury vapor arc. The electrode chamber was placed about 18 cm. from the arc, this being as close as was convenient. Light directly from the arc was not allowed to strike the platinum electrode. The voltage across the arc was 90 volts ± 2 volts. When it fell much below 85 volts most of the effects recorded in this study did not occur. We are now attempting, in this laboratory, to obtain more information concerning the wavelengths or bands in the spectrum and the amount of energy necessary to produce these effects.

Because of the recent suggestion that the physiologic activities of the amino acids bear some relation to their optical activities,[2] the chemicals used in these experiments have been tabulated.

As before, in the experiments with ultraviolet light, 100 c.c. of a 1/100 molar solution of amino acid buffered to pH 10 with disodium phosphate and sodium hydroxide was used. Two hundred milligrams of one of the sugars and 1 c.c. of Lilly's iletin were added when specified. The 0.03 per cent

Substance	Source	Rotation of polarized light
Dextrose	Merck White Label	d
Levulose	Pfanstiehl Special C.P.	l
Glycine	Pfanstiehl and Eastman	inactive
Alanine	Eastman	dl
Phenylalanine	Pfanstiehl	dl
Tyrosine	Eastman	l
Valine	Eastman	dl
Leucine	Eastman	dl
Glutamic acid	Eastman	d
Aspartic Acid	Eastman	dl
Cystine	Eastman	l

solution of hydrogen peroxide was prepared fresh for each run by diluting Merck's Blue Label Superoxol and titrating by iodine liberation against standard sodium thiosulphate.

Attention is once more directed to the qualitative nature of oxidation potential data obtained with these complex systems. The shapes of the curves in which form the data are presented are, however, fairly reproducible and probably indicate the general trends of the reactions. In considering the individual curves, then, general shapes and approximate values alone are significant. Since freak results are not uncommon with these systems, the particular curves presented have been selected from among many as the most representative of the usual course of reaction in each case.

Experiments and Discussion

As is well known, alkaline solutions of dextrose and levulose are strongly reducing, a property which is often made use of in their quantitative determination. The intensity of this reducing power increases as the alkalinity increases, but it has not been possible to formulate an accurate expression for the relation between pH and the reduction potential acquired by platinum electrodes in these solutions. It is usually impossible to get very accurate checks with different electrodes, and one given electrode will show drifting potentials in the same solution, and when placed in a fresh solution often will not closely reproduce its former behavior. Nevertheless in all cases the reduction potential acquired will be within a range considerably below that of a simple buffer of the same pH, and will depend on the concentration of the sugar, the rate of stirring, the electrode, and some other unknown factors.

I have previously shown[6,7] that when even a very minute amount (0.5 c.c. of a 0.03 per cent solution) of hydrogen peroxide is added to one of these sugar solutions (0.2 gm. dextrose in 100 c.c. of sodium hydroxide and sodium phosphate at pH 10) the entire reducing intensity is instantly destroyed. The reduction potential is at once replaced by an oxidation potential, the shift amounting at times to 0.5 volt or more. Thus 0.0000044 mol of an oxidant brings about this rather extensive change in oxidation-reduction conditions, although for every molecule of hydrogen peroxide there are 230 molecules of sugar present. Within a short time, however, the oxidation potential will begin to fall, indicating the removal of the oxidant, and in a few hours the original reducing intensities will be restored. Such sugar solutions when made up exposed to the air, as they usually are, will not immediately develop strong reducing intensities, but, as the dissolved air is removed by bubbling nitrogen gas through the liquid, the potentials on the electrodes will gradually become more negative. After fifteen hours the drift is usually slight.

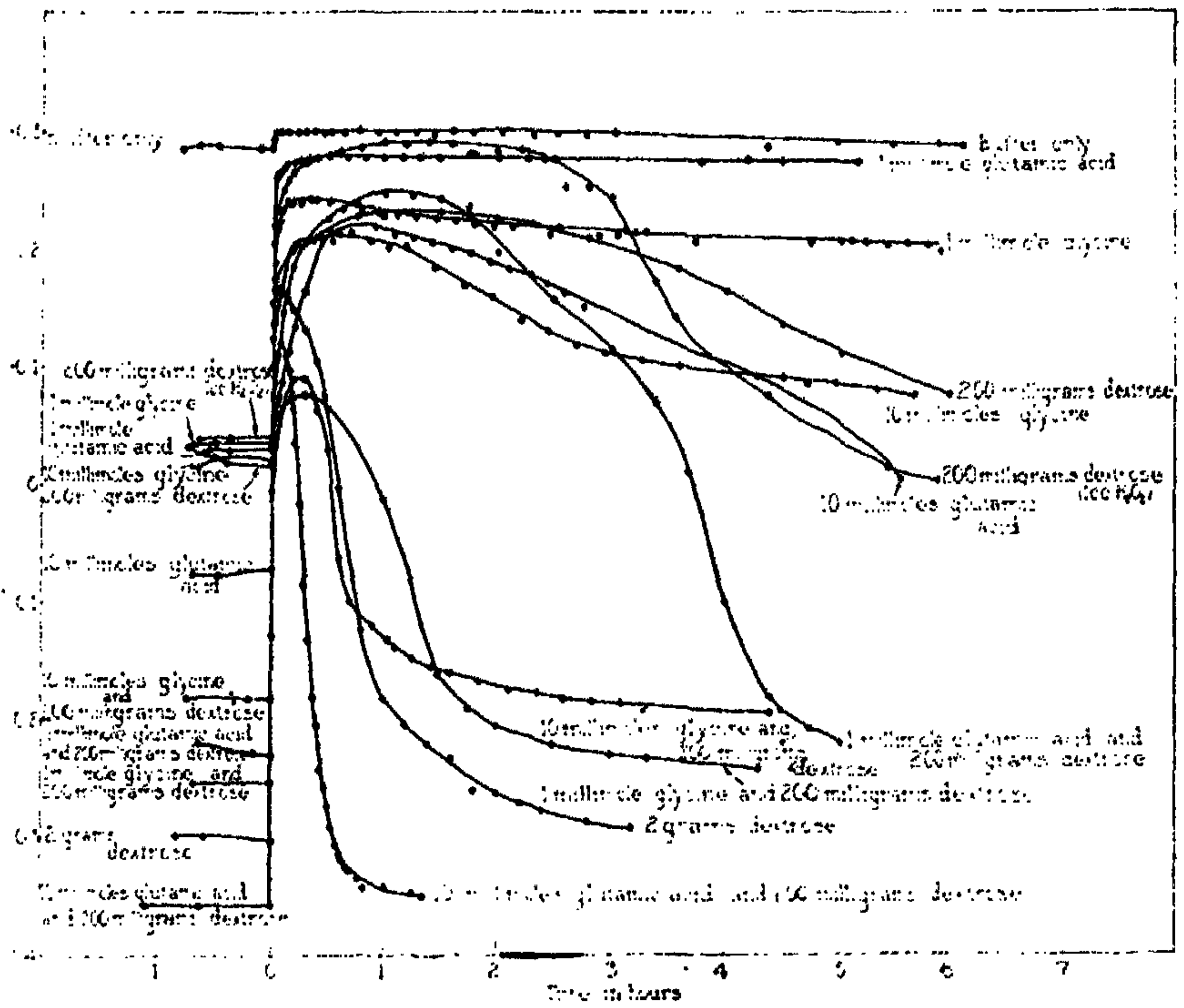

Fig. 1
Controls. No ultraviolet light.

Thus only a very small amount of the sugar present apparently is responsible for the reduction potential acquired by the electrode and is in a state in which it can quickly react with oxidants, in spite of the fact that the latent reduction capacity may be comparatively enormous. These facts agree with the well-known theory[4] that there is an "active sugar" present, small in amount but in equilibrium with the large bulk of the remainder of the sugar which exists in comparatively inactive form. The experiments reported in this and former papers are studies on the reactions of these active sugars or, in other words, on the very first steps in sugar oxidation, since the most reactive form will be the first to be attacked by oxidants. If the amount of oxidant be small enough this will be the only form attacked. This phase of the problem will be discussed in a future paper.

In Fig. 1 are presented some curves from former papers, together with some from later experiments, which will serve as controls for those with ultraviolet light. It can be seen that when sugar is absent high voltages exist for hours. Except when the amino acid concentration is comparatively high, they remain quite positive for many hours and sometimes for days in the buffer alone. Either sugar or its reaction products simply catalyze the decomposition of hydrogen peroxide or remove it by reduction, or both.

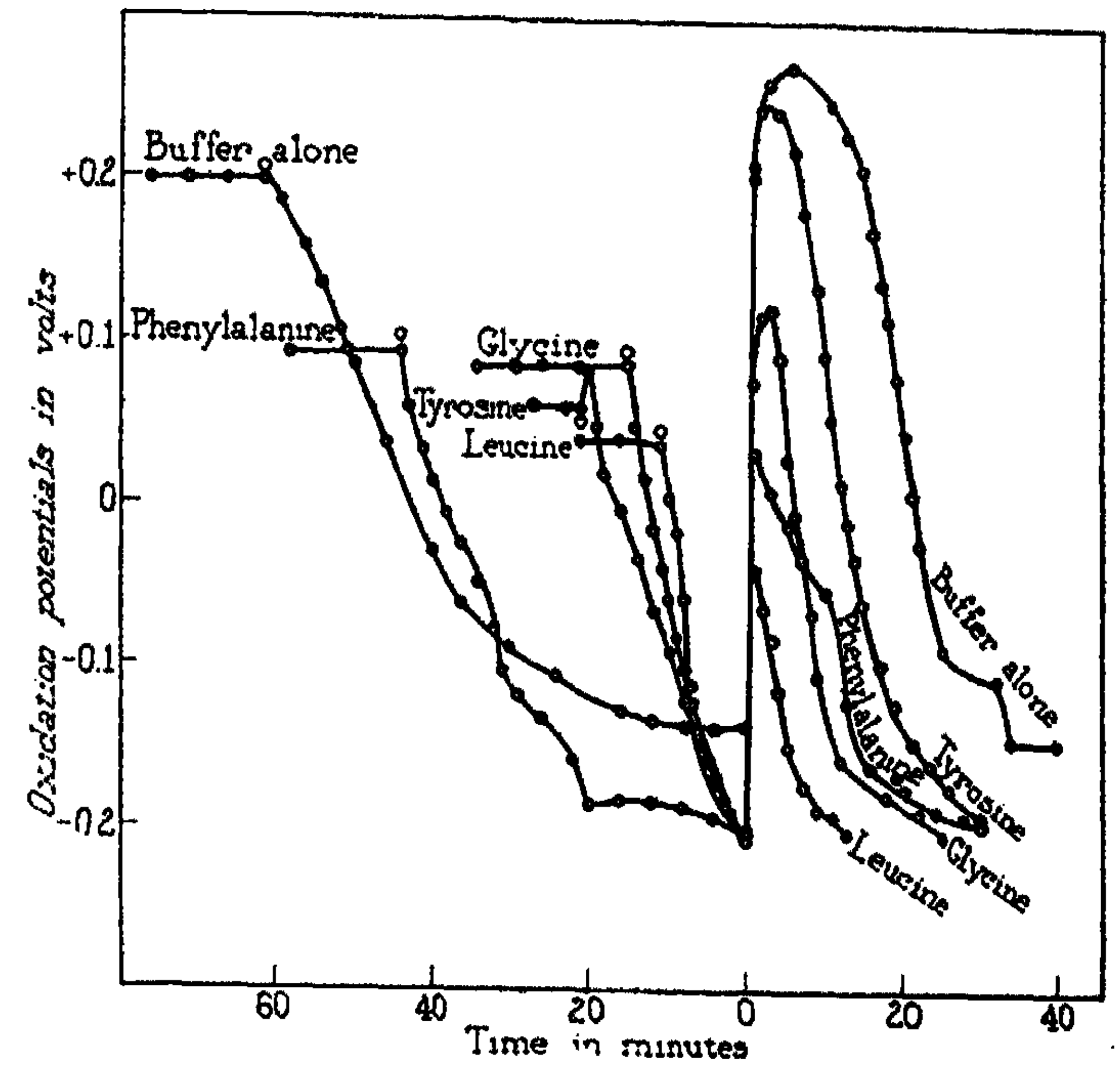

FIG. 2

Controls. Neither sugar nor insulin. Solutions irradiated with ultraviolet light.

Sugar oxidation starts, then, by the oxidation of whatever active form is present. But any appreciable amount of oxidant is sufficient to remove completely such a small amount of reductant. Hence reduction potentials which were indicative of the presence of this active form are followed by oxidation potentials which are the electrical expression of the excess oxidant. However, the oxidation and removal of the active reductant is accompanied by the constant formation of more active sugar to maintain the equilibrium. When this process is continued long enough the excess oxidant is finally completely removed and the oxidation potential again drops. The addition of an oxidant sufficient in quantity and intensity to bring about an analytically determinable amount of reaction forces these solutions to oxidizing intensities considerably above the level around which sugar oxidation can start. It seems certain that this intensity is a very important factor in determining through which of the many theoretically possible courses this reaction will go. In vivo, sugar oxidation is undoubtedly restricted as to oxidation intensity as well as to hydrogen-ion concentration.

In attempting to correlate the data presented in this and the former papers, it is pointed out that the curves showing the fall of the oxidation potentials from the high values reached soon after the addition of hydrogen peroxide are of the same general shape for all, including even those representing the experiments with ultraviolet light (Figs. 2 to 7). The obvious inference is that qualitatively the same thing happened in every case, at least at the start, although at a slower rate where the curves are flatter. Now under the influence of ultraviolet light this recovery occurs quite rapidly even in the absence of any added chemical reducing agent (Fig. 2, curve for buffer alone). Probably, then, the upper parts of all the curves simply represent the influence of hydrogen peroxide on the electrode. When the peroxide is being destroyed and the oxygen from it removed, the potential falls. When a chemical reducing agent is not present, the flattening out of the curves at the bottom simply represents the approach toward an absence of appreciable amounts of an active oxidant.

The removal of oxygen, however, from dissolved air or decomposing hydrogen peroxide by the nitrogen gas alone or with the help of certain of the amino acids or by the action of ultraviolet light, is not all that happens when dextrose or levulose is present. At least four facts prove this: (1) repeated additions of a small amount of hydrogen peroxide or, under certain conditions, one addition of a larger amount will destroy an analytically detectable amount of sugar; (2) the presence of sugar hastens the fall of oxidation potentials whether due to dissolved air or hydrogen peroxide; (3) reduction potentials ultimately developed in sugar solutions are always lower than those in the buffer alone, and (4) oxidation potentials are lowered faster and the ultimate reduction potentials reached are lower the more concentrated the sugar solutions are. These facts show that there is some reaction between the oxygen from one source or another and the sugar, and that the electrode is giving some response to such action.

A trace of methylene blue in the sugar solutions concentrated enough to produce reduction potentials below the methylene blue range will be decolorized when these potentials are reached. If an oxidant is then added, the electrode shows instantly the positive charge indicative of a loss of reducing intensity and a blue color develops in the solution. When in time the electrode again registers a strong reducing intensity, the dye is again colorless. These facts show that the electrode is really indicating changes in oxidation-reduction throughout the solution and not simply a direct effect of oxidant on electrode which is only local and which does not exist throughout the solutions as a whole. Especially when reducing conditions begin to develop is the electrode potential representative of the combined effects of the various sugar equilibriums. At potentials moderately positive the sugars are of effect only indirectly as they may react with and remove the active oxidant.

The effects of the rate of bubbling of the nitrogen gas are significant in this respect. The faster the bubbling the sooner will oxygen, either from dissolved air or decomposing hydrogen peroxide, be swept out of solution. The greater agitation will also hasten the decomposition of the hydrogen peroxide which forms first nascent and then molecular oxygen. Recovery after the addition of peroxide was found to be much faster when the rate was two bubbles a second[6] than when it was twenty-five a minute.[7]

In the first[7] of this series of experiments, solutions of dextrose alone standing over night stirred by twenty-five bubbles of nitrogen each minute acquired reducing potentials of about −0.3 volt. When the rate was two bubbles a second, these potentials only fell to a little below −0.1 volt according to the curve for the second series of experiments.[6] The value for these potentials reached on standing for this length of time (about fifteen hours) is, however, not at all definite. Often they are quite a little more positive (Fig. 1, the two curves for 200 mg. of dextrose). When the rate of bubbles is kept considerably faster the potentials developed over night are somewhat more positive. If a comparatively high reducing intensity be developed in these solutions by slow bubbling, a sudden increase in this rate will often cause an immediate shift to less negative potentials. Fast bubbling, then, while it hastens the removal of the active oxidant at higher oxidation intensities, seems to so affect the complex sugar equilibriums as often to hinder the development of strong reducing intensities. All curves presented in this paper are from experiments in which the rate was maintained at two bubbles a second.

The effects of the common amino acids are also significant in this respect. A bubble rate of two each second with a sugar present is sufficient to remove from these solutions the hydrogen peroxide of 0.5 c.c. of 0.03 per cent solution within a few hours. Under the conditions, after the dextrose solutions have recovered to about +0.1 volt, all the amino acids studied hasten the further development of reducing intensities (Fig. 1 of second series of experiments[6]). This suggests that all these compounds catalyze the reaction between the sugar and the oxidant still left in solution at about +0.1 volt or lower or modify the sugar equilibriums in such a way as to generate more or stronger reductants, or both.

Certain of the amino acids are shown to have still another effect. Glycine, alanine, and phenylalanine prevent a rise to much higher oxidation intensities and speed up the drop back to the negative potentials. In Fig. 1 curves for glycine and glutamic acid are plotted as examples of amino acids that do and do not have this effect. In the same concentrations used in former experiments, 1 millimole for each 100 c.c., but without any sugar, the curves for these two compounds are not much separated. For ten times this concentration, also without sugar, the curves are not far apart, glutamic acid causing a faster drop below +0.1 volt. When dextrose is present along with the 1 millimole of amino acid, the different actions of the two types of these compounds become apparent. Considering the curves for 10 millimoles of amino acid with the usual 200 mg. of dextrose, it can be noted that again glutamic acid is the more active under greater reducing conditions.

Apparently, then, once the hydrogen peroxide is practically all removed by the sugar or otherwise, so that the solution is no longer more than feebly oxidizing, all the amino acids aid in the further drop toward stronger reducing conditions. The type represented by glutamic acid, however, is the more effective in this respect, especially with the higher concentrations of sugar. On the other hand, if the amount of sugar present is small, the type represented by glycine promotes recovery much earlier and prevents the hydrogen peroxide from creating within the solution its usual oxidation intensity. This fact, together with the observation that when larger amounts of peroxide are added to glycine solutions many tiny bubbles of oxygen gas form throughout the liquid, suggests that the more rapid recovery is due to a catalytic decomposition of the peroxide. When sugar is not present to react with and remove the active oxidant so formed, this action as revealed by electrode potentials is not so obvious. Solutions of glutamic acid do not exhibit this phenomenon. There is no evidence that the amino acids themselves, under these conditions, are very much oxidized. The addition of comparatively enormous amounts of peroxide, followed, after standing for a day, by removal by manganese dioxide leaves the amino acid still in a condition to repeat its catalytic effects. Levulose by itself even without ultraviolet light is comparatively active in reacting with small amounts of hydrogen peroxide and restoring the more negative potentials (Fig. 2, second series of experiments[8]). Hence with levulose in the non-irradiated solutions the recovery curves for all the amino acids are more nearly alike.

The division of the amino acids as to their influence on the reactions of small amounts of dextrose and hydrogen peroxide, as has been pointed out,[6, 7] parallels their division in vivo according to their specific dynamic action. Perhaps this effect may be due in part to similar catalytic decomposition of the oxygenated compounds of the blood, thus furnishing more of a more active oxidant which may produce the increased metabolism noticed after ingestion of these compounds.

If the law of mass action applies, the speed of sugar oxidation should vary directly with the product of the concentrations of active oxidant and active sugar. Some of the evidence discussed above seems to agree with this principle. The effect of a greater sugar concentration in furnishing more active sugar and so lower initial potentials and more rapid recovery is shown in Fig. 1. The greater combined effects of glutamic acid and higher sugar concentrations in doing the same thing is also evident. The concentration of active oxidant can be increased either by adding more hydrogen peroxide or by decomposing faster that which is already present. This is illustrated in the quicker fall in voltage with the glycine type of amino acids.

As to increasing the concentration of the peroxide, the two curves for 200 mg. of dextrose alone (Fig. 1), one for the addition of 0.5 c.c. of a 0.03 per cent hydrogen peroxide solution as usual, and the other for an addition of 1 c.c., do not conflict with this idea. At the end of these runs both had recovered to the same general region of oxidation intensity. It cannot be definitely said however, that twice the amount of actual oxidation of sugar occurred in the one with twice the oxidant. Some of the oxidant in both cases may have been removed as oxygen gas. In this particular case the question cannot be settled by chemical analysis because the amounts involved are far too small.

Still more of the oxidant was added to similar solutions in an effort to cause sufficient oxidation in a reasonable time to be determined by the usual analytic methods. The "paralyzing" effect[6] was encountered. At a bubble rate of twenty-five a minute, the addition of only a few cubic centimeters of a 0.03 per cent solution of hydrogen peroxide produced oxidation potentials which were often still high after a day or two. Subsequent analysis showed that little oxidation had occurred although the oxidation potential was rather high and the sugar in great excess.

At faster rates of bubbling the paralyzing effect of the smaller additions of peroxide does not last so long. At a rate of two bubbles each second, however, the following phenomena were observed: 1 c.c. of a 30 per cent hydrogen peroxide solution was added to 8 gm. of dextrose in 100 c.c. of a buffer at pH 10. The oxidation potential rose at once to about +0.3 volt. The next morning it had risen to about +0.5 volt and remained at this level for several days.

When the hydrogen peroxide was removed by manganese dioxide from these intensely oxidizing solutions, analysis showed that very little of the total reducing capacity of the sugar had been destroyed. There had been but little oxidation of the sugar although it was in considerable excess and a high oxidation intensity existed within the solutions for many hours. In a similar experiment the strong hydrogen peroxide was added to a buffer alone and nitrogen gas bubbled through for fifteen hours. The oxidation potential was about +0.4 volt or not so positive as when the sugar had been present. The addition of sugar at this point caused a gradual drift to the more positive values around +0.5 volt and over. If to these solutions any one of the glycine group of amino acids be added, the potentials soon drop and strong reduction intensities develop. If present from the start these high positive potentials are never seen. The glutamic acid group does not have this effect. At no time under any circumstances was it possible to produce the highest oxidation intensities with hydrogen peroxide in the absence of sugar. Sugar, then, a source of considerable reduction intensity and capacity in alkaline solutions, is able to produce and maintain with the hydrogen peroxide an oxidation intensity greater than any quantity of the oxidant alone can produce.[8]

A rapid rate of nitrogen bubbles (ten to twenty each second) during the usual fifteen-hour period of these experiments, will be found to have prevented these more concentrated sugar and peroxide solutions from developing their highest oxidation intensities. If the rate is suddenly increased in solutions which have developed high oxidizing intensities, the oxidation potentials will quickly drop. At a rate of about two bubbles each second minor changes do not have any important effect.

When these larger quantities of peroxide are added to the sugar solutions **the liquid soon becomes filled with a multitude of tiny bubbles of oxygen gas.** This continues for some time during which the voltage slowly rises, and the highest oxidation potentials are acquired after this evolution ceases. In the buffer alone this evolution does not immediately occur, and when after some time it does start, it is very feeble and sometimes is hard to detect. The glycine group of amino acids, either alone or with sugar, hastens this evolution while the others do not. Glycine will even start an evolution of oxygen bubbles in sugar solutions which have long ceased visibly to give off this gas and have acquired the stronger oxidation intensities.

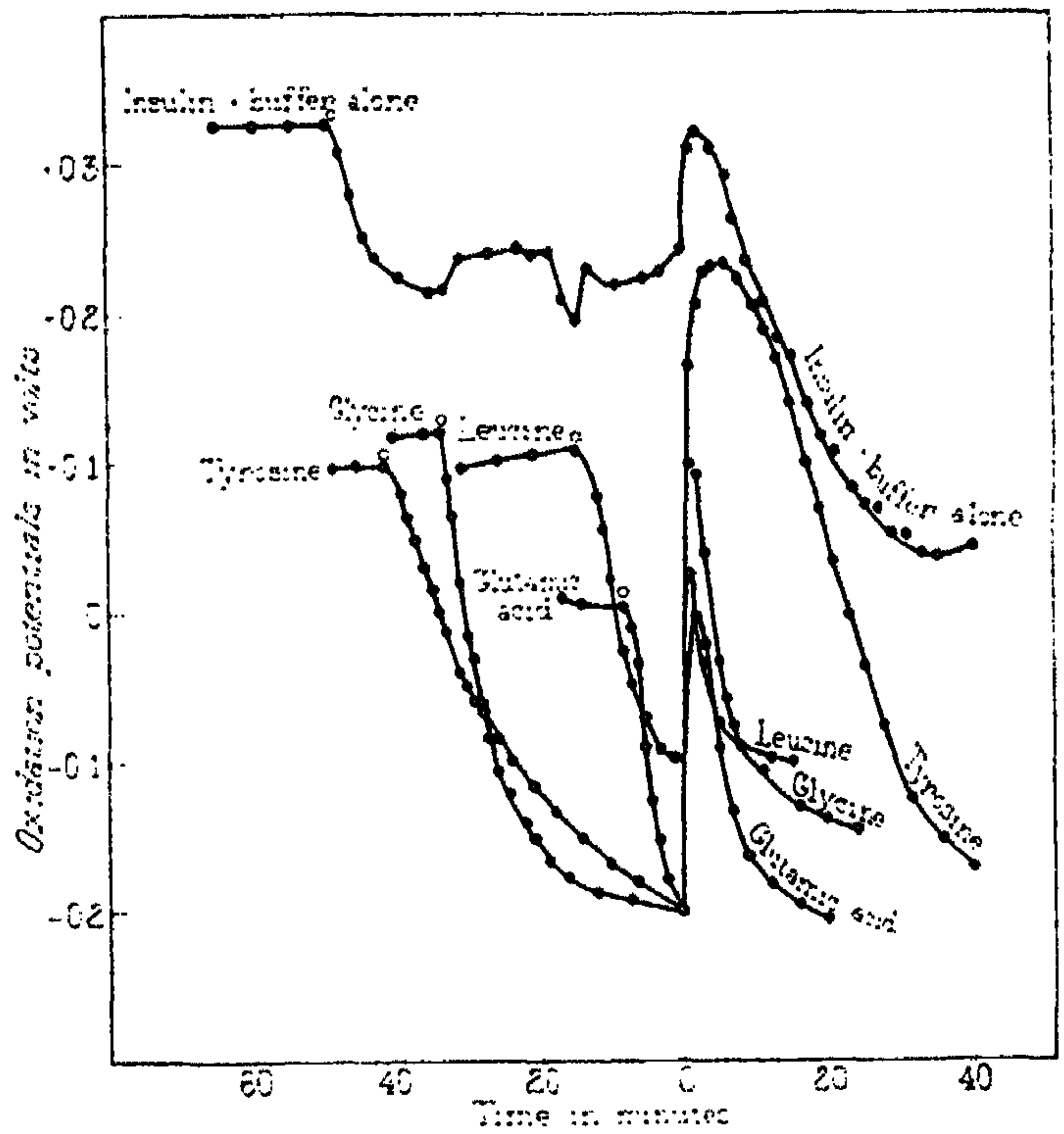

Fig. 3

Controls. Insulin but no sugar. Solutions irradiated.

The evidence from these experiments with the larger concentrations may be summarized as follows:

The law of mass action apparently is not verified, for even in the presence of rather large amounts of hydrogen peroxide, high oxidation potentials, and an excess of sugar, little oxidation of the sugar occurs. The glycine group of

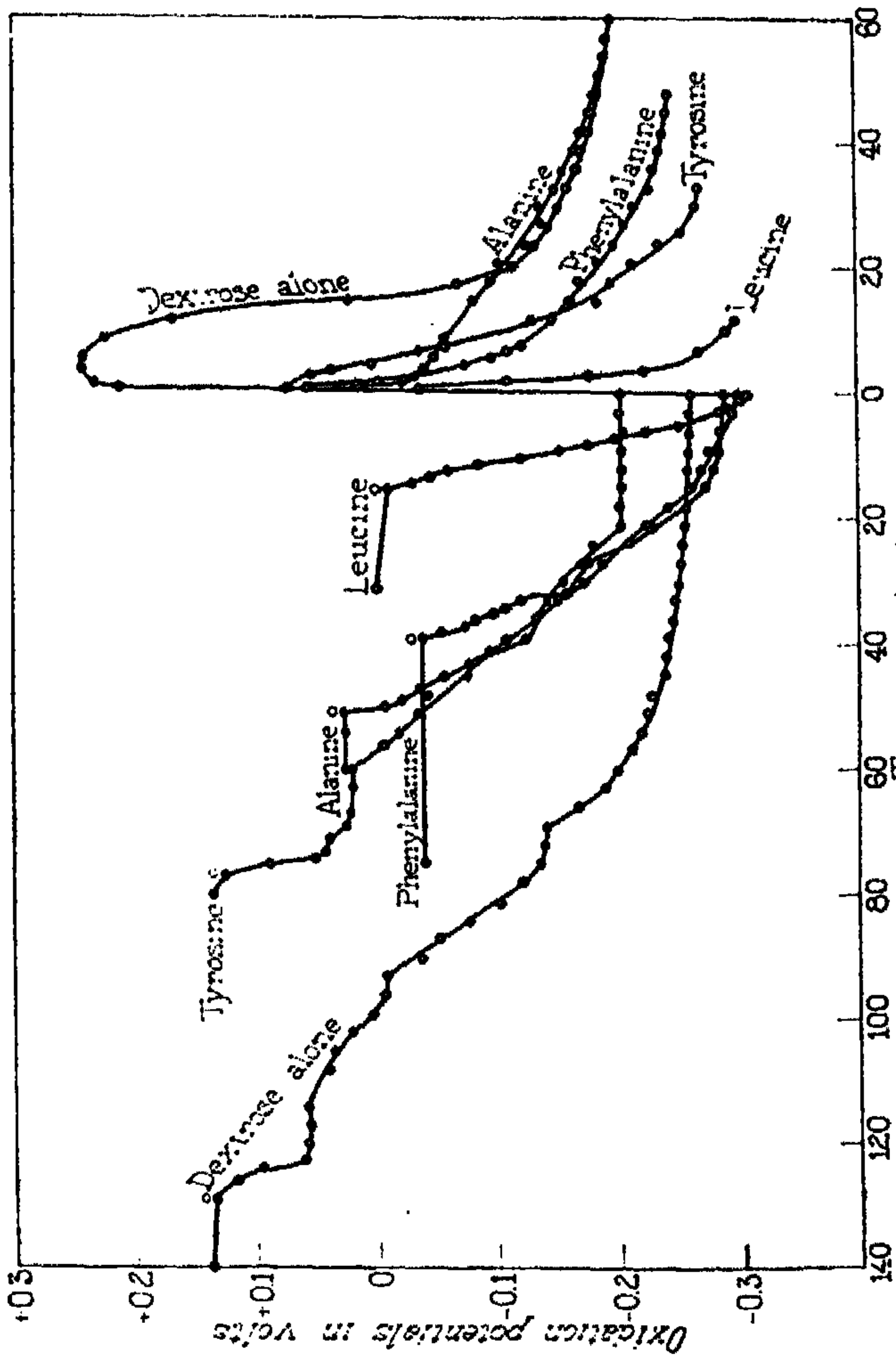

FIG. 4

Irradiated dextrose solutions without insulin.

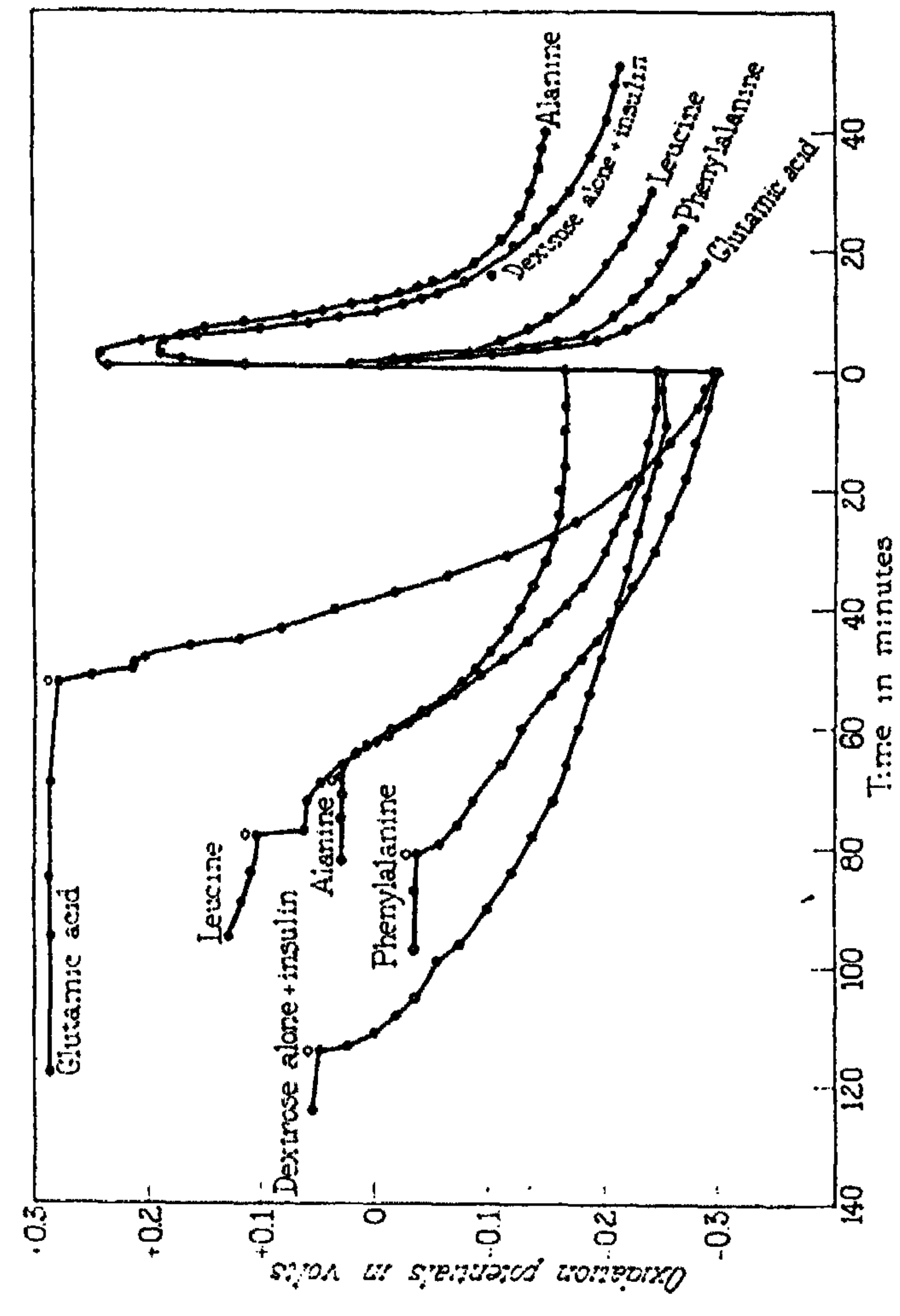

FIG. 5

Irradiated dextrose solutions with insulin.

amino acids again exhibit their catalytic decomposition of the hydrogen peroxide and the prevention and destruction of high oxidation intensities. Sugars or their oxidation products catalyze the decomposition of hydrogen peroxide. Sugar with hydrogen peroxide is able to develop in these solutions oxidation potentials appreciably higher than the peroxide alone can develop. The rate of the nitrogen bubbles again helps to determine the oxidation potentials observed. Agitation breaks up or prevents the formation of complex combinations of the oxidant and the sugar, which when present are responsible for the very high oxidation intensities observed in the more quiet solutions.

Admitting the truth of the foregoing facts and assumptions, the behavior of the irradiated solutions can be fairly well understood, as far as the more general aspects of the first steps of sugar oxidation go, and these experiments will now be considered in more detail.

The most outstanding effect of the ultraviolet light is the increased speed of reaction. The horizontal time scale for the curves presented was lengthened threefold, while the vertical voltage scale was kept as before. Yet the curves are so much steeper, that, in general, the speed of reaction is shown to be ten times greater (Figs. 2 to 7).

The next most obvious effect is the rapid loss of oxidizing intensity when sugar is not present (Figs. 2 and 3). When insulin is absent, even in the buffer alone, the recovery following the addition of hydrogen peroxide is more rapid than was previously reported for solutions of sugar and the amino acids when not irradiated. As is well known, ultraviolet light decomposes hydrogen peroxide. When more concentrated solutions of hydrogen peroxide were irradiated, many minute bubbles of oxygen gas appeared.

Some retarding action of insulin, as was observed in the former experiments, was again noted. A comparison of all the sets of curves shows the general tendencies of insulin to prevent the development of strong reducing intensities when the air is removed, to permit the hydrogen peroxide to produce somewhat higher oxidizing potentials, and to retard the return to reducing conditions. These effects are more evident in solutions without any sugar or with levulose. When dextrose is present, this action is, under certain conditions, not so noticeable. Ahlgren,[1] working with tissues and tissue extracts, has also found that insulin in certain concentrations has a retarding influence on oxidation. Whether irradiated or not it seems to catalyze negatively the decomposition of hydrogen peroxide.

It was found that within an hour the ultraviolet light could produce a reducing intensity of approximately −0.2 volt with most of the amino acids even in the absence of sugar. To lower the voltage further required much longer irradiation in some cases, and was not possible in others. Accordingly this value was selected for the controls and hydrogen peroxide was added when this value was reached or, if this was impossible, when the drifts became slow (Figs. 2 and 3). If dextrose was present, the drop in some cases was comparatively rapid until −0.3 volt was reached. Many of the drifts became slow at about this point. When possible, this potential was selected as the point for the addition of hydrogen peroxide (Figs. 4 and 5). For similar reasons −0.2 volt was chosen when levulose but *not insulin* was present (Fig. 6). It was difficult to obtain low potentials when insulin was present with levulose (Fig. 7) and the hydrogen peroxide was added in most cases whenever the drifts became fairly slow.

In the absence of insulin, some dextrose solutions after several hours of irradiation developed reducing potentials as low as from −0.85 to −0.90 volt, that is, more negative than a hydrogen electrode in the same solutions. Under these conditions it is known[10] that hydrogen and other reducing gases are evolved from such solutions. Particular attention was not given to this phase of the subject although it was noticed that the addition of 0.5 c.c. of a 0.03 per cent hydrogen peroxide solution almost instantly destroyed the greater part of this extreme reducing intensity, just as had always happened in the nonirradiated solutions.

Although nitrogen gas with ultraviolet alone will remove dissolved oxygen or hydrogen peroxide with comparative rapidity, this action was increased by every amino acid studied (Figs. 2 and 3).

The curves for valine and alanine would be similar to the one for glycine, and those for glutamic acid and aspartic acid to that for leucine (Fig. 2). In Fig. 3 the curves for valine and alanine would also be similar to the one for glycine, and the aspartic acid curve to that for glutamic acid. The curve for phenylalanine in Fig. 3 would be similar to that shown in Fig. 2 except that the tendency of insulin to prevent development of strong reducing potentials and rapid recoveries after the addition of hydrogen peroxide would cause it to be flattened out a little. These curves are omitted to prevent confusion.

Glutamic acid, aspartic acid, and leucine were especially effective in developing reduction potentials, exceeding glycine, alanine, and phenylalanine in this respect. This is quite different from their action in the non-irradiated solutions reported previously. As has been pointed out, however, once most of the hydrogen peroxide is removed from solution and the potential reaches +0.1 volt or lower, the glutamic acid group is the more effective of the two groups of amino acids in developing potentials which are still more reducing. The glycine group is the more active in decomposing hydrogen peroxide. Under these conditions the ultraviolet light so strongly decomposes the peroxide that the catalytic effect of the glycine group in this respect is not noticeable, while the effect of the glutamic acid group at the lower potentials is brought out. Hence with and without sugar or insulin (Figs. 2 to 7), the glutamic acid group of amino acids as a rule shows the greater catalytic effect in promoting greater reducing intensities, although most of the amino acids are active to some extent in this respect in most cases.

Tyrosine, as in the non-irradiated solutions, exhibits the least catalytic action of all in the absence of sugar. When dextrose is present and irradiated, however, tyrosine falls more in line with the other amino acids (Fig. 4). Either with or without sugar, solutions of tyrosine when irradiated become amber-colored in daylight. At the point the ultraviolet light enters the solutions they appear blue, and at the back reddish. It is known[3, 9] that tyrosine has absorption bands in the ultraviolet region and its action in this case may be different from that of the other amino acids.

Alanine in the presence of dextrose either with or without insulin seems to lose all catalytic influence when irradiated (Figs. 4 and 5). When it was present it was also found impossible to get reducing intensities much below −0.2 volt within a time of irradiation at all comparable to that necessary for the other amino acids. For the other amino acids the presence of dextrose does not seem greatly to affect the speed of recovery after the addition of hydrogen peroxide. The reducing intensity ultimately developed is, however, greater. The failure to observe any marked difference in the speed of recovery in the presence of dextrose may be due to the comparatively much greater speed of simple decomposition of the hydrogen peroxide by the light. Although ultraviolet light has a profound effect on dextrose solutions after longer periods of irradiation and may thereby actually increase the speed of oxidation, this effect might be masked by that of the much faster simple removal of the peroxide, when so small an amount is added. Lowry and Courtman[5] found that ultraviolet light does not accelerate the isomeric change of dextrose.

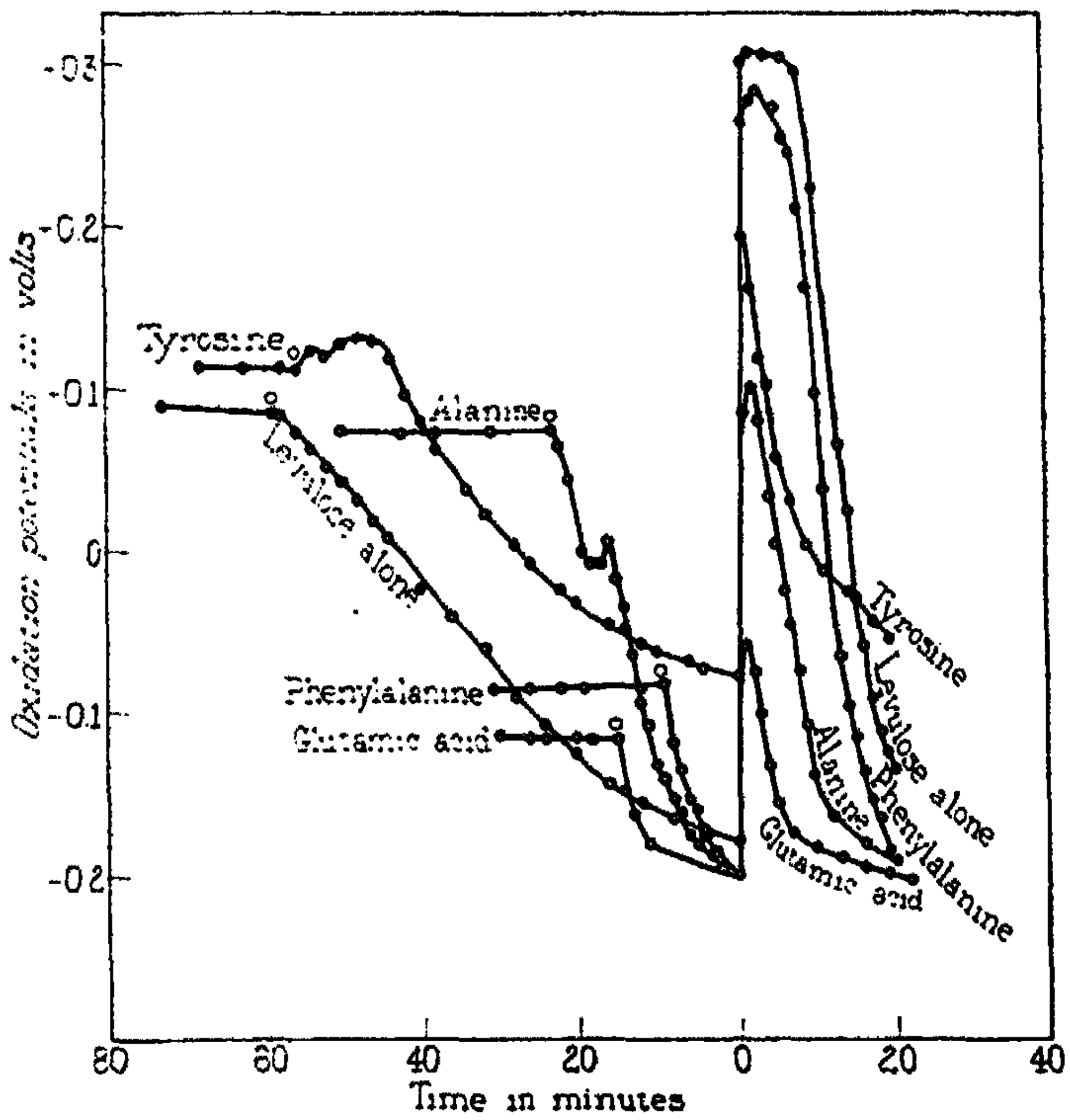

FIG. 6
Irradiated levulose solutions without insulin.

Valine, glutamic acid and aspartic acid would have curves similar to that of leucine in Fig. 4. When glycine is present, the reactions are somewhat slower than for leucine. In Fig. 5, before the hydrogen peroxide was added, the curve for valine would be similar to that for sugar alone, and after hydrogen peroxide was added, to that for leucine; the curve for aspartic acid would be similar to that for leucine; before the addition of the peroxide, the reaction with glycine present is much like that for aspartic acid and after the addition, the reaction is similar to that with glutamic acid; insulin seems to have little effect on the action of tyrosine in the irradiated dextrose solutions.

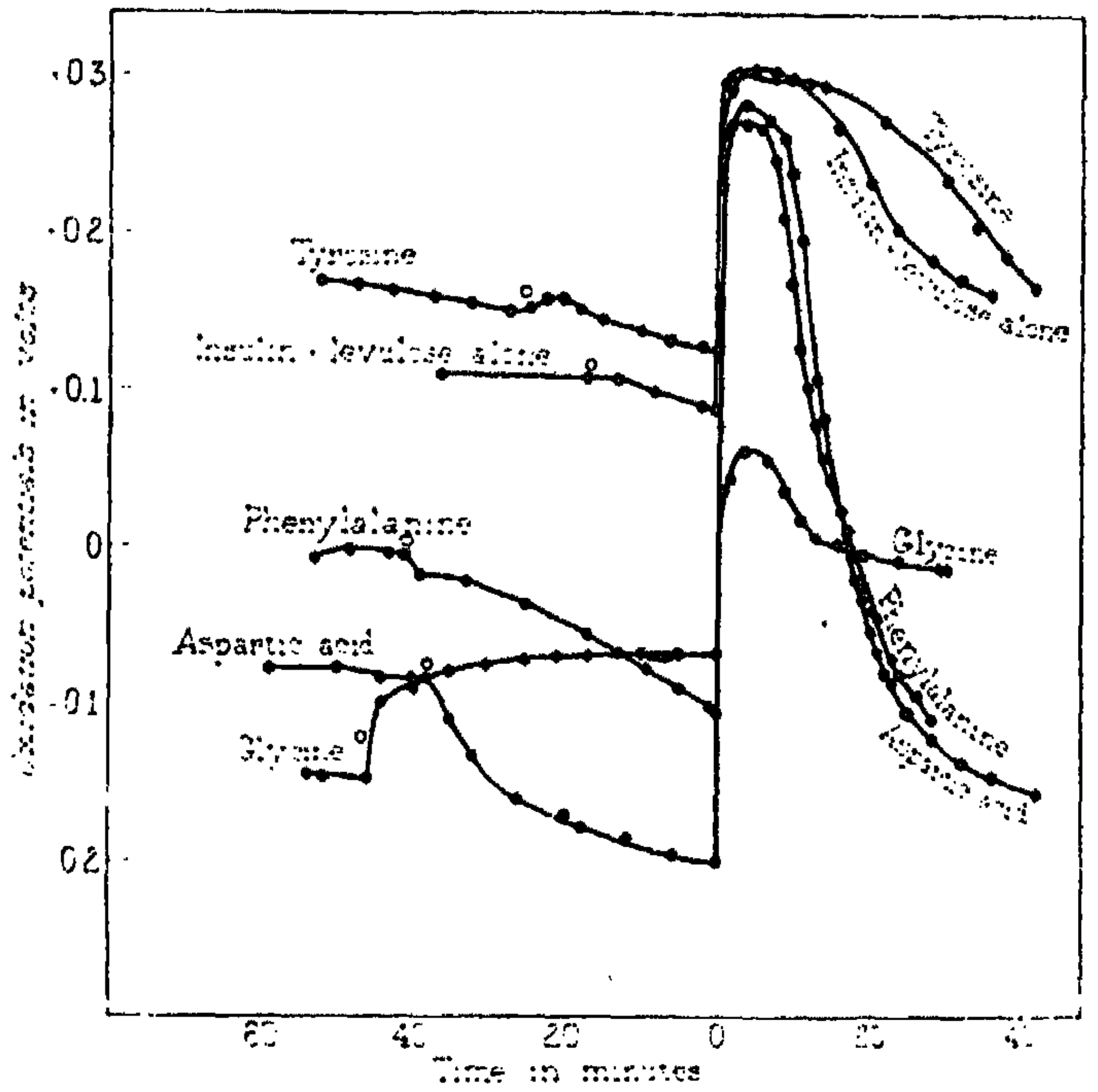

FIG. 7
Irradiated levulose solutions with insulin.

When solutions of levulose without insulin were irradiated the recovery curves (Fig. 6) were somewhat steeper than for the dextrose solutions or those of the amino acids alone. Apparently, then, the oxidation of levulose is appreciably hastened by ultraviolet light. But when insulin is also present (Fig. 7) the recovery is greatly retarded. It is even slower than when levulose is absent from this combination (Fig. 3). Either with or without insulin, tyrosine exerts a retarding influence on the recovery of irradiated levulose solutions. The slow actions of levulose with glycine and an alanine (Fig. 7) were unexpected.

In Fig. 6, after the addition of the peroxide, the curves of glycine, valine, leucine and aspartic acid would lie between those for alanine and glutamic acid. Before the addition, the curves for glycine and aspartic acid would lie between those of glutamic acid and phenylalanine, and those of leucine and valine would be between the curve for alanine and the single vertical line above O time which is common for all curves. In Fig. 7, the curve for alanine would be like that for glycine, and those for glutamic acid, valine and leucine would be similar to that of phenylalanine.

Chemical analysis by the ordinary blood sugar method of Folin shows that both dextrose and levulose when irradiated are attacked much faster by large excesses of hydrogen peroxide. With the addition of 1 c.c. of a 30 per cent solution of hydrogen peroxide, ten-minute irradiation, followed by the decomposition of the excess peroxide with manganese dioxide and a sixteen-hour standing period, the loss of total reducing capacity was found at times to be nearly 80 per cent. Under similar conditions, but without irradiation, the loss was never more than 20 per cent even in the presence of the amino acids, and after having stood for several days with the excess peroxide.

Summary

In this and other recent papers, studies by the oxidation potential method on the first steps of sugar oxidation have been reported. Always, even under many different conditions, a comparatively minute amount of oxidant in the form of air or hydrogen peroxide, has been sufficient to destroy temporarily or prevent the formation of the reducing intensity of dextrose and levulose solutions at pH 10, even though the sugars were present in comparatively enormous excesses. This is evidence in support of the view that the great bulk of the sugar in solutions can not be directly attacked by oxidants except under comparatively intense oxidizing conditions. That is, the reduction intensity developed in these solutions is due to the presence of a very small amount of an active form which is in equilibrium with a comparatively inactive and vastly more abundant form. It is suggested that the oxidation intensity at which sugar solutions are oxidized is probably one of the factors determining the course of the oxidation reactions.

A study has also been made on the effects of certain of the amino acids, insulin, ultraviolet light, and the rate of bubbles of the nitrogen gas stirring these solutions. Certain of the amino acids represented by glycine were shown to catalyze the decomposition of hydrogen peroxide and so promote its reaction with the active sugar. Ultraviolet light has a similar but much greater effect. Other of the amino acids as represented by glutamic acid, while lacking at least to a comparable degree this catalytic effect, seem to be of greater influence in developing further reducing intensities, once most of the oxidant is removed and the stronger oxidizing conditions are gone. These amino acids while therefore not so effective with small concentrations of sugars in nonirradiated solutions, exhibit their action more in concentrated sugar solutions or in solutions irradiated by ultraviolet light in which the excess oxidant is otherwise removed. Insulin, in the concentration used, seemed to catalyze negatively the decomposition of hydrogen peroxide. Hence, as a rule, solutions recovered their reduction potentials more slowly when it was present.

Apparently the law of mass action does not hold in the oxidation of these sugars by air or hydrogen peroxide. The addition of enormous excesses of oxidants to nonirradiated solutions produces very little oxidation of sugar. Additions of large amounts of peroxide to solutions of these sugars are followed by the appearance of innumerable tiny bubbles of oxygen gas throughout the solution, indicating that sugar or its first oxidation products catalytically decompose hydrogen peroxide. A similar phenomenon is observed in the presence of the glycine group of amino acids or when the solutions are irradiated. After these bubbles have disappeared from the nonirradiated solutions of the sugars alone, the oxidation potential goes higher than when sugar is absent even though any amount of the peroxide be added. Glycine prevented this, and glutamic acid did not. Fast bubbling also tended to keep down these excessive oxidation intensities as well as to prevent the formation of the more negative reduction potentials in the deaërated solutions.

When sugar solutions were treated with an excess of hydrogen peroxide and irradiated with ultraviolet light, as much as 80 per cent of the sugar could be destroyed in a short time as compared to less than 20 per cent under all other conditions tried. When irradiated for several hours after deaëration, dextrose solutions without insulin developed reduction potentials exceeding even that of a hydrogen electrode in similar solutions.

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Section on Biophysics,
The Mayo Foundation,
Rochester,
Minnesota.

THE CONCEPTIONS OF ELECTRICAL POTENTIAL DIFFERENCE BETWEEN TWO PHASES AND THE INDIVIDUAL ACTIVITIES OF IONS

BY E. A. GUGGENHEIM

It has long been realised that one cannot accurately determine in a solution the activity or chemical potential of an individual ion, because of the existence of liquid junction potentials whose magnitude cannot be computed without a previous knowledge of the individual ionic activities that one wishes to measure. This vicious circle has generally been regarded as an unfortunate accident and attempts have frequently been made to overcome the dilemma by the use of cells in which the liquid junction potentials, though unknown, were probably small. For example the introduction of a bridge of a concentrated solution of potassium chloride will in many cases reduce the uncertainty to a few millivolts. It is however easy to convince oneself that under the most favourable circumstances the uncertainty due to the liquid junction potential is more than equivalent to the difference between the individual chemical potentials of two different ions of the same charge when present at the same concentration in the same solution. It is in fact impossible by any such device to distinguish between the values of the activity coefficients of different ions with the same charge.

In agreement with this point of view it has recently been shown by Taylor[1] that "the E.M.F. of the cell with transference is thus a function of molecular free energies solely and is not a function of ionic free energies. It therefore can yield no information concerning ionic free energies" and that "with the possible exception of single electrode potentials and rates of reaction there appears to be no occasion for the use of ionic free energies as experimental quantities, but only as a mathematical device.[2] It will be shown that Taylor's first conclusion may be considered as a corollary to a more general principle, from which it also follows that to his second conclusion there are no "possible exceptions."

The general principle referred to may be expressed as follows. "The electric potential difference between two points in different media can never be measured and has not yet been defined in terms of physical realities; it is therefore a conception which has no physical significance." The electrostatic

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[1] P. B. Taylor: J. Phys. Chem., 31, 1478 (1927).

[2] Taylor uses the expression "free energy" for Gibbs' "chemical potential" μ. Lewis and Randall ("Thermodynamics" (1923)) call it the "partial free energy" and use the symbol $\bar{F}$. We prefer to retain the nomenclature of Gibbs, as μ is related equally intimately to the "free energy" F, the "affinity" A, the "heat content" H and the "internal energy" E; this may be seen from the relations

$$\mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,P} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P} = \left(\frac{\partial E}{\partial n_i}\right)_{S,V}$$

where T, S, P, V denote temperature, entropy, pressure, volume respectively and n_i is the number of moles of the species in the system.

potential difference between two points is admittedly defined in electrostatics, but this is the mathematical theory of an imaginary fluid 'electricity,' whose equilibrium or motion is determined entirely by the electric field. 'Electricity' of this kind does not exist; only electrons and ions have physical existence and these differ fundamentally from the hypothetical fluid 'electricity' in that the particles are at all times in movement relative to one another; their equilibrium is thermodynamic, not static.

The electrostatic potential ψ determines the equilibrium or change towards equilibrium of the hypothetical fluid 'electricity,' whereas the chemical potential μ_i determines those of an uncharged molecule of type *i*. But the equilibrium of an ion of type *i* and charge ϵ_i is determined neither by ψ nor by μ_i but by the function $\bar{\mu}_i = \mu_i + \epsilon_i\psi$ which it is suggested should be called the "electrochemical potential." If is therefore $\bar{\mu}$ that has a real physical significance. The conception of splitting the electrochemical potential $\bar{\mu}_i$ of an ion of type *i* into the sum of a *chemical term* μ_i and an electrical term $\epsilon_i\psi$ has no physical significance; for one can assign an arbitrary value to ψ for some point in each medium and this will for the ions of each type *i* determine μ_i, so as to give $\bar{\mu}_i$ the value which determines all the physical processes involving ions of type *i*; amongst such processes may be mentioned in particular diffusion, partition between two media, membrane equilibria, cells without and with liquid junctions, and even reaction rates. A word of explanation is required concerning our use of the word medium; the medium may be considered the same so long as the solvent is the same and all the solute species behave independently. For example two aqueous solutions of the same salt at different concentrations may, or may not, be considered as the same medium according as we neglect, or take account of, specific 'salt effects.' Thus the liquid junction potential between two salt solutions in different solvents has no physical meaning; for two aqueous salt solutions in contact it can be computed only with an accuracy that neglects specific 'salt effects.'

Although μ_i has no physical significance for a single ionic species, yet certain linear combinations of the μ_i have one; the necessary and sufficient condition for this is that they should be expressible in terms of the $\bar{\mu}_i$. For example if we consider two ionic species i and k in the same medium and write formally

$$\mu_i = \mu_i + \epsilon_i \psi$$

$$\bar{\mu}_k = \mu_k + \epsilon_k \psi$$

then these equations have no physical significance as the value of ψ is quite arbitrary. If however we eliminate ψ we obtain

$$\frac{\mu_i}{\epsilon_i} - \frac{\mu_k}{\epsilon_k} = \frac{\bar{\mu}_i}{\epsilon_i} - \frac{\bar{\mu}_k}{\epsilon_k}$$

so that the combination $\frac{\mu_i}{\epsilon_i} - \frac{\mu_k}{\epsilon_k}$ has a definite value although μ_i and μ_k have not. In general, the condition that the sum $\sum\limits_i \lambda_i \mu_i$ should have a definite value, where the λ_i are numerical coefficients, is that $\sum_i \lambda_i \epsilon_i = 0$ for under this condition $\Sigma \lambda_i \mu_i = \sum_i \lambda_i \bar{\mu}_i$ and this defines $\Sigma \lambda_i \mu_i$.

Since the activity a_i of an ion of type *i* is defined by

$$\mu_i = R\,T \log_e a_i + \mu_i^\circ$$

where μ_i° depends on the temperature and pressure, but not on the medium, and its activity coefficient f_i is defined by

$$a_i = f_i\, C_i$$

it follows that the relation $\sum_i \mu_i \epsilon_i = 0$ is also the necessary and sufficient condition for the products $\prod_i a_i^{\lambda_i}$ and $\prod_i f_i^{\lambda_i}$ to be physically defined although the individual a_i and f_i are not. Thus, in particular, the 'mean activity coefficient' of a salt is defined, as is also the ratio of the activities or activity coefficients of two ionic species with the same charge.

We shall now illustrate our general principle by showing that the phenomena of diffusion, partition between two media, membrane equilibria, cells without and with liquid junctions, and reaction rates are completely describable in terms of the electrochemical potentials $\bar{\mu}_i$ (or alternately such linear combinations of the μ_i as are expressible and so definable in terms of the $\bar{\mu}_i$) and that in no case does either μ_i or ψ occur separately from the other.

Diffusion. The driving force on an uncharged molecule of type *i* determining its diffusion is $-\text{grad}\ \mu_i$, the component in the *x* direction being $-\dfrac{\partial \mu}{\partial x}$. For an ion of type *i* and charge ϵ_i the corresponding chemical force is the same, but there is also an electrical force $-\epsilon_i\ \text{grad}\ \psi$ with an x-component $-\epsilon_i \dfrac{\partial \psi}{\partial x}$ Hence the total driving force on the ion determining its diffusion is $-\text{grad}\ \mu_i - \epsilon_i\ \text{grad}\ \psi = -\text{grad}\ (\mu_i + \epsilon_i \psi) = -\text{grad}\ \bar{\mu}_i$ with an x-component

$$-\frac{\partial \mu_i}{\partial x} - \epsilon_i \frac{\partial \psi}{\partial x} = -\frac{\partial}{\partial x}(\mu_i + \epsilon_i \psi) = -\frac{\partial \bar{\mu}_i}{\partial x}$$

No experiment on diffusion can distinguish between the hypothetical component parts of $\bar{\mu}_i$.

Partition between two media. If a salt AB is distributed between two phases I and II the equilibrium is completely defined and described by the conditions

$$\bar{\mu}^{I}_{A} = \bar{\mu}^{II}_{A} \qquad \bar{\mu}^{I}_{B} = \bar{\mu}^{II}_{B}$$

and any decomposition of $\bar{\mu}_i$, into the sum $\mu_i + \epsilon_i \psi$ is arbitrary and without physical significance. No measurements can give any information about ψ or the separate μ_i.

Membrane equilibria. If a membrane permeable to some ions, but impermeable to others and to the solvent[1] separates two phases I and II, then the equilibrium of any diffusible ion of type *i* is completely determined by the condition

$$\bar{\mu}_i^{\mathrm{I}} = \bar{\mu}_i^{\mathrm{II}}$$

Only if the medium is the same in both phases (same solvent with neglect of specific salt effects) has it any physical significance to split $\bar{\mu}_i$ into a part μ_i depending only on the concentration of *i* and an electrical part $\epsilon_i\,\psi$. Thus in the special case of an ideal solution

$$\begin{aligned}\epsilon_i(\psi^{\mathrm{I}} - \psi^{\mathrm{II}}) &= \mu_i^{\mathrm{II}} - \mu_i^{\mathrm{I}} \\ &= \mathrm{RT}\log_e\frac{C_i^{\mathrm{II}}}{C_i^{\mathrm{I}}}\end{aligned}$$

where R is the gas constant, T the absolute temperature and C_i the concentration of the species *i*. But in general for a non-ideal solution any analogous equation would have no physical meaning.

Cell without liquid junction. It is here convenient to take as a concrete example the cell

Cu	Solution containing Cu^{++} and Zn^{++}	Zn	Cu
I	II	III	IV

with the circuit broken in the copper; the irreversible deposition of copper on the zinc electrode is to be ignored. Let the phases be numbered in order I, II, III, IV. Then the two electrode-solution junctions and the metal-metal junction may be regarded as membranes permeable respectively to copper ions Cu^{++}, zinc ions Zn^{++} and electrons El^{-} only. The equilibria at these three junctions are completely described by the conditions

$$\bar{\mu}_{Cu^{++}}^{\mathrm{I}} = \bar{\mu}_{Cu^{++}}^{\mathrm{II}} \qquad \bar{\mu}_{Zn^{++}}^{\mathrm{II}} = \bar{\mu}_{Zn^{++}}^{\mathrm{III}} \qquad \bar{\mu}_{El^{-}}^{\mathrm{III}} = \bar{\mu}_{El^{-}}^{\mathrm{IV}}$$

and the vexed question whether the electrical potential difference is seated at the electrodes or at the metal-metal junction has no physical meaning.

Since the phases IV and I are the same medium, copper, the potential difference between them has a physical meaning as in electrostatics. We have in fact

$$\bar{\mu}_{Cu^{++}}^{\mathrm{IV}} = \mu_{Cu^{++}}^{\mathrm{Cu}} + \epsilon_{Cu^{++}}\,\psi^{\mathrm{IV}}$$

$$\bar{\mu}_{Cu^{++}}^{\mathrm{I}} = \mu_{Cu^{++}}^{\mathrm{Cu}} + \epsilon_{Cu^{++}}\,\psi^{\mathrm{I}}$$

By subtraction we obtain for ϕ the E.M.F. of the cell

$$\phi = \psi^{\mathrm{IV}} - \psi^{\mathrm{I}} = \frac{\bar{\mu}_{Cu^{++}}^{\mathrm{IV}} - \bar{\mu}_{Cu^{++}}^{\mathrm{I}}}{\epsilon_{Cu^{++}}}$$

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[1] If the membrane is permeable to the solvent a pressure difference (differential osmotic pressure) is necessary for equilibrium; the treatment thus becomes slightly more complicated but the same conclusions hold.

By making use of the three junction equilibrium conditions this can be transformed to

$$\phi = \left(\frac{\bar{\mu}_{Cu^{++}}}{\epsilon_{Cu^{++}}} - \frac{\bar{\mu}_{El^{-}}}{\epsilon_{El^{-}}}\right)^{IV} + \left(\frac{\bar{\mu}_{El^{-}}}{\epsilon_{El^{-}}} - \frac{\bar{\mu}_{Zn^{++}}}{\epsilon_{Zn^{++}}}\right)^{III} + \left(\frac{\bar{\mu}_{Zn^{++}}}{\epsilon_{Zn^{++}}} - \frac{\mu_{Cu^{++}}}{\epsilon_{Cu^{++}}}\right)^{II}$$

The first two pairs of terms on the right are quantities which are constants for Cu and Zn respectively, so that the equation for ϕ can be written

$$\phi = \phi^{\circ} + \left(\frac{\bar{\mu}_{Zn^{++}}}{\epsilon_{Zn^{++}}} - \frac{\bar{\mu}_{Cu^{++}}}{\epsilon_{Cu^{++}}}\right)^{II}$$

where ϕ° is independent of the composition of phase II. The usual formula for ϕ

$$\phi = \phi^{\circ} + \left(\frac{\mu_{Zn^{++}}}{\epsilon_{Zn^{++}}} - \frac{\mu_{Cu^{++}}}{\epsilon_{Cu^{++}}}\right)^{II}$$

of course involves the μ in just such a linear combination as can be expressed in terms of the $\bar{\mu}$ and is so defined.

Cells with liquid junction. As already mentioned it has been shown by Taylor[1] that cells with liquid junctions can yield no information (except concerning mobilities) that cannot be obtained at least equally well from cells without liquid junctions. The description of a cell with liquid junction is straightforward and the treatment follows that of cells without liquid junction combined with the treatment of diffusion. Let us consider as a special case the cell

Cu	Solution X	Diffusion layer	Solution Y	Cu
I	II	III	IV	V

where the phases are numbered in order I, II, III, IV, V; solutions X and Y contain copper ions as well as various other ions of both signs. Then the diffusion conditions in phase III are completely defined in terms of the electrochemical potentials $\bar{\mu}_i$, of the various ions. The diffusion layer is then completely defined by the concentration C_i and electrochemical potential $\bar{\mu}_i$ of the ions of each type i at each part of the layer. In particular the diffusion conditions fix the values of $\bar{\mu}_{Cu^{++}}$ at the two ends of the layer, that is to say the values of $\bar{\mu}^{II}_{Cu^{++}}$ and $\bar{\mu}^{IV}_{Cu^{++}}$. But the electrode equilibria are determined by

$$\bar{\mu}^{I}_{Cu^{++}} = \bar{\mu}^{II}_{Cu^{++}} \qquad \bar{\mu}^{V}_{Cu^{++}} = \bar{\mu}^{IV}_{Cu^{++}}$$

and finally since phases I and V are the same medium the E.M.F. of the cell is given by

$$\phi = \psi^{V} - \psi^{I} = \frac{\mu^{V}_{Cu^{++}}}{\epsilon_{Cu^{++}}} - \frac{\bar{\mu}^{I}_{Cu^{++}}}{\epsilon_{Cu^{++}}} = \frac{\bar{\mu}^{IV}_{Cu^{++}}}{\epsilon_{Cu^{++}}} - \frac{\bar{\mu}^{II}_{Cu^{++}}}{\epsilon_{Cu^{++}}}$$

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[1] P. B. Taylor: J. Phys. Chem., 31, 1478 (1927).

The usual formula is

$$\phi - \frac{\mu^{IV}_{Cu^{++}}}{\epsilon^{Cu}_{++}} - \frac{\mu^{II}_{Cu^{++}}}{\epsilon_{Cu^{++}}} + \psi^{IV} - \psi^{II}$$

and $\psi^{IV} - \psi^{II}$ is called the "diffusion potential", but, as seen from the above treatment and already pointed out by Taylor, this splitting up of ϕ into "electrode potentials" and "diffusion potential" is quite arbitrary.

Reaction rate. The velocity of the primary process

$$\lambda_A A + \lambda_B B + \ldots \longrightarrow \text{products}$$

is given by[1]

$$V = k\, C^{\lambda_A}_{A} \cdot C^{\lambda_B}_{B} \ldots \quad \frac{f^{\lambda_A}_{A} \cdot f^{\lambda_B}_{B} \cdot \ldots}{f_x}$$

where k depends on the temperature and solvent only, C_i is the concentration and f_i the activity coefficient of the species *i* with charge ϵ_i; f_x is the activity coefficient of a "complex" $(A_{\lambda_A} \cdot B_{\lambda_B} \ldots)$. There is still some difference of opinion as to the nature of this complex[2], but in any case its charge ϵ_x satisfies the relation

$$\epsilon_x = \lambda_A \epsilon_A + \lambda_B \epsilon_B + \ldots$$

which is just the condition that the product

$$\frac{f^{\lambda_A}_{A} \cdot f^{\lambda_B}_{B} \cdot \ldots}{f_x}$$

should have a physical meaning although the individual f_i have not.

We thus see that all the phenomena generally associated with the individual ionic chemical potentials μ_i and electrical potential differences between two media are equally well describable in terms of the electrochemical potentials $\bar{\mu}_i$ without introducing the former conceptions, which have no physical meaning. If one describes the phenomena in terms of the fictitious individual ionic chemical potentials μ_i, then only such linear combinations of the μ_i occur in the treatment as are expressible in terms of the electrochemical potentials $\bar{\mu}_i$. It has previously been realised that only these and not the μ_i have any THERMODYNAMIC importance, but we maintain that only they have any PHYSICAL significance, for only they are definable in terms of physical realities.

It is perhaps worth while emphasizing that not even when one thinks in terms of simple atomic models does the conception of the chemical potential of an individual ion become of physical significance. For example one might assume that at a given low concentration the difference for two media I and II in the chemical potential of an ion *i* with the spherical symmetry of a rare gas atom would differ from that for such an uncharged atom of the

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[1] Brönsted: Z. physik. Chem., **102**, 169 (1922); Bjerrum: **108**, 82 (1924).

[2] Brönsted: loc. cit. and **115**, 337 (1925); Bjerrum: loc. cit. and **118**, 251 (1925).

same size by an amount $\frac{\epsilon_i^2}{2r_i}\left(\frac{1}{D''} - \frac{1}{D'}\right)$ where r_i is the radius of the ion and D' D'' are the dielectric constants of the media. But such a definition would have no physical significance, because $\frac{\epsilon_i^2}{2r_i}\frac{1}{D}$ is a measure of the electric work of removing the charge from the ion *i* to a large sphere (virtually infinitely large) in the same medium. Hence the expression $\frac{\epsilon_i^2}{2r_i}\left(\frac{1}{D''} - \frac{1}{D'}\right)$ is not a measure of the work of transferring the charge from an ion *i* in medium I to a particle of the same size and structure in medium II, but differs from this work by the unknown work of transferring the charge from the large sphere in medium I to the large sphere in medium II, that is to say by the amount $\epsilon_i (\psi'' - \psi')$, where $\psi'' - \psi'$ is the electric potential difference between the two media and so is indeterminate. Only when we consider the simultaneous transfer of λ_i ions of each type *i* where the relation $\sum_i \lambda_i \epsilon_i = 0$ is satisfied, does the indeterminateness cancel.

Again, if we attribute the 'salt effects' in dilute solutions in a given solvent to the interionic field, it is clear that the interionic energy is stored in the whole assembly and any partition of it amongst the separate types of ions would be arbitrary. In the theory of Debye and Hückel,[1] which treats the ions as rigid spheres, this shows itself by the fact that the specific quantities, which distinguish solutions of the same electric type, are not the diameters of the individual ions, but the distances of closest approach of the various pairs of ions.

It is thus clear that if one sets out to measure the activity or chemical potential of an individual ion the dilemma, with which one is in every case confronted, is not an accident, but is the natural consequence of trying to measure a quantity which physically does not exist.

We see then that the equilibrium and change towards equilibrium of charged particles are in all cases completely defined by the electrochemical potentials μ_i, one of which corresponds to each species *i* including electrons El^-. It might be suggested that the electric potential ψ be defined by the relation

$$\bar{\mu}_{El^-} = \epsilon_{El^-}\ \psi$$

and then the μ_i could be defined by

$$\mu_i = \bar{\mu}_i - \epsilon_i \psi = \mu_i - \frac{\epsilon_i}{\epsilon_{El^-}} \bar{\mu}_{El^-}$$

There is no physical or logical objection to this, but this use of the expression 'electrical potential' would be so far removed from that of 'electrostatic potential' that it is not to be recommended. Consider for example the description of the Volta effect. If we define as "uncharged" a piece of metal

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[1] Debye and Hückel: Physik. Z., 21, 185 (1923).

in which the number of free electrons is exactly equivalent to the number of metallic ions, then the electrochemical potential $\bar{\mu}_{\mathrm{El}^-}$ of electrons will not be the same in a piece of uncharged zinc and a piece of uncharged copper. If two such pieces of zinc and copper be brought into contact there will then be a flow of electrons from the zinc to the copper until the difference in $\bar{\mu}_{\mathrm{El}^-}$ is annulled. On the other hand in electrostatic theory the flow of electrons is usually said to create, not annul, an electrostatic potential difference. Hence if instead of 'electrochemical potential $\bar{\mu}_{\mathrm{El}^-}$ of electrons' we were to write 'electric potential ψ', the above description would be likely to sound strange. It is therefore probably best to restrict the expression 'electric potential' to mean the 'electrostatic potential' of electrostatics, and avoid its use in the description of physical phenomena involving ions and electrons.

In conclusion the author wishes to thank Professor Bjerrum for his kind criticism.

Copenhagen,
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KINETICS AND TEMPERATURE COEFFICIENTS OF SOME PHOTOCHEMICAL REACTIONS IN RADIATIONS OF DIFFERENT WAVE-LENGTHS

BY B. K. MUKERJI AND N. R. DHAR

In a recent paper we have determined the quantum efficiencies of fourteen photochemical reactions and have found that the quantum efficiency depends on the wave-length of the radiation employed and on the temperature of the reacting system. We have made a special study of the influence of temperature on numerous thermal and photochemical reactions in these laboratories.[1]

As there is very little experimental work on the relation between the temperature coefficient and the frequency of the radiation, we have made a systematic investigation on the kinetics of several reactions both in the dark and in the light of different wave-lengths at different temperatures.

The experimental arrangement is the same as described in the paper on the quantum efficiency.

The results obtained are recorded in the following tables:—

(1) Bleaching of Dicyanin

The bleaching of dicyanin in air is very probably caused by its oxidation by the atmospheric oxygen. We have observed that by passing oxygen through the dye solution in light the bleaching is accelerated. As there is no experimental work on the kinetics of this change we have made a systematic investigation on the kinetics at different temperatures in the dark and under the influence of radiations of different wave-lengths. The velocity of the reaction was followed by measurements of the extinction coefficient spectrophotometrically.

The following results have been obtained:—

Concentration of Dicyanin —M/24,166

λ	k_1 at 25°	k_1 at 30°	k_1 at 40°
4725Å	0.00337	0.00379	0.00450
5650Å	0.00317	0.00353	0.00422
7304Å	0.00309	0.00340	0.00397
Sunlight	0.090(15°)	0.101(25°)	0.103(35°)
Dark	0.00099	0.00127	0.00172

Kinetics in pure light				$k_{40°}/k_{30°}$	Arrhenius A
λ	k_1 at 25°	k_1 at 30°	k_1 at 40°		
4725	0.00238	0.00252	0.00278	1.099	835
5650	0.00218	0.00226	0.00250	1.106	846
7304	0.00210	0.00213	0.00225	1.056	448
Sunlight	—	—	—	1.02	225
Dark	—	—	—	1.354	2680

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[1] J. Chem. Soc., 111, 707 (1917); 123, 1856 (1923); Z. anorg. allgem. Chem., 134, 172 (1924); 121, 1561 (1922); Z. Elektrochemie, 32, 586 (1926).

We have measured photometrically the percentage of incident light transmitted by the different combination of light filters used in these investigations. Moreover, we have calculated the amount of energy content in the radiations employed in this investigation by applying Planck's well known formula:—

$$E_\lambda = \frac{8\pi ch}{\lambda^5}\cdot\frac{1}{e^{ch/\lambda kT} - 1}$$

The "T" in the above formula was taken to be the temperature of the *filament of the lamp and this temperature could be ascertained by measuring* the resistance of the filament and by applying the empirical formula[1]:—

$$R/R_0 = (T/T_0)^{1.200}$$

The ratio of the energy given out by the 1000-watts lamp in the mean wave-regions are:—

$$\lambda_{4725} : \lambda_{5650} : \lambda_{7304} \equiv 1 : 2.54 : 5.8$$

we have assumed that this ratio remains constant for 500 c.p. and 100 c.p. lamps which have also been used in these experiments.

In the following table the true accelerations are shown taking into consideration the energy distribution at the wave-regions employed and the percentage absorption of light by dicyanin.

Temperature 40°C

	Percentage incident radiation transmitted by filters	Number of times acceleration in light over the dark reaction for 100% transmission by filters	Number of acceleration over the dark reaction for the relative values of E_λ	% absorption by dicyanin	Number of times acceleration over dark reaction for 100%
4725Å	29.6	5.41	5.41	32.44	16.67
5650Å	3.2	45.62	17.96	60.31	29.78
7304Å	2.86	45.78	7.9	29.08	27.17

Similar results are obtained at 25° and 30°.

The foregoing results show that the percentage of absorption is maximum at $\lambda = 5650$Å and this also produces the maximum acceleration of velocity in that region.

(2) Sodium Citrate and Iodine

The rate of disappearance of iodine in the dark follows the unimolecular formula. The following results were obtained with different concentrations of sodium citrate using N/100 iodine and N/30 KI in the dark.

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[1] Worthing and Forsythe: Phys. Rev., (2) **18**, 144 (1921).

Concentration of Sodium Citrate	k_1 at 33°	Number of molecules of Sodium Citrate reacting
N/5.76	0.00188 ......(1)	
		1.63 (from (1) and (2))
N/3.2	0.00476 ......(2)	
		1.59 (from (1) and (3))
N/2.88	0.00582 ......(3)	

It appears therefore that the reaction between sodium citrate and iodine in the dark is *bimolecular* with respect to sodium citrate and *unimolecular* with respect to iodine and hence the total reaction is *trimolecular*.

Kinetics at different temperatures.

	$k_{½}$ at 33° (Semi-molecular)	$k_{½}$ at 33°
4725Å	0.0108	0.0180
7304Å	0.00831	0.0148
Dark	0.00115	0.00188
	(unimolecular)	(unimolecular)

Kinetics in pure light

Wave length	$k_{½}$ at 23°	$k_{½}$ at 33°	k_{33}/k_{23}	Arrhenius A
4725Å	0.00506	0.0074	1.46	3425
7304Å	0.00257	0.0042	1.63	4420
Dark	—	—	1.64	4430

Temperature 23°

Wave length	% of incident light transmitted by filters	Number of times acceleration in light for 100% transmission	Relative values of $E\lambda$	Number of times acceleration over the dark reaction for equal values of $E\lambda$
4725 Å	29.6	2.7	1	1
7304 Å	2.86	15.6	5.8	2.7

(3) Sodium Malate and Iodine

In this reaction the rate of disappearance of iodine in the dark follows the unimolecular formula. The following results were obtained with different concentrations of sodium malate using N/125 I_2 and N/36.2 KI in the dark.

Concentration of Sodium Malate	k_1 at 30°	Number of molecules of Sodium Malate reacting
N/8	0.000949.......(1)	
		1.62 (from (1) and (2)
N/6	0.00152........(2)	
		1.64 (from (2) and (3)
N/4	0.00291........(3)	

It appears therefore that the reaction between sodium malate and iodine in the dark is *bimolecular* with respect to sodium malate and *unimolecular* with respect to iodine and hence the total reaction is *trimolecular*.

Kinetics at different temperatures

Wave length	$k_{\frac{1}{2}}$ at 30° (Semi-molecular	$k_{\frac{1}{2}}$ at 40° (Semi-molecular)
4725 Å	0.00618	0.00925
7304 Å	0.00417	0.00612
Dark	0.000949 (unimolecular)	0.00153 (unimolecular)

Kinetics in pure light

Wave length	$k_{\frac{1}{2}}$ at 30°	$k_{\frac{1}{2}}$ at 40°	$k_{40°}/k_{30°}$	Arrhenius A
4725 Å	0.00231	0.00360	1.56	4211
7304 Å	0.00030	0.00047	1.57	4273
Dark	—	—	1.61	4510

Temperature 30°

Wave length	% of incident light transmitted by filters	Number of times acceleration over dark reaction	Relative value of E_λ	Number of times acceleration over dark reactions for equal values of E_λ
4705 Å	29.6	2.03	1	2.03
7304 Å	2.86	2.8	5.8	0.48

(4) Sodium Formate and Mercuric Chloride

0.898 N sodium formate, H/15 $HgCl_2$ and 0.2813 gram sodium acetate in 20 c.c. of the reacting mixture.

Kinetics observed			Kinetics in pure light	
λÅ	k_1 at 20°	k_1 at 30°	k_1 at 20°	k_1 at 30°
4725	0.000985	0.00385	0.000323	0.00086
5650	0.00100	0.00368	0.000338	0.00069
7304	0.000808	0.00359	0.000146	0.00060
Dark	0.000662	0.00299		

λÅ	$k_1 30°/k_1 20°$	mean "A"	% incident light transmitted by filters	Number of times acceleration per 100% transmission at 30°	Number of times acceleration over the dark reaction at 30° for equal values of E_λ
4725	2.66	8675	29.6	0.767	0.767
5650	2.04	6323	3.2	6.968	2.74
7304	4.11	12533	2.86	6.615	1.14
Dark	4.52	13377			

(5) Potassium Oxalate and Iodine

N/2.95 $K_2C_2O_4$, N/11.36 I_2 and N/29.35 KI

Kinetics

λÅ.	$k_{\frac{1}{2}}$ at 20°	$k_{\frac{1}{2}}$ at 30°	$k_{\frac{1}{2}}$ at 36°
4725	0.00489	0.0147	0.0271
5650	0.00425	0.0136	0.0261
7304	0.00368	0.0131	0.0256

The velocity of the reaction in the dark being very small in comparison with that in light, the former is altogether left out of consideration when dealing with the total velocity obtained in light.

λÅ	$k_{\frac{1}{2}}$ 30°/$k_{\frac{1}{2}}$ at 20°	Mean values for Arrhenius A
4725	3.01	9791
5650	3.20	10313
7304	3.56	11261

Temp. 36°C

λÅ	% transmission of incident light through filters	Velocity Constant *for 100% transmission*	Velocity Constant for *equal values of* E_λ
4725	29.6	0.0916	0.0916
5650	3.2	0.816	0.3213
7304	2.86	0.781	0.1347

(6) Sodium Potassium Tartrate and Bromine

N/12.23 sodium-potassium tartrate, N/121.2 Br_2, and N/6.6 sodium acetate.

Kinetics

λÅ	k_1 at 20°	k_1 at 25°	k_1 at 30°
4725	0.00850	0.0173	0.0248
5650	0.0137	0.0210	0.0325
7304	0.0133	0.0242	0.0321
Dark	0.00372	0.00674	0.0122

λÅ	Kinetics in pure light k_1 20°	k_1 25°	k_1 30°	$\frac{k_1\ 30°}{k_1\ 20°}$	Mean "A"
4725	0.00478	0.01056	0.0126	2.64	8609
5650	0.00998	0.01426	0.0203	2.03	6279
7304	0.00958	0.01746	0.0199	2.08	6493
Dark				3.28	10536

Temperature 20°C

Mean λÅ	% of incident light transmitted by filters	Number of times accelerated for 100% transmission by filters	Number of times acceleration over the dark reaction for equal values of E_λ
4725	29.6	4.37	4.37
5650	3.2	83.75	32.9
7304	2.86	90.23	15.6

(7) Quinine Sulphate and Chromic Acid

M/89 Quinine Sulphate in N/2 H_2SO_4, N/80.88 $H_2Cr_2O_7$ and 1.31 N H_2SO_4

Kinetics

Wave length	k_1 at 25°	k_1 at 30°	k_1 at 35°
4725 Å	0.000313	0.000380	0.000450
5650 Å	0.000258	0.000325	0.000400
7304 Å	0.000232	0.000295	0.000365
Dark	0.000204	0.000262	0.000326

Kinetics in pure light

Wave length	k_1 at 25°	k_1 at 30°	k_1 at 35°	$\frac{k_{35}}{k_{25}}$	Arrhenius A
4725 Å	0.000109	0.000118	0.000124	1.14	1253
5650 Å	0.000054	0.000063	0.000074	1.39	2925
7304 Å	0.000028	0.000033	0.000039	1.40	3052
Dark	—	—	—	1.60	4257

Temperature 30°

Wave length	Number of times acceleration over dark reaction	Number of times acceleration for equal values of E_λ
4725 Å	1.52	1.52
5650 Å	7.52	2.96
7304 Å	4.41	0.76

(8) Potassium Permanganate and Oxalic Acid

N/421.3 $KMnO_4$, N/19.12 $H_2C_2O_4$, N/337 $MnSO_4$ and N/2.78 H_2SO_4

Kinetics

Wave length	k_1 at 8.5°	k_1 at 14.5°	k_1 at 24.5°
4725	0.0429	0.0865	0.2550
5650	0.0386	0.0741	0.2003
7304	0.0351	0.0652	0.1886
Dark	0.0220	0.0466	0.1440

Kinetics in pure light

Wave length	k_1 at 8.5°	k_1 at 14.5°	k_1 at 24.5°	$\frac{k\ 24.5°}{k\ 14.5°}$	Arrhenius A
4725 Å	0.0209	0.0399	0.1110	2.78	8676
5650 Å	0.0166	0.0275	0.0563	2.05	5922
7304 Å	0.0131	0.0186	0.0446	2.4	7472
Dark	—	—	—	3.09	9542

Temperature 14.5°

Wave length	Number of times acceleration for 100% transmission	Number of times acceleration over dark
4725	2.89	2.89
5650	18.44	7.26
7304	13.95	2.41

(9) Sodium Formate and Iodine

N/7.17 sodium formate, N/111.42 I_2, N/28.12 KI and N/4.44 sodium acetate.

Kinetics

λÅ	$k_{\frac{1}{2}}$ at 20°C	$k_{\frac{1}{2}}$ at 30°C
4725	0.0134	0.0641
5650	0.0127	0.0618
7304	0.0128	0.0647
Dark	0.0087	0.457

λÅ	Kinetics in pure light $k_{\frac{1}{2}}$ 20°	 $k_{\frac{1}{2}}$ 30°	$\frac{k\ 30°}{k\ 20°}$	Arrhenius A	% incident light transmitted by filters	No: of times accelerated for 100 % transmission at 20°C	No: of times acceleration for equal values of E_λ
4725	0.0047	0.0184	3.92	12114	29.6	1.83	1.83
5650	0.0040	0.0161	4.03	12360	3.2	14.38	5.66
7304	0.0041	0.0190	4.63	13591	2.86	16.49	2.84
Dark	—	—	5.25	14706			

(10) Sodium Nitrite and Iodine

2 N/3 $NaNO_2$; N/32 I_2; N/8.04 KI and N/6 Ch_3COONa.

Kinetics

λÅ	$k_{\frac{1}{2}}$ at 20°	$k_{\frac{1}{2}}$ at 25°	$k_{\frac{1}{2}}$ at 30°
4725	0.0125	0.0163	0.0270
5650	0.00809	0.0152	0.0225
7304	0.00772	0.0136	0.0220
Dark	0.000353 (Unimolecular)	0.000574 (Unimolecular)	0.000955 (Unimolecular)

λÅ	Kinetics in pure light $k_{\frac{1}{2}}$ at 20°	 $k_{\frac{1}{2}}$ at 25°	 $k_{\frac{1}{2}}$ at 30°	$\frac{k\ 30°}{k\ 20°}$	Arrhenius A
4725	0.0100	0.0122	0.0199	1.99	6104
5650	0.00559	0.0111	0.0144	2.57	8370
7304	0.00522	0.00953	0.0139	2.66	8676
Dark	—	—	—	2.71	8841

Temperature 30°C

λÅ	Number of times acceleration for 100% transmission by filters	Number of times acceleration for equal values of E_λ
4725	9.26	9.26
5650	67.31	26.5
7304	72.94	12.58

(11) Ferrous Sulphate and Iodine

Kinetics

λÅ	k_1 24.5°	k_1 30°	k_1 34.5°
4725	0.00658	0.0111	0.0174
5650	0.00585	0.00996	0.0162
7304	0.00358	0.00903	0.0128
Dark	0.000373	0.000675	0.00109
	(Unimolecular)	(Unimolecular)	(Unimolecular)

	Kinetics in pure light				
λÅ	k_1 at 24.5°	k_1 at 30°	k_1 at 34.5°	$\frac{k\ 34.5°}{k\ 24.5°}$	Arrhenius "A"
4725	0.00453	0.00754	0.0118	2.61	8765
5650	0.00380	0.00640	0.0106	2.79	9377
7304	0.00198	0.00399	0.00564	2.85	9570
Dark	—	—	—	2.92	9768

Temperature 30°C

λÅ	Number of times accelerated for 100% transmission by filters	Number of times accelerated in light for equal values of E_λ
4725	7.16	7.16
5650	57.5	22.63
7304	54.65	9.4

(12) Chromic Acid and Oxalic Acid

(In presence of manganous sulphate and sulphuric acid).

N/421.3 $H_2C_2O_4$; N/1947 $(COOH)_2$; N/337 $MnSO_4$ and N2.78 H_2SO_4 acid.

Kinetics λÅ	k_0 at 21°	k_0 at 31°C
4725	0.230	0.545
—	—	—
7304	0.197	0.504
Dark	0.147	0.433

	Kinetics in pure light				
λÅ	k_0 21°	k_0 31°		$\frac{k_0\ 31°}{k_0\ 21°}$	Arrhenius "A"
4725	0.083	0.112	—	1.35	2677
7304	0.050	0.071	—	1.42	3130
Dark	—	—	—	2.94	9626

Temperature 31°

λÅ	% incident light transmitted by filters	Number of times accelerations for 100% transmission by filters	Relative values of E_λ	Number of times accelerations over dark reaction for equal values of E_λ
4725	29.6	0.87	1	0.87
5650	2.86	5.73	5.8	0.99

(13) Mercuric Chloride and Ammonium Oxalate

(In presence of eosin as sensitiser.)

M/82 mercuric chloride; M/11.4 ammonium oxlate and M/15.500 eosin.

[$HgCl_2$ and $(NH_4)_2SO_4$ were saturated with CO_2 before mixing].

λÅ	$k_{26°}$	$k_{36°}$	$k_{46°}$
5400	0.00119	0.00228	0.00418
4950	0.00461	0.00756	0.0125
4350	0.00109	0.00211	0.00408

This reaction does not take place in the dark.

				Temperature 46°		
λÅ	$\frac{k_{46°}}{k_{36°}}$	Arrhenius "A"	% light transmitted by filters	Velocity constants for 100% transmission by filters	Relative values of E_λ	Velocity constants for equal values of E_λ
5450	1.83	5950	49	0.00853	3.9	0.00219
4950	1.65	4931	40	0.0313	1.19	0.00263
4350	1.93	6475	35	0.0117	1	0.0117

(14) The Photo-Oxidation of Iodoform by Atmospheric Oxygen

M/40 CHI_3

(Total light from a 1000 watts tungsten filament lamp was used.)

Kinetics

Solvent Amyl alcohol			Solvent Benzene		
$k_0(15°)$ (Zero-molecular)	$k_{0\ 25°}$ (Zero-molecular)	$k_{35°}$ (Zero-molecular)	$k_{0\ 24°}$ (Zero-molecular)	$k_{0\ 34°}$ (Zero-molecular)	$k_{0\ 44°}$ (Zero-molecular)
0.0111	0.0130	0.0150	0.421	0.496	0.521

Solvent Amyl alcohol		Solvent Benzene	
$\frac{k_{35°}}{k_{25°}}$	Arrhenius "A"	$\frac{k_{44°}}{k_{34°}}$	Arrhenius "A"
1.15°	1235	1.05	607

Discussion

Our experimental results show that in all cases the temperature coefficients of the photochemical changes are less than those of the corresponding thermal reactions. Moreover, the values of the temperature coefficients and Arrhenius A depends on the wave-length of the incident radiation. The results show in general that, the greater the observed acceleration of the reaction by light of different wave-lengths, the less is the temperature coefficient. These results support our views emphasized in the foregoing papers. We have repeatedly observed that the temperature coefficient of a photochemical reaction depends on the amount of acceleration over the thermal reaction.

We have proved from the measurements of the extinction coefficients that there is increased absorption when the temperature of the system is increased. From our experimental results already recorded on the temperature coefficients of purely photochemical reactions it will be seen that the temperature-coefficient is always greater than unity. In deducing these temperature coefficients the velocity of the thermal reactions has always been subtracted from the total velocities obtained by exposure to light. Even with this precaution the temperature coefficient of the purely light reaction is always found to be greater than unity. These results are very likely due to the fact that the absorption increases with temperature and consequently the photochemical change becomes greater at higher temperatures.

Some work in this line has been carried out by Padoa and coworkers[1] and their results show that the temperature coefficients of the photochemical reactions increase as the frequency of light diminishes, the only exception being the oxidation of hydriodic acid where a diminution of temperature coefficient is observed as the light frequency falls. Similarly Griffith and McKeown[2] have shown that the temperature coefficient of the photochemical decomposition of ozone is greater the greater the wave-length of the radiation.

We are of the opinion that these results are due to the fact that the light of shorter wave-lengths producing greater acceleration of the reactions causes greater lowering of the temperature coefficient than radiations of longer wave-lengths. In the case of the oxidation of hydriodic acid the iodine produced absorbs light in the visible spectrum and thus the reaction is markedly accelerated by radiation of longer wave-lengths. Hence Padoa observed smaller temperature coefficients with longer wave-lengths than with shorter ones in the oxidation of H I.

We have calculated the true accelerations due to light in several of these photochemical changes taking into consideration the energy distributions at different wave-regions applying Planck's formula and the percentage of adsorption by the reacting substances. In several cases the absorption is maximum at λ5650 Å and in this region the true acceleration of the photochemical change is also maximum.

From our experimental results it is evident that all the foregoing reactions are appreciably accelerated in the regions of the mean wave-lengths λ4725, 5650 and 7304 Å. It should be made clear at this stage that all the reactions investigated in this paper proceed with measurable velocity in the dark. In other words, radiation acts as an accelerator in these reactions. One fact will be clear from our experimental results that all the reactions are appreciably accelerated in the region λ7304 Å, which practically lies in the infra-red region of the spectrum. There is a belief in the minds of photochemists that photo-chemical reactions are brought about only by violet and ultra-violet radiations and the majority of the photo-chemical changes studied are under the influence of radiations solely of the above type. Some years ago Rideal and Hawkins showed that the hydrolysis of methyl acetate is accelerated by sun-light, but these observations have now been ascribed

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[1] Atti Accad. Lincei (5), 25, II, 168, 215 (1916); Gazz., 55, 87 (1925).

[2] Faraday Soc. Discussion October, 1925.

to experimental errors.[1] Another case investigated was by Griffith and Shutt[2] who found that under the influence of infra-red radiation ozone decomposes slowly. Our investigations carried on in a systematic manner under the influence of the visible and infra-red radiations will convince the photo-chemists that chemical changes can be accelerated by infra-red wave-lengths as well as by shorter wave-lengths.

The acceleration of the reactions having iodine as one of the reactants can be readily explained from the following point of view:—

The heat of dissociation of iodine molecule is 34,400 cal. and the corresponding wave-length comes out to be 0.836μ. Consequently, we can assume that even in presence of radiations of λ7304 the iodine molecule will be atomised. Hence in presence of radiation of λ7304 the reaction is accelerated because of the presence of the atomic iodine.

The main difficulties of the Perrin-Lewis radiation hypothesis of chemical activity are as follows:—

(i) The observed velocity of a reaction is much greater than the calculated velocity on the assumption that the entire energy is derived from the temperature of the system.

(ii) From the critical increment as obtained from the temperature coefficient of the reaction one can easily calculate the wave-length which should markedly accelerate a chemical change. But usually no acceleration is observed in the region of the calculated wave-length. In other words, the region where the chemical change is fastest is not the same as predicted by calculation. Moreover, in many cases it has been observed that the reacting mixtures do not show appreciable absorption in the region obtained by calculation from the temperature coefficients. In order to explain away these difficulties it has been assumed that most chemical changes take place in stages and instead of one single frequency a series of frequencies is active in bringing about the total reaction. There is considerable experimental evidence in support of these assumptions because we know that many chemical changes can take place under the influence of a series of wave-lengths and that reactions do actually occur in stages.

From the experimental results recorded in this paper it will be observed that the reactions investigated can be accelerated by radiations of the infra-red type. In the following table the wave-lengths obtained by calculation from the thermal temperature coefficients of some of the reactions are given:—

Potassium oxalate and iodine—0.86μ
Potassium permanganate and oxalic acid—1.44μ
Ferrous sulphate and iodine—1.46μ
Bleaching of dicyanin—5.64μ
Sodium nitrite and iodine—1.69μ
Mercuric chloride and ammonium oxalate—2.62μ
Chromic salt and oxalic acid etc.—1.59μ

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[1] Compare Taylor: "Physical Chemistry", 2, 1273.

[2] J. Chem. Soc., 123, 2752 (1923).

Rochelle salt and bromine—1.38μ
Sodium formate and mercuric chloride—1.07μ
Quinine sulphate and chromic acid—3.47μ

It is evident therefore, that all these reactions should be accelerated by short infra-red radiations. As a matter of fact, we have observed accelerations by radiation of wave-length λ7304 Å. We are of the opinion therefore, that these wave-lengths which are obtained by calculation from the thermal temperature coefficients may be regarded as the *threshold limit*, no chemical change is possible, with radiations of longer wave-lengths. This may also be made clear from another line of argument. Following Arrhenius it has been shown in previous papers[1] from these laboratories that there are active and inactive molecules in a system and that chemical changes take place between the active molecules only and it has also been held that an increase in temperature means an increase in the number of the activated molecules. Now, those dark reactions which are very sensitive to the influence of temperature are evidently the ones where the difference in energy between the active and inactive molecules is very marked. In other words, in activating the inactive molecules in such a system absorption of energy in quanta of greater energy content would be necessary than in a system where the difference in energy levels between the active and inactive molecules is not so prominent.

Dhar[2] has shown that fast reactions have smaller temperature coefficients than comparatively slow ones. It is because, in a fast reaction the number of active molecules is much greater than in the slower ones. Morevoer, it can be assumed as well that in a fast reaction the molecules can be activated more easily than in a slow reaction. Consequently, a fast reaction need not be so sensitive to the influence of temperature. Hence, it appears that those reactions which have small temperature coefficients could be activated by quanta of smaller energy content and consequently such reactions should be accelerated by short infra-red wave-lengths. On the other hand, those thermal reactions which are very sensitive to the influence of temperature should be activated by radiations of larger energy quanta and ought to be sensitive to shorter wave-lengths.

Hence, we venture to suggest that the threshold frequency of thermal reactions having high temperature coefficients, when carried on in presence of light should be much larger than that of the reactions having a smaller temperature coefficient. Consequently, we are definitely of the opinion that the conception of the threshold frequency is of great importance in understanding the mechanism of photo-chemical reactions. It should be made clear that the threshold frequency really depends on the temperature coefficient of the thermal reactions.

Daniels and Johnston[3] have found that 1.16u as the wave-length which would activate the decomposition of N_2O_5 but they have reported that this

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[1] J. Chem. Soc., 111, 707 (1917); Z. anorg. allgem Chem., 159, 103 (1926).
[2] J. Chem. Soc., 111, 707 (1917).
[3] J. Am. Chem. Soc., 43, 53 (1921).

reaction is not sensitive to this wave-length. We would suggest, however, that this reaction will progress by exposure to intense light of this wave-length for a longer period.

From our experimental results it is quite clear that chemical changes can be accelerated by short infra-red radiation in such cases where the values theoretically obtained predict that possibility.

The depolymerization of dianthracene to anthracene gives a critical increment of 41,300 calories corresponding to 0.707μ. It was found that exposure of the system to radiations with 0.7μ brings about the depolymerisation of anthracene and it is very likely that a solution of dianthracene will show a feeble absorption in this region.

It must be pointed out clearly that according to the views advanced in the foregoing pages we can get the threshold frequencies from the measurements of the temperature coefficients. Radiations of longer wave-lengths will not promote the reaction in question. The main difference between this conception and the Perrin-Lewis Radiation theory is that according to the latter theory the wave-length calculated from the temperature coefficient should bring about the maximum speed of the reaction in question whilst according to the conception now put forward the threshold frequency is the minimum frequency necessary for the carrying out of the reaction. Radiations of shorter wave-lengths will be effective while radiations of longer wave-lengths will be incapable of accelerating the reaction.

Rideal and Williams[1] have suggested that the wave-length λ5448 Å which corresponds to the resonance potential of iodine is the limit. With longer wave-length no reaction takes place between iodine and ferrous sulphate. We have however, proved that the same reaction can be accelerated by wave-length λ7304 Å. Consequently, the suggestion of Rideal and Williams is erroneous. That these authors are in error is also held out in a very recent communication by Kistiakowsky[2] who shows that the suggested relation of the wave-length to the critical potential of gaseous iodine is highly improbable, the volt equivalent of effective radiation varying from 1.9 (λ6500) to 2.4 V. It was shown by Dymond[3] that gaseous iodine is dissociated into atoms only on absorption of radiation of wave-lengths shorter than λ5000 Å (2.48 V).

Summary

(1) The bleaching of dicyanin in presence of air follows the uni-molecular formula. The temperature coefficient of this reaction is 1.35 in the dark and is slightly greater than unity in light.

(2) The reactions between sodium citrate and iodine and sodium malate and iodine are both trimolecular in the dark and the temperature coefficients are 1.64 and 1.61 respectively.

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[1] J. Chem. Soc., 127, 258 (1925).

[2] J. Am. Chem. Soc., 49, 976 (1927).

[3] Z. Physik, 34, 553 (1925).

(3) Our experiments on the influence of light of different wave-lengths on fourteen photochemical reactions show that the greater the acceleration of the reaction due to light the smaller is the temperature coefficient of the photochemical change. The temperature coefficients in light ar greater than unity.

(4) We have been able to show satisfactorily that infra-red radiation of mean wave-lengths λ7304 Å can accelerate all the chemical changes investigated in this paper.

(5) We have calculated the true accelerations due to light in several of these photochemical changes taking into consideration the energy distributions at different wave-regions applying Planck's formula and the percentage of absorption by the reacting substances. In several cases the absorption is maximum at λ5650 Å and in this region the true acceleration of the photochemical change is also maximum.

(6) We have calculated the threshold frequency of photochemical reactions from the temperature coefficients of the same reactions carried on in the dark. Radiations of frequencies smaller than the threshold frequeney will not promote the reaction in question, whilst radiations of larger frequencies will accelerate the reaction. This conception of the photochemical threshold frequency seems to have considerable experimental support.

Chemical Laboratory,
University of Allahabad,
Allahabad, India.
December 6, 1927.

STUDIES IN PHOTOGRAPHY*

I. The Nature of Sensitivity and the Latent Image

BY FRANK E. E. GERMANN AND DZU-KUN SHEN

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I. Introduction

The nature of sensitivity and the latent image has been subjected to many proposed theoretical modifications. Since no difference whatsoever has ever been observed between an exposed and an unexposed plate except the developability of those grains which have received an exposure, greater than the induction value and less than that for reversal, the only method available for the study of the nature of the latent image is through the observation of the behavior of the exposed grains towards developers. The observation of the development centres, first by Hodgson,[1] followed by the exhaustive study of Svedberg, opened a new road for studying the mechanism by which the latent image is formed by the action of light. The existence of the special sensitive specks situated haphazardly upon the grains and the identification of the sensitivity promoting material present in the gelatin marked a great advance in the solution of the problem.[2] Photographic sensitivity as a whole, however, is by no means perfectly understood and many phenomena, such as reversal, are still more or less of a mystery.

It seems at present very improbable that the problem of what constitutes sensitivity can be solved by a direct method. We know, however, numerous substances which can affect the sensitiveness of a photographic plate making it either more or less sensitive. It is our belief that the key to the solution of the nature of photographic sensitivity rests upon the careful study of the mechanism of sensitization and desensitization.

Many investigations have supported the conclusion that the sensitivity of gelatino-silver bromide emulsions is due in a large measure to the presence on or in the grains of traces of substances other than silver bromide. It is, therefore, generally accepted that the formation of the latent image can not be represented by a simple chemical reaction as $2AgBr = 2Ag + Br_2$, although the decomposition of silver bromide into silver and bromine through the action of light is a well-established fact.[3] Since the mechanism of latent image formation, though not clearly understood, is not likely to be explained by such a simple chemical equation, any theory based upon such an assumption will probably have to be modified. Substances which can sensitize a photographic plate are termed chemical sensitizers; their sensitizing action

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* Contribution from the Department of Chemistry of the University of Colorado.

[1] M. B. Hodgson: J. Franklin Inst., **184**, 705 (1917); T. Svedberg: Z. wiss. Phot., **20**, 36 (1920); Phot. J., **61**, 325 (1921); **62**, 186, 310 (1922); **64**, 273 (1924).

[2] Toy: Trans. Faraday Soc., **19**, 290 (1923); Sheppard: Phot. J., **65**, 380 (1925).

[3] Hartung: J. Chem. Soc., **121**, 682 (1922); **125**, 2198 (1924).

is attributed to the power of halogen absorption.[1] The fact that silver iodide gelatin emulsions are much less sensitive than those containing silver bromide is explained by the inability of the gelatin to react with iodine, while gelatin acts as a chemical sensitizer in the case of silver bromide emulsions[2]. That gelatin can react with bromine is a well-established fact. If the halogen absorbing power were the only factor of importance essential to sensitizers, many substances such as alkalies, sulphites and nitrites would have been better sensitizers than gelatin. Many organic compounds, developers in particular, are chemical sensitizers as proven by the fact that they have a sensitizing effect on silver iodide emulsions. However, many cases are known in which the so-called sensitizers actually decrease the sensitiveness of a silver bromide emulsion;[3] the nature of chemical sensitizers and the mechanism of chemical sensitization seem to deserve careful study in the hope that additional facts may be discovered bearing on the nature of photographic sensitivity.

The importance of silver iodide incorporated in the silver bromide emulsions has been recognized since the early days of photography. The remarkable and distinctive effects produced by the introduction in various ways of a small amount of silver iodide into the silver bromide emulsions are still very little understood. Silver iodide collodion plates[4] are very sensitive while pure silver iodide gelatin emulsions are relatively insensitive but possess many peculiarities. The sensitizing action of many developers upon the silver iodide emulsions was recorded by many early investigators,[5] but interest was recently aroused by a patent issued to Johnson[6] who claimed to have found many substances having sensitizing action upon silver iodide emulsions. Germann and Hylan[7] undertook the investigation of the process and explained the mechanism of the sensitizing action and the cause of the lack of sensitiveness of the silver iodide emulsion on the basis of adsorption. They extended their theory to the discussion of the relationship between sensitivity

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[1] Vogel: "Handbuch der Photographie," 4th Ed. 1, 73 (1890); Bancroft: J. Phys. Chem., 12, 230 (1908); 14, 128 (1910).

[2] Lüppo-Cramer: Phot. Korr. 38, 218, 422, 427 (1901); 40, 25, 174 (1903); 43, 433 (1906); Bancroft: J. Phys. Chem., 14, 144 (1910); Germann and Hylan: J. Am. Chem. Soc., 45, 2486 (1923).

[3] Lüppo-Cramer: "Wissenschaftliche Arbeiten," 31 (1902); Phot. Korr., 40, 25 (1903); 49, 76 (1912); 50, 58 (1913); 52, 278 (1915); Phot. Ind., 18, 505, 664 (1920); Duce: Brit. J. Phot., 69, 296 (1922).

[4] Henderson: Brit. J. Phot., vol. 32, 201 (1885); Schumann: Phot. J., 35, 204, 229, 283, 320 (1895); Schleusser and Beck: Z. wiss. Phot., 21, 105 (1921); Renwick: 2nd Coll. Symp. Mon., 37 (1924); Phot. J., 61, 12 (1921); 64, 360 (1924); 66, 163 (1926); J. Soc. Chem. Ind., 39, 156 T (1920); Lüppo-Cramer: Phot. Ind., 18, 211 (1920); 19, 417 (1921); 22, 375 (1924); 23, 110, 1116 (1925); 25, 806 (1927); Phot. Korr., 47, 239 (1910); 49, 262, 440 (1912); 50, 460, 503, 509, 561 (1913); 51, 402 (1914); Eder's Jahrb., 40 (1903); Sheppard: J. Franklin Inst., 196, 653 (1923); Phot. J., 60, 12 (1920); 62, 88 (1922); Archey: Phot. J., 61, 235 (1921); Trivelli: Rec. Trav. chim., 42, 714 (1923); J. Soc. Chem. Ind., 42, 908 (1923).

[5] Vogel: "Handbuch der Photographie," 4th Ed. 1, 73 (1890); Lüppo-Cramer: Phot. Korr., 38, 218, 422, 427 (1901); 40, 25, 174 (1903); 43, 433 (1906); 49, 76 (1912); 50, 58 (1913); 52, 278 (1915); Bancroft: J. Phys. Chem., 12, 230 (1908); 14, 128, 144 (1910).

[6] Johnson: Chem. Abs., 16, 3270 (1922); Brit. Pat., 178, 828; French Pat., 550, 439.

[7] Germann and Hylan: Science, 58, 332 (1923); J. Am. Chem. Soc., 45, 2486 (1923); J. Phys. Chem., 28, 449 (1924).

and grain size, arguing that the large grains are in general not more sensitive than small grains, but that the greater sensitivity of large grains is due to causes other than size. The intensive studies on sensitivity carried on by Svedberg, Toy, Clark and Sheppard in recent years have given great impetus to photographic research.[1] It is assumed that the conclusions drawn from the studies on grain sensitivity of silver bromide should be applicable to the case of silver iodide, concerning which the mechanism of sensitization by the so-called chemical sensitizers demands theoretical modification.

II. Experimental

The preparation of an emulsion having a wide range of grain size offered a great deal of difficulty. In a fine-grained pure silver iodide emulsion, the grains do not grow readily during ripening. They also show a strong tendency to coagulate and give clumps of crystals, which would be useless in an accurate study of individual grains. After many unsuccessful attempts, it was found that the following formula, if prepared according to directions, will always give an emulsion having a wide range of grain size, and free of aggregates of crystals.

Solution I.	Potassium iodide	21.500 grams
	Gelatin (Nelson No. I)	6.000 grams
	Water	80 cc.
Solution II.	Silver nitrate	7.000 grams
	Water	20 c.c.
	Ammonium Hydroxide (Sp. Gr. 0.90), sufficient to redissolve the precipitate.	
Solution III.	Silver nitrate	13.000 grams
	Water	20 c.c.
	Ammonium Hydroxide (Sp. Gr. 0.90) sufficient to redissolve the precipitate.	
Solution IV.	Gelatin (Nelson No. I)	30 grams
	Water	70 c.c.

Solution I is prepared by soaking the gelatin in the water solution of the iodide for fifteen minutes at room temperature. Solutions I and II are then placed in a thermostat whose temperature does not vary more than a half

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[1] Svedberg: Z. wiss. Phot., 20, 36 (1920); Phot. J., 61, 325 (1921); 62, 186, 310 (1922); 64, 273 (1924); Toy: Phot. J., 61, 417 (1921); Brit. J. Phot., 69, 443 (1922); Phil. Mag., 44, 352 (1922); 45, 715 (1923); 48, 147, 947 (1924); 49, 1104 (1925); 53, 482 (1927); Trans. Faraday Soc., 19, 290 (1923); Clark: Phot. J., 63, 230 (1923); 64, 91 (1924); 66, 78 (1926); Trans. Faraday Soc., 19, 309 (1923); Brit. J. Phot., 69, 462 (1922); 70, 223, 717, 763 (1923); 74, 121, 227 (1927); Sheppard: Phot. Korr., 59, 76 (1922): Phot. J., 61, 400, 450 (1921); 62, 196, 407 (1922); 63, 334 (1923); 65, 31, 134, 380 (1925); 66, 399 (1926); 67, 216, 281, 331, 359 (1927); J. Franklin Inst., 194, 485 (1922); 195, 337 (1923); 196, 653 (1923); 198, 629 (1924); 200, 51 (1925); 201, 335 (1925); 203, 829 (1927); 204, 491 (1927); J. Phys. Chem., 25, 181, 561 (1921); 27, 1, 466 (1923); 28, 529 (1924); 29, 1568 (1925); Phot. Ind., 25, 412, 598, 781 (1927); J. Am. Chem. Soc., 49, 1814 (1927); 1st Col. Symp. Mon., 346 (1923); 3rd Col. Symp. Mon., 76 (1925); Brit. J. Phot., 73, 33 (1926); Science; 469 (1923); Sci. Ind. Phot., 7M, 17, 31, 42 (1927); J. Opt. Soc. Am., 5, 913 (1922).

degree from 88°C. When equilibrium is attained, solution II is poured into a water-jacketed burette, also maintained at 88° C. From this burette it is run into solution I with constant stirring, the rate being such as to require one and three-quarter minutes for the entire quantity to be delivered. The emulsion is then allowed to ripen with constant stirring at the temperature of the thermostat, for a period of ten minutes. Solution III, which is also at 88°, is then placed in the water-jacketed burette and delivered to the mixture of solutions I and II in forty-five seconds, after which it is allowed to ripen with constant stirring for fifteen minutes at 88°C. The emulsion is then cooled in four minutes to 40°C., and then solution IV is added. After ripening for fifteen minutes at 40°, it is allowed to stand in cold running water over night, during which time it sets to a rigid gel. It is then shredded and washed in running water to free it from soluble salts. This is usually accomplished in three hours, as evidenced by the fact that diphenylamine in sulphuric acid will no longer show the presence of nitrates in the emulsion.

After the emulsion was thoroughly washed, it was melted at 40°C and diluted with a 1% gelatin solution to such a concentration that it would give a one-grain layer coating on the glass plate. The diluted emulsion was twice filtered through an open Whatman No. 41 paper on a Buechner funnel, and a solution of chrome alum was added with rapid stirring, using one gram of chrome alum per 100 grams of gelatin used in the emulsion.

Glass plates, 14″ × 10″ in size, were washed with 20% caustic soda solution followed by rinsing with water, then soaked in chromic acid solution for two hours, again thoroughly washed with water and allowed to dry. The washed plates were never allowed to be exposed to air longer than necessary for drying; prolonged exposure would result in the deposition of grease from the air, and uniform coating of the emulsion would be impossible.

After thorough mixing, a small portion of the emulsion was poured from a separatory funnel upon the clean and carefully levelled glass plates, and allowed to dry at room temperature. Each large plate was cut into four pieces, seven inches long and five inches in width. One of these plates was placed in a plate holder and exposed behind an interchangeable mask so that twelve different exposures could be made on the same plate. A 15-watt tungsten filament lamp was used as a light source, with a six-volt storage battery as a source of steady current, the constancy of the current consumption being checked by means of an ammeter. Uniformly diffused light was obtained by inserting a piece of thin ground glass about three inches from the light source, and the plate to be exposed was placed half a meter away from the latter. The whole was enclosed in a black wooden box. Since it was desired to study the behavior of individual grains and the relationship between the sensitiveness and the size of grains, Svedberg's statistical method was found the most satisfactory. His method was followed, with the exception that the exposed plates were developed in a pyro-soda developer free from soluble halide and both the developed and undeveloped grains were directly counted under a microscope without dissolving off the silver grains; this would avoid the possible error pointed out by Renwick[1] that a partly developed grain might be mistaken for an undeveloped grain. The plates were developed in the following developer at a temperature of 18°C.

Solution A.	Water	1000 c.c.
	Pyro	60 grams
	$K_2S_2O_5$	12 grams
Solution B.	Water	1000 c.c.
	Na_2SO_3	95 grams
Solution C.	Water	1000 c.c.
	Na_2CO_3	70 grams

For use, make solution consisting of 10% A, 10% B, 10% C and 70% water.

After the plate was thoroughly washed and dried, it was cut into sections each representing a definite exposure. They were examined under a Bausch and Lomb microscope fitted with a 1.9 mm. oil emersion objective and a 25X Huyghenian occular. Both the developed and undeveloped grains were counted and the percentage number made developable was plotted against the corresponding exposure. At least ten fields, amounting approximately to two thousand grains were counted on each section, and the average percentage number of grains made developable was taken.

Luminescence Phenomenon

It will be observed that no fixing bath was used in the above outline. The reason for this is to be found in the following observations. While following the procedure outlined by Sheppard,[2] the developed plate was rinsed in 1% acetic acid solution to stop development and then followed by washing with water. At the moment the developed plate came in contact with the acid solution, a faint luminescence was observed. This phenomenon was finally found to be due to the reaction between the spent developer and the acetic acid. A freshly prepared pyro-soda developer did not show such effect, while the luminescence became more pronounced when the pyro-soda developer had been allowed to stand in air for a short time. Besides acetic acid, hydrogen peroxide and mineral acids have also been tried and found to give the same phenomenon. Since the absorption of oxygen is necessary for the production of the luminescence, it is suggested that pyrogallol in alkaline solution absorbs oxygen from the air forming a compound which resembles peroxide, in which the oxygen is very loosely attached. This compound is immediately decomposed by the acid with evolution of oxygen accompanied by luminescence.

Sheppard,[3] in explaining the fogging action of hydrogen peroxide on the photographic plate, suggests that "since hydrogen peroxide is endothermic in its formation from water

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[1] Renwick: Phot. J., **61**, 333 (1921).

[2] Sheppard: J. Franklin: Inst., **195**, 343 (1923).

[3] Sheppard: J. Franklin Inst., **195**, 345 (1923).

$$H_2O_2 = H_2O + \frac{1}{2}O_2 + 25{,}650 \text{ cal.}$$

and is continually decomposing, especially in the presence of catalysts, that the energy is evolved primarily as a chemiluminescence, of short wavelength affecting the silver halide." Chemi-luminescence is fairly general in chemical reactions involving the evolution or adsorption of gases, chiefly oxygen.[1] The observed chemi-luminescence is therefore suggested to give an indirect support to Sheppard's conclusion.

Since the luminescence thus produced might affect the plate and introduce error in the experiment, the plate, after being developed, was immediately placed in running water without rinsing with acetic acid.

Grain Sensitiveness of Silver Iodide

The most apparent difference between silver bromide and silver iodide grains is their reducibility by means of chemical developers, a fact to which Lüppo-Cramer[2] attributes the apparent insensitivity of silver iodide.

The silver bromide emulsion, when coated in a single grain layer, usually developed very quickly with the unbromided developer, even without having received an exposure; in other words, it fogged very readily. Work carried out by previous investigators has been confined mostly to silver bromide grains, and the developers used contained a large amount of potassium bromide to suppress the development. In order to show the development centres, the development had to be stopped at the end of about a minute. In the case of silver iodide grains, the development goes on very slowly; even at the end of fifteen minutes in a developer containing no soluble halide, some grains are still incompletely developed. The fact that a grain will be either completely developed or not at all was confirmed by developing the slides of an evenly exposed plate different lengths of time and counting the percentage number of grains developed, assuming a grain would be completely developed if it contained one or more centres. The plate and the exposure were so chosen that only a small fraction of the grains would be made developable, in order that fog correction, if any, could be made by having an unexposed plate developed along with it. In the short development the centres were so small that they could easily escape observation, but as the development went on, the centres increased in size until the whole grain was developed. Fig. 1 shows that the percentage number of developable grains made visible increases with time of development and becomes practically constant after about ten minutes. The values plotted have been corrected for fog, which, even after thirty minutes of development is less than one per cent. This is a very striking characteristic of silver iodide emulsions. Since prolonged developing does not increase fogging appreciably, fifteen minutes was adopted in all cases for the complete revelation of the centres. Fig. 2 shows the relation between time of exposure and percentage number of developable grains when a one grain layer silver iodide

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[1] Trautz: Z. Elektrochemie, 14, 453 (1908).

[2] Lüppo-Cramer: Eder's Jahrb. 40 (1903).

plate is exposed, developed and examined as detailed above. It is to be noted that the maximum developability is almost reached at the exposure of 64 seconds, and that only 17% of the total silver iodide grains are ever made developable. Further increase in exposure decreases the number of developable grains, that is, the period of reversal is entered.

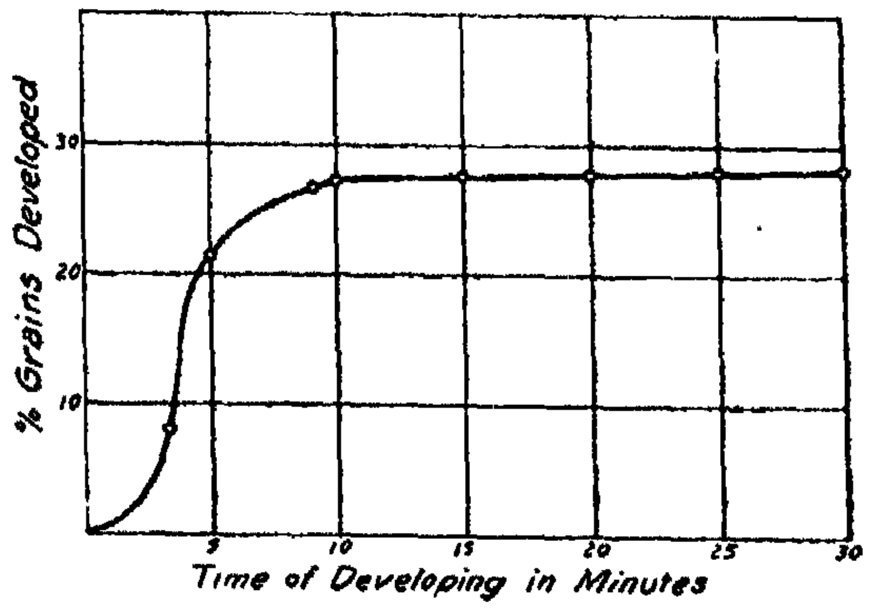

FIG. 1

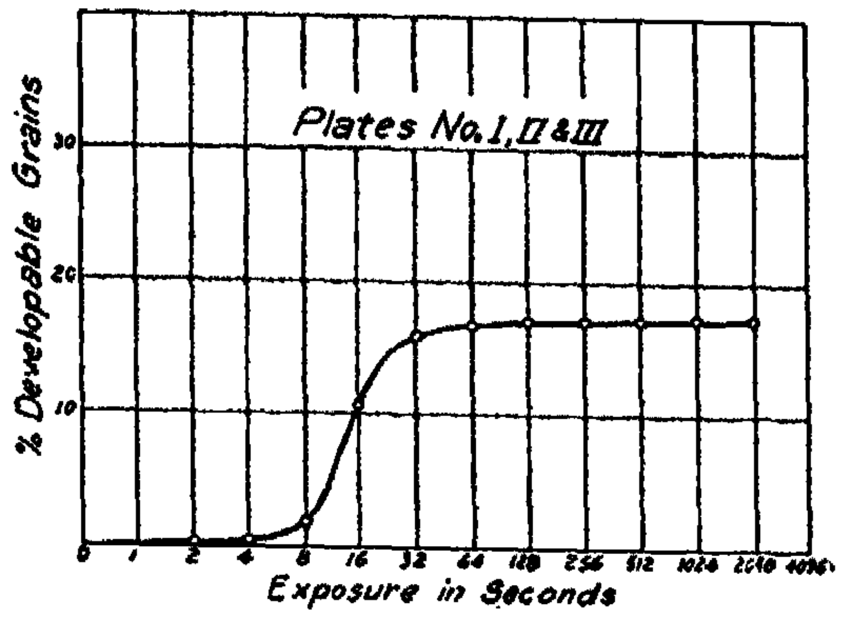

FIG. 2

Sensitivity and the Size of Grains

The relationship between sensitivity and grain size has been realized since the early days of photography. Fast emulsions usually consist of large grains, but it is not at all true that the sensitivity of any large-grained emulsion exceeds that of any small-grained one.[1] Furthermore, emulsions having identical grain characteristics may differ considerably in sensitiveness.[2] The fact that only in one and the same emulsion, are the large grains more sensitive than the small ones, makes it apparent that grain size is not the

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[1] Renwick: Phot. J., 61, 333 (1921).

[2] Sheppard: 1st Col. Symp. Mon., 346 (1923).

sole factor determining high sensitivity.[1] We still do not know what causes sensitivity; we know, however, that the sensitivity of an emulsion can be increased through processes which simultaneously increase the size of grains. We do not know the mechanism by which the sensitivity is increased; it seems justifiable to believe that the factors which govern the increase in sensitivity coincidently favor the growth of grains. In one and the same emulsion, the conditions under which the large grains are produced are decidedly different from those in formation of the small grain fraction; a difference in sensitiveness between these two classes of grains should not be surprising.

If the sensitivity is due to the presence of some impurity in the gelatin, allyl thiocarbamide, according to Sheppard,[2] and the degree of sensitivity depends upon the size of the sensitive specks situated on or in the silver halide grains,[3] the large grains would be more sensitive because the sensitive specks on the large grains are likely to be larger. If we assume that the amount of the sensitive material is limited in the gelatin, the amount adsorbed on the silver halide grain would be greater in the earlier stages of precipitation when the concentration of the sensitive material is the greatest. When an emulsion is made by pouring a silver nitrate solution into the soluble halide solution to which gelatin is added, it is obvious that at the earliest stage of precipitation, the concentration of the soluble halide is also the greatest, which favors the so-called Ostwald ripening, i.e., the grains produced will attain the largest size. From these considerations, therefore, the large grains which are more sensitive are produced during the earlier stages of precipitation, during which time the concentration of both soluble halide and sensitizing material is greatest.

The insensitiveness of the silver iodide emulsion cannot be explained to be merely due to the incapability of the normal developers to reduce the silver iodide grains, as suggested by Lüppo-Cramer, because such explanation cannot satisfy the fact that seventeen per cent of the total grains are developable, unless the assumption is made that the rest of the grains are materially different and entirely lacking in sensitivity. If sensitivity is due to the presence in the grain of some foreign material derived from gelatin, then only this seventeen per cent of the total grains is supplied with such material, and the lack of sensitivity of the rest of the grains would be due to deficiency of the sensitivity material on account of the fact that they are formed during the latter stage of precipitation in which the sensitivity material is practically exhausted. If this were the case, the developable grains would have been those formed at the earlier stage of precipitation, i.e., those of the largest size.

In order to test the above conclusions, two extreme fractions containing the largest and smallest grains of an emulsion were obtained by repeated

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[1] Svedberg: Z. wiss. Phot., 20, 36 (1920); Phot. J., 61, 325 (1921); 62, 183, 186, 310 (1922); 64, 272 (1924); Renwick: 64, 360 (1924); 66, 163 (1926); Sheppard: J. Franklin Inst., 203, 829 (1927).

[2] Sheppard: Phot. J., 65, 380 (1925).

[3] Sheppard: J. Franklin Inst., 200, 51 (1925); 3rd Col. Symp. Mon., 86 (1925).

centrifuging, and coated on separate glass plates. The emulsion was made exactly as before except taking four minutes for the first mixing and twenty minutes for the first ripening in order to obtain a wider range in grain size. Both plates were exposed and developed in exactly the same manner; it was found that the developability-exposure curves for the large and small grained fractions coincided with that of the uncentrifuged emulsion. This is shown in Fig. 2, plates I, II, and III representing the uncentrifuged, large and small grained emulsions respectively, all of which coincide. This would indicate that the undevelopability of eighty-three per cent of the grains cannot be due to the depletion of the sensitivity promoting material in the solution. It would, furthermore, indicate that there is no appreciable difference in sensitivity between the large and small grains of the same emulsion.

In a later paper the effect of sensitizers on these same emulsions will be presented, and data will be given which seem to prove that the insensitivity of silver iodide emulsions is due to quick reversal.

Summary

1. Photographic sensitizers are discussed, and a complete bibliography on the sensitizing effect of silver iodide in silver bromide emulsions is given.

2. A formula is given which yields emulsions of a large range of grain size.

3. A luminescence phenomenon resulting from the contact of spent developer with acids is studied and an explanation given. As a result of this observation, the plates studied are washed in running water rather than placed in a fixing bath.

4. Grain sensitivity of silver iodide emulsions is studied and it is found that in the unsensitized emulsions only seventeen per cent of the grains ever develop.

5. A silver iodide emulsion of wide range of grain size was centrifuged and the large and small-grained fractions coated on different plates. Both showed identical developability curves which also coincided with that of the uncentrifuged emulsion.

6. It would therefore appear that both large and small grains are alike and that the insensitivity is not due to an exhaustion of a sensitivity-promoting material.

7. It is suggested that the apparent insensitivity is due to a rapid reversal, evidence for which will be presented in a future paper.

THE VAPOR PRESSURE OF ETHYLENE CHLORIDE BETWEEN −30° AND 100°.

J. N. PEARCE AND PAUL E. PETERS

In some work which we are doing on the adsorption of vapors by charcoal a knowledge of the vapor pressure of ethylene chloride is very essential. Rex[1] has measured the vapor pressure of ethylene chloride at 0°, 10°, 20° and 30°, but his results are probably in error, since the boiling point of his sample varied from 83.7° to 84.3°. Staedel[2] has determined the boiling points of this liquid under pressures varying between 400 mm. and 1080 mm.

The normal boiling point of ethylene chloride, as given by Thorpe,[3] is 83.5°; that given in the Critical Tables[4] is 83.7°. Schiff[5] reports the boiling point as 83.3° at 749 mm., while Brühl[6] gives it as 84.5° to 85° at 750.9 mm.

Eastman's C.P. ethylene chloride was fractionally distilled five times by means of the improved fractionating still recommended by Loveless.[7] The fraction finally collected consisted of about 200 cc. which was distilled during a period of two hours, the maximum change in temperature being 0.01° while the pressure remained constant at 747.3 mm.

The mercury used in the manometers was purified in the usual way by repeated spraying through an acid solution of mercurous nitrate, and then distilling in a current of air under reduced pressure.

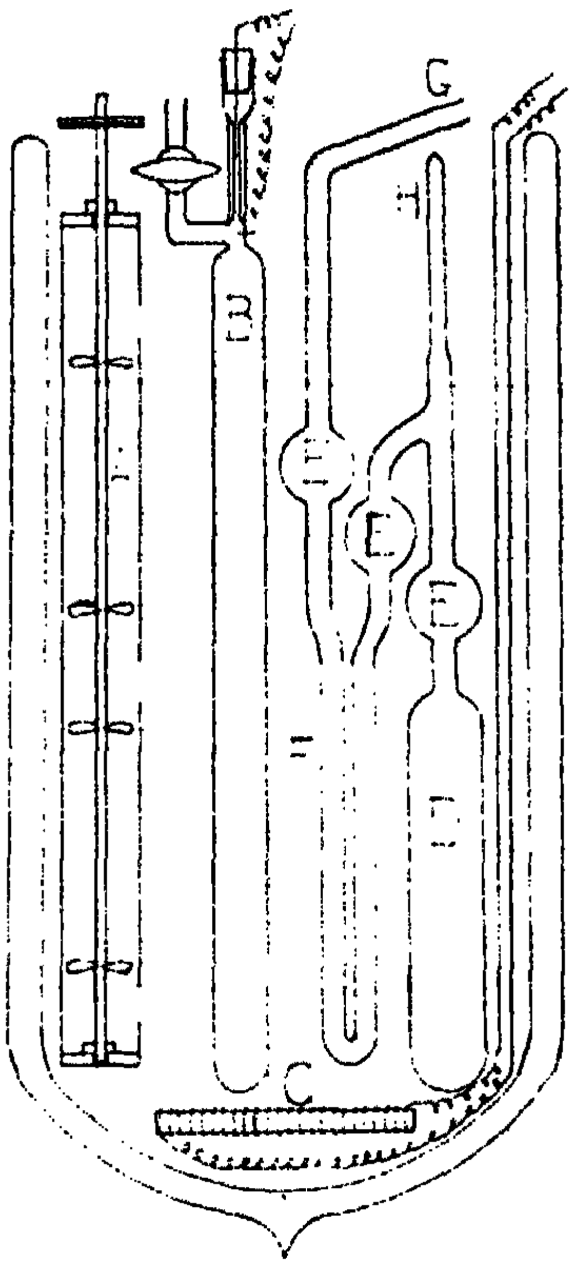

Fig. 1

The apparatus used, Fig. 1, is similar in principle to that first used by Johnston,[8] and later modified by Smith and Menzies.[9] The *isotenoscope is maintained* at any desired temperature in a water bath contained within a large unsilvered Dewar flask. The bath

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[1] Rex: Z. physik. Chem., 55, 358 (1906).
[2] Staedel: Ber., 15, 2559 (1882).
[3] Thorpe: J. Chem. Soc., 37, 182 (1880).
[4] "International Critical Tables," 1, 179 (1926).
[5] Schiff: Ann., 220, 96 (1883).
[6] Brühl: Ann., 203, 10 (1880).
[7] Loveless: Ind. Eng. Chem., 18, 826 (1926).
[8] Johnston: Z. physik. Chem., 62, 333 (1908).
[9] Smith and Menzies: J. Am. Chem. Soc., 32, 1412 (1910).

is electrically heated by means of a nichrome coil C, and the temperature is electrically controlled by the thermo-regulator B; adequate stirring of the bath liquid is provided by the rotary stirrer A. Below 60° the maximum variation did not exceed ±0.01°; at higher temperatures the variation never exceeded ±0.02°. In this way it is possible to keep the temperature constant until vapor pressure equilibrium is established.

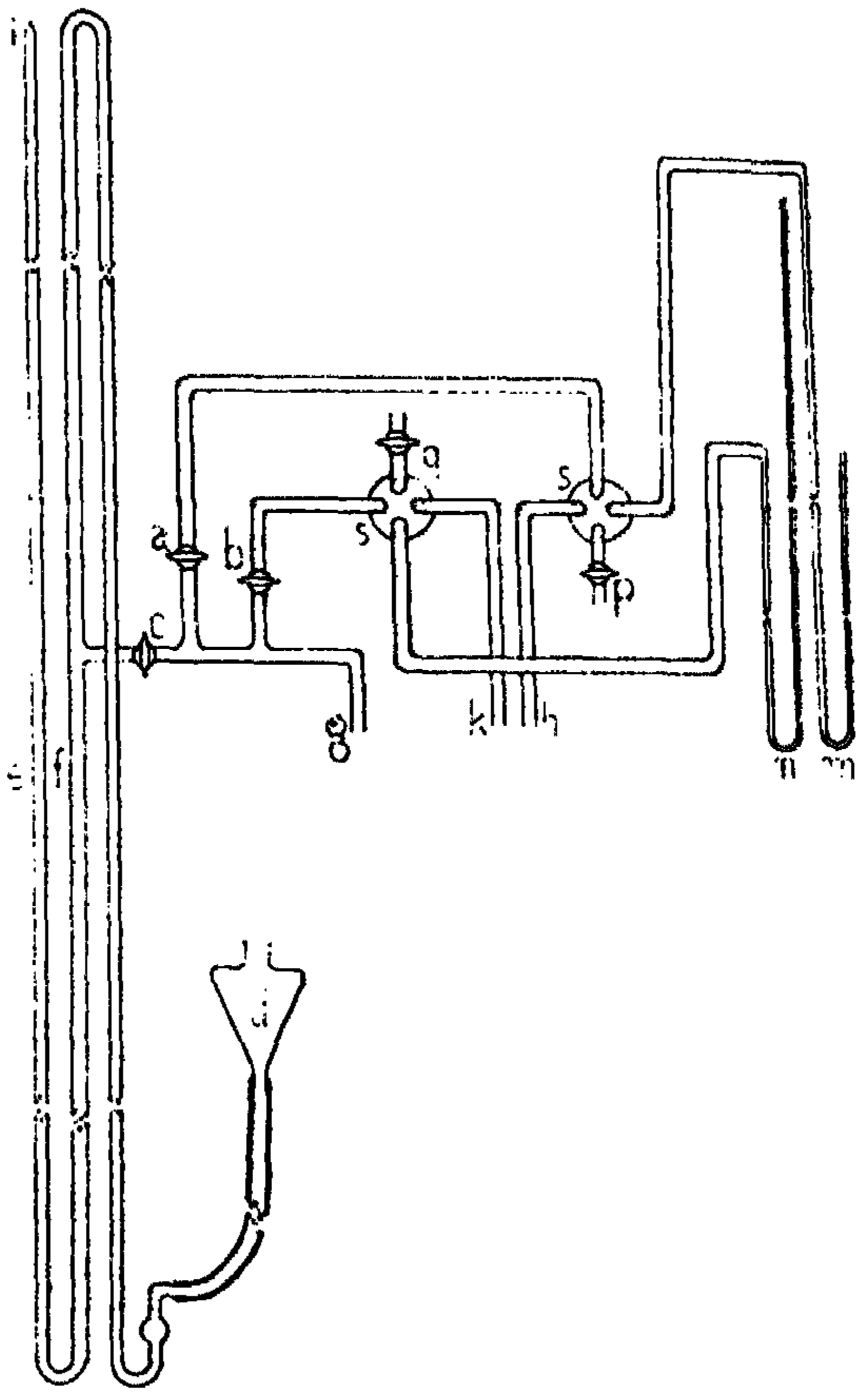

FIG. 2

For temperatures below 0° the isotenoscope is placed in a second Dewar flask containing alcohol. This is then suspended in the larger flask which contains a small quantity of liquid air, and by varying the height of the inner flask above the liquid air the rate of cooling of the alcohol bath is quite easily controlled. After the necessary low temperature is reached the bath is allowed to warm and readings are taken at intervals of 2°. Owing to the small thermal leak the rise in temperature is quite slow.

The 45 cc. bulb D which contains the liquid ethylene chloride is 25 cm. in diameter; this gives a flat surface which eliminates the effects of capillarity.

Further, the vibration produced by the stirrer sufficiently agitates the surface of the liquid in D so that any error due to the presence of a perfectly quiet liquid surface is avoided. The bulbs E serve to prevent the liquid from being carried over with the vapor and to prevent the escape of mercury from F in case of bumping or sudden change in pressure. The isotenoscope is connected (G to *g*) by a system of stopcocks with the closed manometer *e*, (Fig. 2), and with vacuum and pressure tanks, *ss*, each of about 20 l. capacity. The mercury in both *e* and *f* was subjected to long continued boiling under a very high vacuum before sealing at *i*; the barometer thus created checked exactly the readings of atmospheric pressure read from a standard precision barometer.

In making a determination the tube F was filled about three-fourths full of mercury and then heated under reduced pressure to drive out any dissolved gases. Next, the liquid ethylene chloride was introduced into D through H. Then with both arms of the isotenoscope attached to the vacuum line the liquid was gently boiled to remove the dissolved gases and to displace the air above the liquid. At the same time the glass tube above the liquid was heated to a much higher temperature to expel adsorbed gases and vapors. When about 5 or 6 cc. of the liquid had been boiled away the tube H was sealed and a vapor pressure reading was made at 0°. The tube H was then broken in vacuo, to prevent entrance of air into D, and about 5 cc. more of the liquid was removed by boiling as previously described. The tube H was again sealed and a second pressure reading was made at 0°. This process of alternate evacuation and reading was repeated until consecutive readings at 0° showed no further decrease in pressure, indicating that all of the air and other gases has been completely expelled. Four separate individual samples, each treated as described, gave an uncorrected minimum value of 21.1 mm.; this after the necessary corrections are applied gives the vapor pressure of the liquid at 0°.

When the liquid in the isotenoscope has attained temperature equilibrium at a given temperature, the pressure is roughly adjusted by stopcocks *a* and *b* leading to the vacuum and pressure tanks, respectively; only the stoppers, *ss*, of these are indicated in the diagram. Tubes *h* and *k* are connected to the vacuum and compressed air lines, respectively; manometers *m* and *n* merely indicate the approximate vacuum and pressure. After the pressure has been so adjusted that the two mercury columns in F stand practically at the same level, the final equalization of pressure in F is accomplished by means of a leveling bulb *d* which is provided with a delicate screw adjustment. In this way we are able to obtain adjustments of pressure with a high degree of precision. When the pressure is so adjusted that the mercury in both arms of F stands at exactly the same level, as observed by means of a cathetometer, the stopcock *c* is closed and the pressure is read directly from the difference in levels of the mercury in *e* and *f*.

A cathetometer, readable by vernier to 0.05 mm., was used for reading pressures up to 500 mm.; higher pressure readings accurate to 0.1 mm. were read from a steel tape mounted between *e* and *f*. All pressures were reduced to mms. of mercury at 0°. Temperatures above 0° were read from a standard normal thermometer graduated in 0.1° and standardized against a second thermometer recently standardized by the Bureau of Standards. A normal pentane thermometer graduated in 1° intervals was used without standardization for temperatures below 0°.

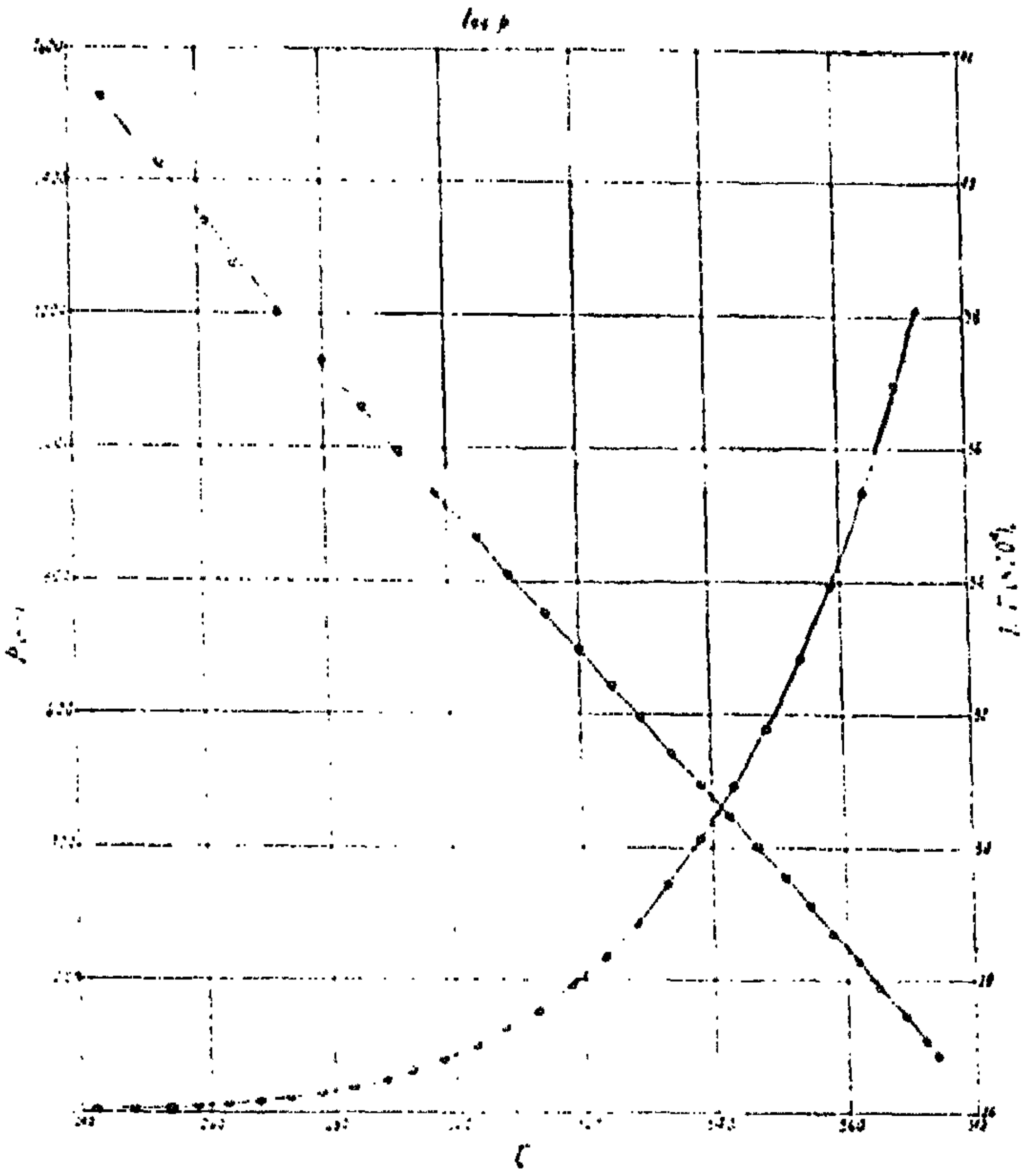

Fig. 3

Experimental Results

The vapor pressures which were obtained at intervals of approximately 5° are recorded in columns 2 and 5 of Table I. The fact that all of the points fall very nearly on a smooth curve, Fig. 3, speaks for the accuracy obtained. In Table II are collected the values of the vapor pressure for rounded temperatures in 5° intervals. These were read from a large scale plot. It has been found that the vapor pressures can be calculated very approximately by means of the equation:

$$\log p = -\frac{4481.12}{T} - 52.3092 \log T + 0.07153T - 0.000041847T^2 + 128.756.$$

For temperatures between −30° and 90° this equation gives pressures which are accurate to within 1 mm. The values thus calculated are given in columns 3 and 6 of each Table.

In Fig. 3 are plotted also the values of log p against the reciprocals of the corresponding absolute temperatures. In general, the points fall on a smooth curve; the slight deviation from the straight line indicates that the heat of vaporization varies slightly with the temperature.

TABLE I

Observed Vapor Pressures of Ethylene Chloride between −30° and 100°.

t°C	p obs.	p (Eq.)	t°C	p obs.	p (Eq.)
−30.82	3.2 mm.	2.6 mm.	39.79	153.2 mm.	153.9 mm.
−24.92	4.6	4.1	45.13	191.6	192.2
−19.32	6.6	6.1	50.12*	234.8	234.8
−15.02	8.2	8.1	55.22	285.0	286.1
−10.42	11.6	11.0	60.28	344.8	344.8
− 5.12	15.9	15.4	65.27	412.8	412.2
+ 0.07*	21.0	21.0	70.27	490.9	489.4
5.09	28.2	26.9	75.36*	579.2	579.1
10.07	36.7	36.6	80.43	682.9	680.6
15.52	49.1	49.2	85.45	794.6	793.7
20.21	62.1	62.4	91.03*	934.6	934.4
25.25*	79.8	79.8	96.03	1095.6	1075.9
30.23	100.9	100.7	99.40	1208.6	1178.8
35.24	126.3	126.3			

* Data used in deriving equation.

TABLE II

Vapor Pressures of Ethylene Chloride at Round Temperatures

t°C	p curve	p (Eq.)	t°C	p curve	p (Eq.)
−30	3.2 mm.	2.6 mm.	40	155.8 mm.	155.3 mm.
−25	4.5	4.1	45	191.6	191.3
−20	6.0	5.8	50	233.3	233.6
−15	8.3	8.1	55	282.9	283.3
−10	11.5	11.3	60	341.8	341.5
− 5	15.7	15.4	65	408.7	408.4
0	21.0	20.9	70	485.4	484.9
5	28.1	27.9	75	572.9	572.4
10	36.8	36.8	80	673.8	671.6
15	47.9	47.9	85	784.5	783.5
20	61.6	61.7	90	907.5	907.1
25	78.9	78.9	95	1059.0	1045.2
30	100.1	99.7	100	1231.0	1200.3
35	125.4	125.0			

A careful interpolation of the large scale plot of the vapor pressure-temperature curve shows the normal boiling point of ethylene chloride to be 84.1°. The molal heat of vaporization of ethylene chloride at its boiling point as calculated by the Clapeyron equation,

$$\frac{dp}{dT} = \frac{\Delta H}{T(V-v)},$$

is 7745 cals.

Using this value for the heat of vaporization we find the molal entropy of vaporization, $\Delta H/T_b$, at the boiling point to be 21.68 cals. This is in close agreement with the values calculated by means of the two equations proposed by Nernst,[1] viz.,

$$\Delta H/T_b = 8.5 \log T_b = 21.70 \text{ cals., and}$$
$$\Delta H/T_b = 9.5 \log T_b - 0.007\, T_b = 21.75 \text{ cals.}$$

Employing the formula of Bingham,[2] we obtain

$\Delta H/T_b = 17 + 0.011\, T_b = 20.93$ cals., while that obtained in applying de Forcrand's equation[3] is

$\Delta H/T_b = 10.1 \log T_b - 1.5 - 0.009\, T + 0.0000026\, T^2 = 21.40$ cals.

The ratio of the absolute boiling points for vapor pressures of 760 mm. and 200 mm., respectively, is 1.119. This value is almost identically the same as that obtained by Ramsay and Young[4] for normal liquids.

Prud'homme[5] connects the freezing point, the boiling point and the critical temperature of a liquid in the form of the expression,

$$\frac{T_f\,(T_c - T_f)}{T_b\,(T_c - T_b)} = 1.00.$$

The value of T_f as given in the International Critical Tables is −35.3°. Using this value and the value of T_b obtained above, viz., 84.1°, the critical temperature of ethylene chloride is calculated to be 321.9°C. This value differs considerably from the somewhat questionable value of 283° as determined by Pawlewski.[6]

Summary

The vapor pressure of ethylene chloride has been determined for temperatures between −30° and 100°. Between 243°K and 363°K the vapor pressure may be calculated by means of the equation,

$$\log p = -\frac{4481.12}{T} - 52.3092 \log T + 0.07153\, T - 0.000041847\, T^2 + 128.756.$$

The normal boiling point of ethylene chloride at 760 mm. has been found to be 84.1°; the critical temperature is calculated to be 321.9°.

The molal heat of vaporization of ethylene chloride at its boiling point is 7745 cals.; its molal entropy of vaporization is 21.68 cals.

Physical Chemistry Laboratory,
The State University of Iowa.

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[1] Nernst: Göttinger Nachr: (1906).

[2] Bingham: J. Am. Chem. Soc., **28**, 723 (1906).

[3] de Forcrand: Compt. rend., **156**, 1439, 1648 (1913).

[4] Ramsay and Young: Z. physik. Chem., **1**, 249 (1887).

[5] Prud'homme: J. Chim. phys., **18**, 359 (1920).

[6] Pawlewski: Ber., **16**, 2633 (1883); see Landolt, Börnstein and Roth: "Tabellen," **4**, 441 (1912).

STUDIES ON GLASS

III. The Dielectric Constants of Glassy and Liquid Glucose

BY FRANCIS R. CATTOIR AND GEORGE S. PARKS

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In the preceding paper of this series[1] the preparation of glucose glass was described and some data were presented regarding the heat capacities, coefficients of thermal expansion and refractive indices of glassy and liquid glucose. In the present investigation, which is essentially a continuation of that study, we have measured the dielectric constants of glucose in the glassy and liquid states over a temperature range of more than 200°.

Method and Experimental Results

An electrical resonance method was used for the determination of the dielectric constants. As it was substantially similar to that described by Jackson and others,[2] we shall forego a detailed description in the present paper. Two 1000-kilocycle vacuum-tube oscillators were employed. Circuit I was a Hartley oscillator, which contained in addition to an electron tube and suitable inductance a pair of variable condensers, C_1 and C_2, and the dielectric cell, all three capacities being connected in parallel. The frequency of this circuit could be changed and controlled at will by adjustment of these capacities. Circuit II was essentially the familiar Ultraudion. At the start of the investigation it was adjusted to a frequency of 10^6 cycles per second and then maintained constant, thus serving as a means whereby the frequency of oscillation of Circuit I was brought to this standard value. The heterodyne notes set up between these two oscillating circuits were received thru a pair of telephone receivers connected to circuit II by means of an audio transformer. The experimental procedure was then to adjust one of the variable condensers in the Hartley circuit until this beat note fell to zero.

The dielectric cell consisted of two coaxial copper cylinders, resting vertically in a large Pyrex test-tube. This test-tube was fitted with a rubber stopper thru which the wire connections were led out by means of two small glass tubes. The outer copper cylinder had an internal diameter of 2.1 cm. and the inner cylinder had an outside diameter of 1.6 cm.; they were both 4.5 cm. in length. The relative positions of these two cylinders were maintained by three small, tightly-fitting glass rods placed in the space between them. This dielectric cell was then introduced into a 3-liter Dewar jar, equipped with an outer metal jacket which was grounded. The jar was filled with transformer oil for measurements above 0°C. and with kerosene cooled

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[1] Parks, Huffman and Cattoir: J. Phys. Chem., **32**, 1366 (1928).

[2] Jackson: Phil. Mag., **43**, 481 (1922). See also Hyslop and Carman: Phys. Rev., **15**, 243 (1920); Williams and Krchma; J. Am. Chem. Soc., **48**, 1888 (1926); and Matsuike: Science Reports, Tohoku University, **14**, 445 (1925).

with solid carbon dioxide for work below this temperature. Equipped with a stirrer, thermometer, and electrical heating coil, it served splendidly as a small, adjustable thermostat.

Before any measurements were made on the glucose, the apparatus was calibrated by the use of several liquids of known dielectric strength. These liquids and their dielectric constants are given in Table I. The procedure in the calibration was as follows. With air in the dielectric cell, condenser C_1 was adjusted so that condenser C_2 read near but not directly on the upper end of its scale with the beat note at zero. The dial of C_1 was then fixed at this adjustment with a few drops of sealing wax, and benzene was placed in the cell. The reading of C_2 was again noted with the beat note at zero. Readings of C_2 were similarly made with the other liquids in the cell. The various dial readings for C_2 were then plotted against the dielectric constants of the several liquids and a calibration curve (practically a straight line) was thus constructed for the apparatus.

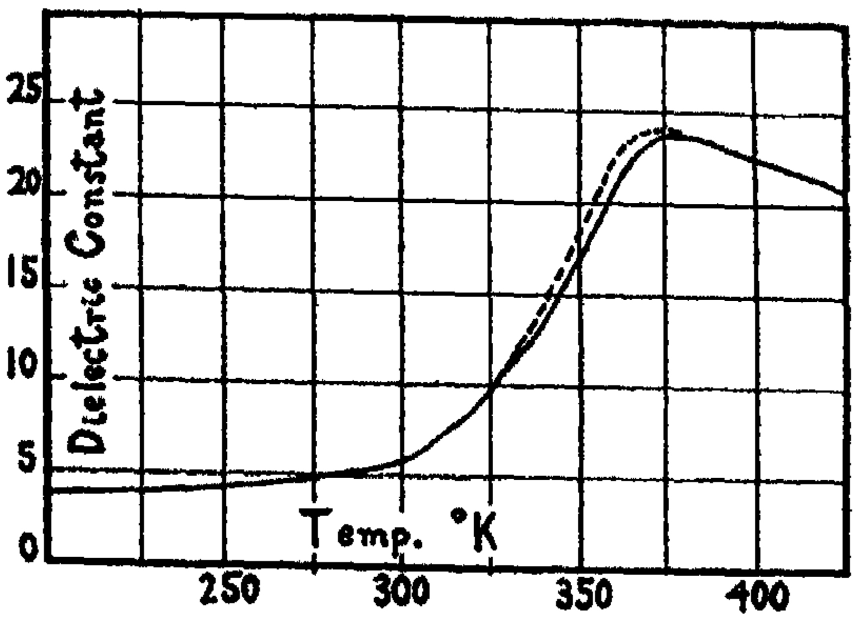

Fig 1

The solid line has been obtained by plotting the data of Table II; the broken line represents the data of Table III.

Table I

Calibration Data*

Substance	Dielectric Constant at 25°C.
Air	1.00
Carbon tetrachloride	2.23
Chloroform	5.0
n-Propyl alcohol	21.6
Acetone	21.2
Ethyl alcohol	25.2
Nitrobenzene	36.0

* These dielectric constants for the calibration substances were selected after a careful survey of the data in the Landolt-Börnstein "Tabellen" (1923 pp. 1035-1040) and in the recent papers of Matsuike (Science Reports, Tohoku University 14, 451 (1925)) and of Krchma and Williams (J. Am. Chem. Soc. 49, 2413 (1927)).

The dielectric cell was next filled with glucose glass. This was accomplished by placing the cell in a paraffin bath at 160°C and pouring in enough liquid glucose to fill it to a depth of about 5 cm. The system was then cooled slowly down to room temperature in order to avoid the development of strains or fractures in the glucose glass thus formed.

Two sets of measurements were made upon this sample. The results are recorded in Tables II and III and are represented graphically in the accompanying figure. The data in Table II were obtained by starting at 200°K. and working upwards to progressively higher temperatures until 423°K. (i.e. 150°C.) was attained. Above this latter temperature the electrical conductivity of the liquid glucose became appreciable and interfered with any further measurements. During the subsequent cooling of the liquid glucose to the glassy state the results in Table III were obtained. In this work temperatures below 270°K. were measured with a copper-constantan thermocouple, accurate to ± 0.5°, and temperatures above were determined by a calibrated mercury thermometer, graduated to 0.1°. Considering the method and the character of the apparatus employed, we estimate the absolute error in the dielectric constants thus obtained to be less than 4%; altho the reliability of the data for comparative purposes is greater than this figure might indicate, inasmuch as the various values were reproducible and consistent among themselves to within one to three-tenths of a unit.

TABLE II

Dielectric Constants of Glassy and Liquid Glucose

(Temperatures increasing; frequency, 10^6 cycles per second.)

Temp., °K.	Dielectric constant	Temp., °K.	Dielectric constant	Temp., °K.,	Dielectric constant	Temp., °K.,	Dielectric constant
200.0	3.8	260.0	4.6	302.9	6.3	374.1	23.7
209.0	3.9	270.5	4.7	307.9	6.8	382.0	23.7
220.0	4.0	279.1	4.9	322.5	9.1	393.	23.0
225.0	4.1	284.1	5.0	331.1	11.2	408.	22.0
232.0	4.2	289.9	5.4	342.2	14.0	413.	21.6
243.0	4.3	294.3	5.4	352.9	18.0	423.	21.0
253.0	4.4	299.0	5.7	362.8	21.7		

TABLE III

Dielectric Constants of Liquid and Glassy Glucose

(Temperatures decreasing; frequency, 10^6 cycles per second.)

Temp., °K.	Dielectric Constant	Temp., °K.	Dielectric Constant
369.9	23.8	316.9	8.0
368.1	23.8	312.1	7.5
357.9	21.5	303.3	6.2
343.7	15.5	289.6	5.2
333.7	12.3		

Discussion

The dielectric constants for glassy glucose were found to vary from 3.8 to 5.4, depending upon the temperature. These values are similar in magnitude to those determined by other investigators for crystalline organic compounds, many inorganic glasses and the so-called non-polar liquids. Between 293° and 310°K. the glucose glass softens and changes into a viscous liquid, while the dielectric constant begins to increase rapidly. The constant for the liquid glucose then continues to rise rapidly with increasing temperatures, reaching a maximum of 23.9 at 378°K. above which point there is a slow falling off to a value of 21.0 at 423°. Thus, within the temperature range thru which the material is a fairly mobile liquid, the value of the constant is comparable to that for other polar liquids, such as acetone and normal propyl alcohol, and is roughly four or five times that of the glassy glucose. Essentially similar data have been obtained by Fleming and Dewar[1] in an earlier investigation of the dielectric constants of liquid and glassy glycerol.

One other point is worthy of brief attention. As the curves in the figure clearly show, the results obtained within the temperature interval 325°-375°K. were distinctly greater when the viscous liquid was cooling down than when it was being heated to progressively higher temperatures. Just why this dielectric hysteresis effect should be obtained is not apparent. Within the same temperature range the power absorption for oscillation in Circuit I was appreciably greater than at either higher or lower temperatures; possibly the two phenomena are related.

Department of Chemistry,
Stanford University, California,
December 17, 1928.

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[1] Fleming and Dewar: Proc. Roy. Soc., 61, 324 (1897).

THE SYNTHESIS OF AMMONIA IN THE GLOW DISCHARGE*

BY A. KEITH BREWER AND J. W. WESTHAVER

A 4 M

The results obtained in a series of experiments on the synthesis of ammonia in glow or Geissler discharge tubes are presented in the present paper. While various phases of this general subject have been studied by a large number of investigators, a comprehensive understanding of the processes involved is still to be had. It is hoped that these experiments will contribute somewhat to our meagre knowledge of chemical action in electrical discharges. Special attention will be given to the yield obtainable as influenced by such factors as current, power, design and dimensions of the tube wherein the synthesis takes place, and the presence of magnetic and electrostatic fields. Also, some suggestions will be made relative to the mechanism of the reaction involved.

Apparatus

The arrangement of the apparatus used throughout these experiments is shown in Fig. 1. The glass system was made entirely of Pyrex. The discharge tube A was so supported between the pole pieces of a powerful electromagnet that it could be immersed in a Dewar flask containing liquid air. Arrangements were made to syphon in liquid air during the course of a run so that the level remained the same. A liquid-air trap at B separated the major part of the apparatus from the discharge tube; mercury vapor was thus kept out of the discharge. A three-liter flask was added to the system to make the pressure changes during the course of the reaction of convenient magnitude for the currents used; it also served to minimize any error that might come in from fluctuations in the discharge temperature and the adsorption of gases. The McLeod gauge used gave accurate relative pressure readings from 4.00 to 0.01 mm. over a single scale; it was possible to take readings at 30-second intervals. A mercury trap separated the system from the pumps and gas supply reservoirs. The system was thus free from stopcocks and could be highly evacuated.

The discharge tubes used were of two general types, one in which a portion of the positive column was immersed in liquid air, and the other in which the entire tube including the electrodes was immersed; the two types are illustrated in Fig. 1. The electrodes were made of aluminum rods or discs clamped to tungsten leads. The exposed tungsten was glass-covered to prevent sputtering. When only the positive column was immersed, tungsten exploring electrodes were sealed into the tube at the liquid air level. The potential drop through the region of the discharge in which the ammonia was being frozen out was measured by an electrostatic volt meter connected to the exploring electrodes. When the entire tube was immersed, the voltmeter was connected directly to the discharge electrodes.

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* Fertilizer and Fixed Nitrogen Investigations, Bureau of Chemistry and Soils, U.S. Department of Agriculture.

Most of the results described here were obtained using a 1 k.w. 20,000 volt transformer for the current supply. The currents through the discharge tube were measured either with an A.C. milliammeter or a vacuum thermocouple and galvanometer. The discharge current was controlled by rheostats in the primary circuit of the transformer. For the D.C. work, the transformer was replaced by a 10,000 volt rotary converter. The electro-magnet as used gave a field strength up to about 1,000 Gauss.

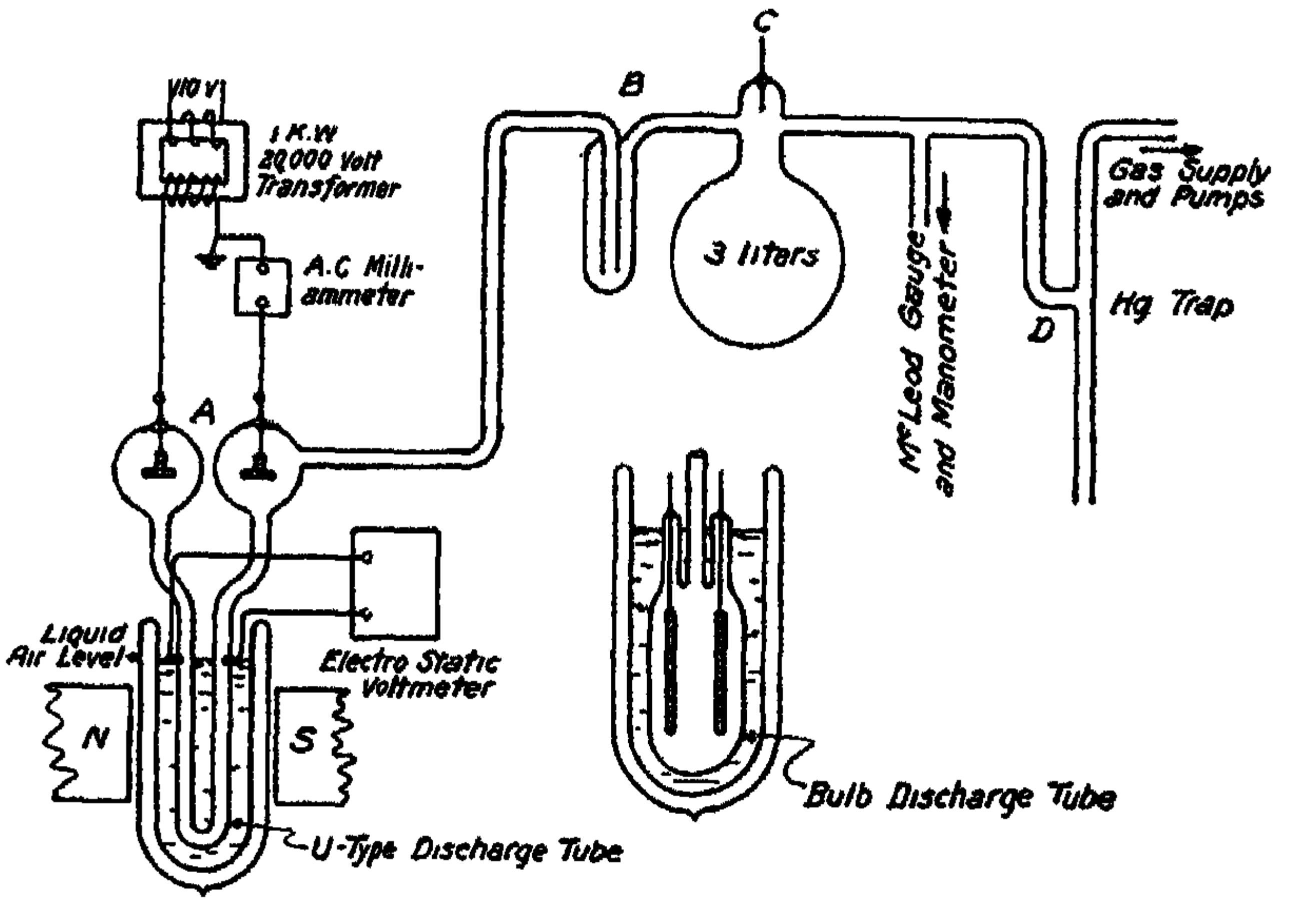


Fig. 1

Method of Procedure

The rate of synthesis of ammonia was determined by measuring the change in pressure of the 3:1 mixture at regular intervals when a constant current was flowing through the discharge tube immersed in liquid air. The ammonia was frozen out on the walls of the discharge tube as fast as formed so there was no delay in obtaining pressure equilibrium.

In order to obtain significant results, it was necessary to have an accurate 3:1 mixture of pure hydrogen and nitrogen. Deviations from this ratio retarded the reaction due to the accumulation of the excess gas in the discharge tube. The desired mixture was obtained by decomposing pure ammonia in the system by means of an electrical discharge. A highly evacuated balloon flask was filled from a tank containing liquid ammonia to which potassium had been added. From this flask it was passed into a liquid air trap connected with the pumps, where it was frozen out and any excess gas pumped off. A portion of this ammonia was distilled into the system and again frozen out in the trap at B. It was then allowed to evaporate through a discharge between C and A. The gas entering the 3-liter reservoir was thus almost completely decomposed. The liquid air was again placed on trap B to prevent any trace of undecomposed ammonia or mercury vapor from entering the discharge tube while the run was in progress.

After filling the system with the pure 3:1 mixture, the discharge tube was immersed in liquid air to the proper level and the current through the discharge tube quickly brought to the desired value. Both the current and the liquid air level were maintained constant during the course of the run. Pressure readings were taken on the McLeod gauge at intervals of one minute; the voltages were also recorded.

As a check on the 3-1 mixture, some runs were continued as long as a discharge could be passed through the tube, and showed as high as a 98% synthesis. Ordinarily a run was continued only so long as a steady discharge could be maintained.

At the end of the run the ammonia was again allowed to evaporate through a discharge from C to A, decomposing it into the original 3-1 mixture. The same gas, therefore, could be used for a large number of runs. To prevent the accumulation of any impurity, the system was highly exhausted at the end of each day, and baked out before refilling with fresh ammonia.

Results

These experiments were carried out with a number of discharge tubes which differed widely in their shape and dimensions. In some cases the ammonia was synthesized only in a part of the positive column, in others the entire discharge tube was immersed in liquid air, again just one electrode and a portion of the adjacent positive column were immersed, and a D.C. current passed through the tube. The character of the discharge was also changed by the presence of powerful magnetic fields, either parallel or perpendicular to the direction of motion of the electrons, and by electrostatic fields placed at right angles to the electron stream. In all these experiments the results obtained were strikingly similar in character and extremely simple in nature.

The summarized results of every experiment may be stated as follows: *The rate of synthesis of ammonia for a given discharge tube and magnetic field strength is proportional to the current passing through the discharge, and remains constant so long as the current is kept constant.* This may be expressed as

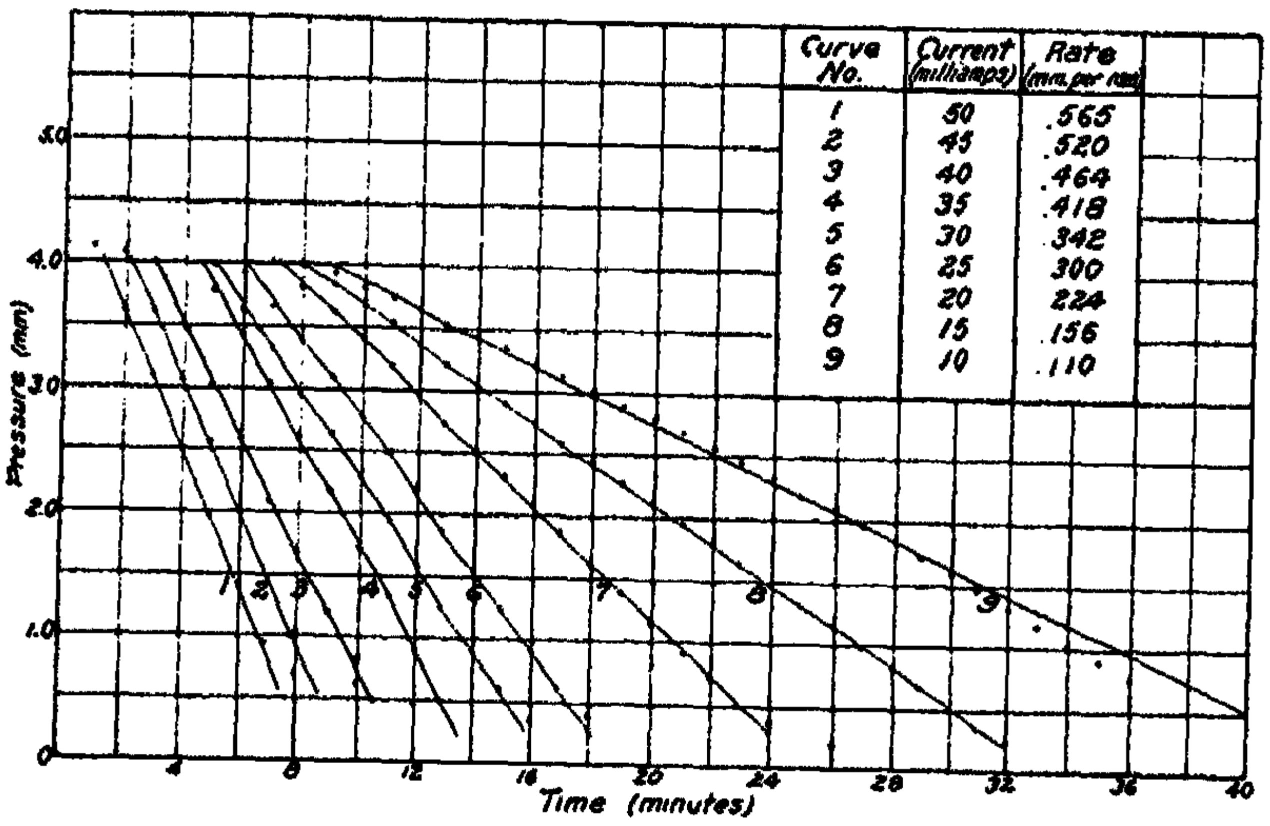
$$dP/dt = \propto I$$

where dP/dt is the rate of formation of ammonia, I is the current, and $\propto$ is a constant depending upon the size and shape of the tube, and the direction and intensity of the magnetic field when it is applied. It will be seen later that for a particular tube $\propto$ is independent of the pressure and potential gradient in the discharge.

Under all conditions in which some accidental disturbance did not enter, a straight line was obtained when the pressure was plotted against time, the slope of this line being proportional to the current passing through the tube. For this reason representative data only will be presented here to show some of the factors influencing $\propto$ and to illustrate certain characteristics of the discharge.

The dependence of the rate of synthesis of ammonia on the current passing through the discharge is shown in Fig. 4. The data obtained with a U-shaped discharge tube are plotted in Fig. 2. The lines for different currents are offset one minute in time to prevent congestion in plotting.

It will be noted that between 4 mm. and 1 mm. pressure, all points fall on straight lines to within the limits of experimental error. The widest deviation is in line 9, where the current was 10 milliamps, the smallest current that could be read on the milliameter, and hence the per cent experimental error for this run was high.



Curve No.	Current (milliamps)	Rate (mm. per min)
1	50	.565
2	45	.520
3	40	.464
4	35	.418
5	30	.342
6	25	300
7	20	224
8	15	.156
9	10	.110

FIG. 2

Results, equally as good as those illustrated, were obtained with every tube used. Line 6 of Fig. 3 was picked at random from the data obtained with a long, spiral tube, of small bore, in which the pressure range from 0.7 mm. to 0.05 mm. was investigated. It will be seen that the straight line relationship between pressure and time still holds to a high degree of accuracy.

Line 3 of Fig. 3 represents corresponding data taken with the bulb illustrated in Fig. 1. Line 1 of Fig. 3 shows an extension of a line similar to 3. This run was started with a current of 40 m.a. A departure from the straight line relationship began in this particlular run at about 0.85 mm. and at 0.63 mm. represented by the point A, no further clean-up was detectable. The current was then reduced to 15 m.a., and a clean-up to 0.3 mm. was obtained. When the current was again raised to 40 m.a., the pressure immediately rose to its former value. This phenomenon is obviously due to an equilibrium between the rate of synthesis of ammonia and the rate of the decomposition of the solid ammonia on the walls of the tube. Such a decomposition is probably due to the bombardment of the walls with high speed electrons and positive ions which becomes pronounced at low pressures and high current densities. For this reason it will be seen in Fig. 2 that line 8 is extended to a considerably lower pressure than is line 1. Further illustrations of the removal of ammonia from the walls will be given when the effects of magnetic fields are discussed. It is clearly evident that the departure from the straight line relationship between pressure and time observed at the lower pressures, in no way disproves the fact that the rate of synthesis is constant for a constant discharge current.

The proportionality between current and rate is illustrated in Fig. 4. The rates as given by the slopes of the lines in Fig. 2 are represented in line 2. Line 1 represents similar data taken with a double U tube with the same bore

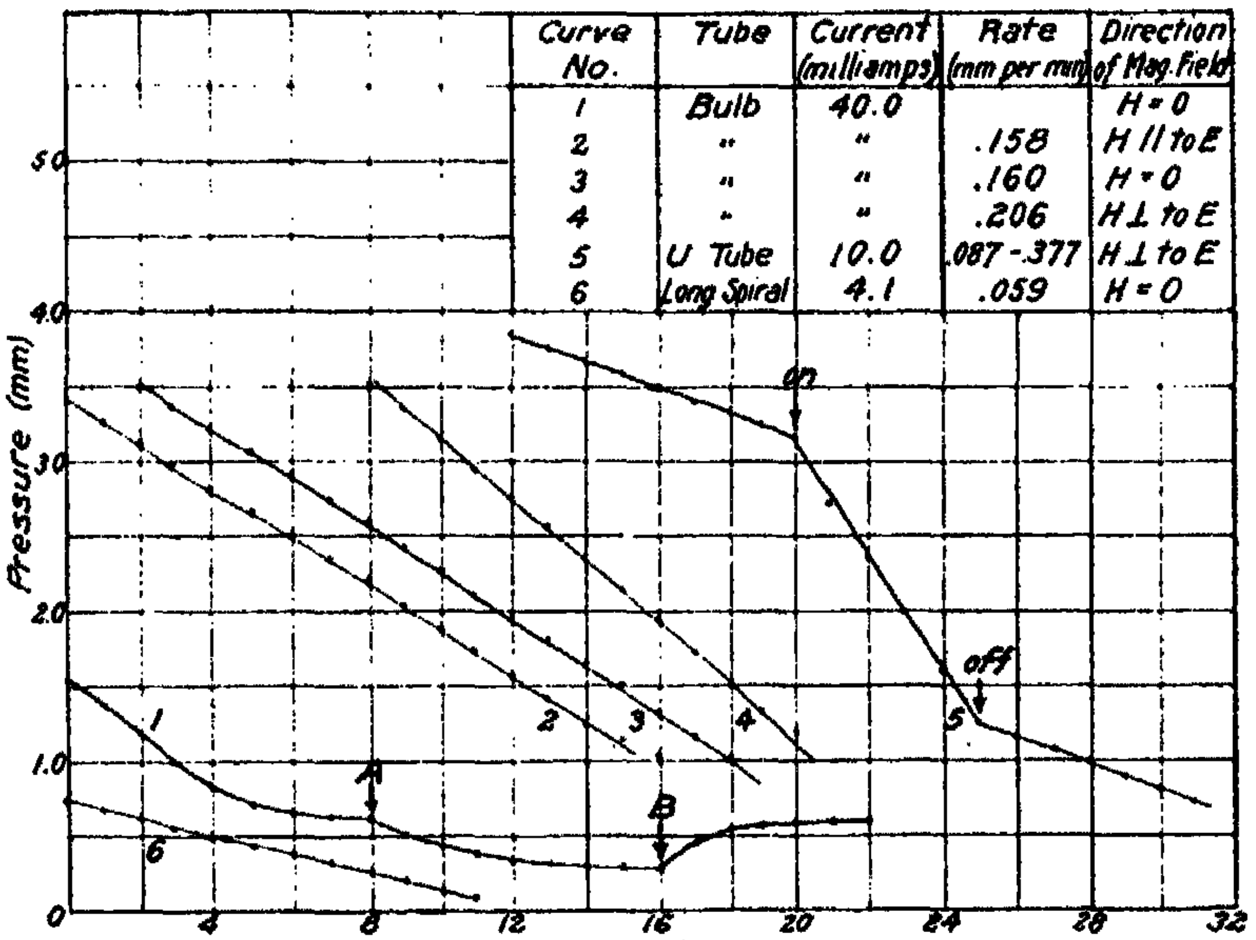


FIG. 3

but about twice the length. Line 4 represents corresponding data taken with the bulb.

It will be seen that the rate of synthesis is proportional to the current within the limits of experimental error.

A strong magnetic field had a pronounced two-fold effect on the character of the discharge; it caused the glow to be concentrated in definite sheets or bands, and when the field was at right angles to the original path of the electron, it materially varied the potential necessary to maintain the discharge. In the case of the U-tube, the glow, rather than being most intense in the center of the tube, was confined to two narrow bands one on either side of the tube farthest removed from the pole pieces. For the bulb, when the field was parallel to the plane of the electrodes, the glow, rather than filling the entire tube, was confined in a single ion sheet, about the width of the electrodes which passed through the electrodes to the walls. When the field was at right angles to the plane of the electrodes, two sheets were formed, one passing through either electrode parallel to the field.

The effects of the magnetic field on the rate of synthesis are illustrated in Fig. 3 and Fig. 4, and are summarized in Table 1.

Line 5 of Fig. 3 shows the results of a field of approximately 1000 gauss at right angles to the axis of the tube. The first and last parts of the line are in the absence of the field while the center part is with the field on. It

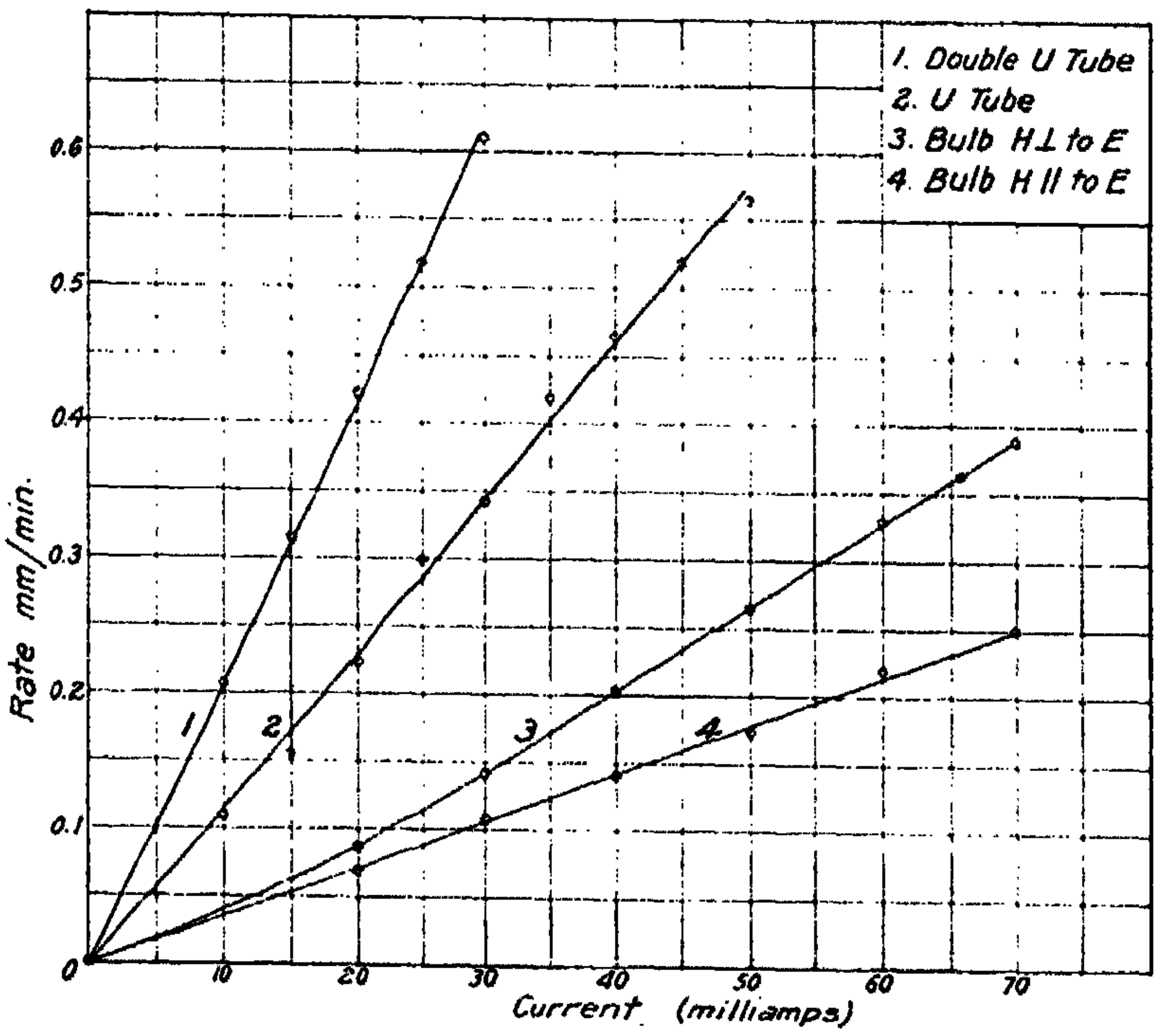


FIG. 4

will be seen that for the same current passing through the tube the rate of synthesis, for the field strength used, was increased from 0.087 to 0.377 mm. per minute; the potential drop between the exploring electrodes was raised from 3200 to 4400 volts.

The effect of a magnetic field on the rate of synthesis in the bulb is illustrated by lines 2, 3 and 4 of Fig. 3. Line 3 is for no field, line 2 shows the field parallel to the plane of the electrodes, hence parallel to the direction of propagation of the electrons, and line 4 shows the effect of the field at right angles to the plane of the electrodes. It will be noted that the parallel field gave no effect whatsoever on the rate of synthesis, while the perpendicular field materially enhanced the rate.

Variations in the magnetic field strength gave the expected results on the rate of synthesis, in that a point could be reached beyond which a further increase in the field produced little increase in the rate.

The removal of ammonia from the walls was clearly illustrated with the magnetic fields. In the case of the bulb at pressures down to about 1.5 mm. the ammonia was found to be evenly distributed over the sides of the tube. As the pressure decreased, however, the film began to disappear where the ion sheets intersected the walls. At pressures of 0.5 mm., the ammonia was completely removed from these junctures, leaving a sharply defined image of the electrodes on the tube walls. While this removal of ammonia due to high speed electron bombardment probably took place to some extent in all the discharge tubes it was inappreciable at the pressures for which the reaction rates were calculated.

In determining the effect of electrostatic fields on the rate of synthesis, the positive column of the U tube was placed between the plates of a condenser and a potential gradient established through the tube perpendicular to the direction of the electrons. A D.C. potential of 4000 volts and an A.C. potential of about 15,000 volts were used. No effect was observed with the D.C., but the A.C. may have shown a slight decrease in rate. This increase, however, was too small to be at all certain. The only observable effect was a slight broadening of the luminous core of the discharge.

The effect of the length of the positive column immersed in liquid air on the rate of ammonia synthesis per unit of current is shown in Fig. 4. Lines 1 and 2 represent data taken with U-shaped tubes of similar bore but differing in the length of the positive column. It will be seen that the longer the positive column immersed the greater the rate of synthesis for a given current. In the short tube 2.06 molecules of ammonia were formed for each electron passing through the tube, while the corresponding value for the longer tube was 3.65. A count of the number of striations in the two tubes showed the ratio of molecules of ammonia formed per electron in the respective tubes was also the ratio of the number of positive ions formed. The power efficiency for the two tubes was the same.

In the expression $dP/dt = \alpha I$, the yield of ammonia for a given tube and applied magnetic field depends only on the current. The relationship between power and yield is far more complex. Since the current is maintained constant during each run, the power input must vary as the voltage. The voltage in turn is a function of the pressure.

The effect of pressure on the voltage and likewise on the power input is shown in Fig. 5.

The power in all cases was taken to be the product of current and potential drop. No allowance was made for the phase relationship between current and voltage. Root mean square currents, and voltages as given by an electrostatic voltmeter were used in the power calculations.

It will be seen that curve 3 for the bulb is entirely different from curves *1* and *2* for the long tubes. This is due to the fact that 3 represents the voltage characteristics for the entire tube, while 1 and 2 represent only the potential drop between the exploring electrodes in the positive column.

In Table I are summarized the data obtained from the different tubes. The efficiency is given in terms of current, i.e., molecules formed per electron passing through the tube, and in terms of power, i.e., watts necessary to produce a unit rate of synthesis at 3 mm. pressure.

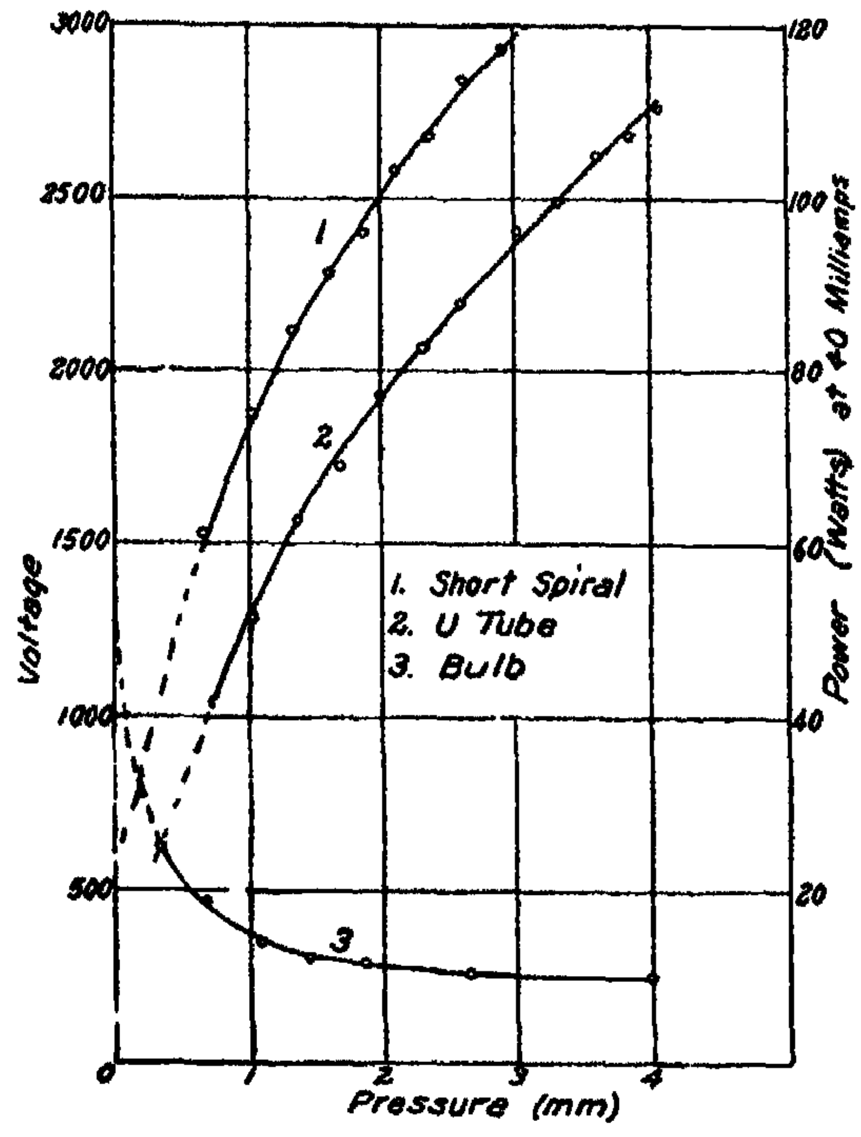


Fig. 5

TABLE I

Type of Tube	Magnetic Field	Average Voltage at 3 mm.	Rate in mm. per min. per m.a.	NH_3 molecules per electron of current	Grams per kwh.	Length of tube immersed (cm.)	Bore of Tube (mm)
Double U	H = O	4,500	.0207	3.66	2.00	66	10
Single U	H = O	2,500	.0116	2.06	2.00	32	10
Single U	H ⊥ to E	4,400	.0330	6.75	3.38	32	10
Bulb	H ⊥ to E	435	.00614	1.08	6.2	9	40
Bulb	H ∥ to E and H = O	264	.00360	0.634	6.03	9	40
Short Spiral	H = O	2,900	.0112	1.98	1.69	40	4.5
Long Spiral	H = O	5,400	.0200	3.53	1.63	75	4.5

The data show that while the current efficiency for the bulb is lower than for the U tube the power efficiency is much higher. From the voltage characteristics, it is evident that the pressure of 3 mm., for which the powers were calculated, was much nearer the pressure for maximum efficiency for the bulb than for the U tube. This will in part account for the fact that about 3 times more power per unit rate was consumed for the U tube than for the bulb. Nevertheless, it is evident that the power efficiency increases with the bore of the tube.

The effect of the magnetic field on the current and power efficiencies is given in Table I. In the case of the bulb, the power efficiency, within the limits of experimental error, was independent of the presence and direction of the magnetic field. The current efficiency, however, was materially higher when the magnetic field was at right angles to the plane of the electrodes, and was unaffected by a parallel field. The U-tube showed an enhanced yield in the presence of the field, the current efficiency being raised from 2.06 to 6.75 molecules of ammonia per electron, and the wattage per unit rate of ammonia synthesized being lowered from 200 to 130.

A Probable Mechanism

The glow discharge tube offers a fertile field for a study of the elementary units initiating chemical action, since within the discharge are to be found electrons, positive ions, neutral ions, and excited molecules. Each of these has been suggested by different investigators as the elementary reacting units. While the theory of the discharge tube is not sufficiently worked out to enable a complete mechanism to be presented at this time, nevertheless, the extreme simplicity of the results obtained in these researches makes it possible to offer some highly probable suggestions regarding the nature of the reaction.

The general theory of the discharge tube has been discussed recently by Sir J. J. Thomson,[1] by Townsend,[2] and by Langmuir,[3] but is still far from complete.

It is well at this time to mention certain facts regarding discharge tubes which will aid in an understanding of the data obtained. The electric current through such a tube is carried by electrons and positive ions, negative ions seldom existing in any appreciable quantity. The amount of current attributed to each of the carriers is in proportion to their relative mobilities. In the present experiments, therefore, a large percentage of the current is carried by the electrons, a small amount by the hydrogen ions, and very little by the nitrogen ions. In the positive column, where the potential gradient is practically uniform, a state of equilibrium exists between the electrons and positive ions. Here the positive ions are formed by collisions of electrons with neutral molecules at the same rate that they disappear by recombination

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[1] Phil. Mag., 48, 1 (1924).

[2] Townsend: "Electricity in Gases."

[3] Langmuir: Gen. Elec. Rev., 27 (1924).

in the discharge and on the negatively charged walls of the tube. The discharge itself is most intense in the center of the tube. The number of positive ions and electrons per unit volume in the positive column is practically the same except in the negative sheath near the walls of the tube. An upper limit for the number of positive ions formed by a single electron in passing through the positive column can be had by dividing the potential difference between the two ends of the column by the ionization potential of the gas, but the value thus obtained is extremely high. Possibly a better approximation of the number can be obtained by dividing the potential difference, not by the ionization potential, but by the potential for optimum ionization, which for nitrogen at 1 mm. pressure, is 100.8 volts and for hydrogen 73.5 volts.[1]

The concentration of excited molecules in a glow discharge depends materially on the character of the discharge, and on the pressure of the gas, in general reaching a maximum at about 2 mm. pressure. On the other hand, few, if any, neutral atoms are to be found at the high pressures, the concentration being a maximum in the case of H_2 at about 0.5 mm. pressure.

The effect of a magnetic field upon excited molecules and atoms is so slight that it may be neglected. Electrons, on the other hand, show a very marked effect, exhibiting a tendency to follow the magnetic lines of force, i.e., an electron moving in the direction of the field is unaffected, but an electron moving at right angles to the field is deflected as depicted by the left hand rule. Positive ions are likewise deflected by magnetic fields but to a very much smaller extent. The effect of a magnetic field perpendicular to the direction of the electric field is to deflect the electrons to the side thus concentrating them near the walls of the tube rather than at the center. The mean free path of the electron in the direction of the electric field is thus materially shortened. The space charge set up in the tube by the deflected electrons causes the positive ions to be likewise pulled to the walls. The resultant effect of the magnetic field is, therefore, to markedly increase the number of electrons and positive ions per unit length of the positive column, and to shift the region of maximum concentration from the center towards the walls of the tube.

In viewing the data presented in these experiments, wherein the rate of synthesis for a given tube is dependent only on the current and is completely independent of the pressure, it seems most probable that the initial reactants must be positive ions rather than atoms or excited molecules formed directly in the discharge. Had the reaction been due to excited molecules, the rate should have decreased rapidly with decreasing pressure. On the other hand, had the reaction been due to atoms, the rate should have increased with decreasing pressure, becoming a maximum at a little less than 0.5 mm.

The fact that the initial reactants are ions is again shown in a very conclusive manner by the action of the magnetic field. In the bulb, the field

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[1] Hughes and Klein: Phys. Rev., (2) 23, 450 (1924); Compton and van Voorhis: 27, 724 (1926).

parallel to the plane of the electrodes completely eliminated the general glow throughout the tube but had no effect on the current nor on the rate of synthesis. The field perpendicular to the plane of the electrodes, while again eliminating the general glow, increased the number of electrons and positive ions in the tube and likewise increased the rate of reaction.

The conclusion that the reaction is initiated by ions and not by excited molecules or atoms, is in complete agreement with the data obtained by Kunsman[1] and by Storch and Olsen[2] who observed no evidence of ammonia formation when a mixture of nitrogen and hydrogen was bombarded with electrons until the energy of the electrons reached the ionization potential of the gas. Bernard Lewis[3] is of a contrary opinion, concluding that the initial reactants are neutral atoms of both nitrogen and hydrogen. In his experiments he was able to detect ammonia when hydrogen from a Woods tube was mixed with nitrogen from an electrodeless discharge tube. Since the life of an ion in either nitrogen or hydrogen is such that the gases may be drawn through many feet of glass tubing before the ions become neutralized, the ammonia formed in his experiments may have resulted from ions entering the reaction chamber from the discharge tubes.

If the initial process in the synthesis of ammonia is the formation of positive ions in the discharge, two possibilities exist as to the final step in the reaction. NH^+_3 may be formed in the gas phase and the neutralization take place on the negatively charged walls of the tube, or the reaction may be independent of the walls, the formation of NH_3 neutral taking place in the gas phase.

A special bulb was constructed to test this point; one electrode was an enclosed aluminum cylinder tightly fitted into a glass bulb, and the other was a small aluminum rod supported in the center of the cylinder by a Pyrex covered tungsten rod entering through a small opening in the top.

With such a tube operated on D.C., it is possible to answer the above question. If NH^+_3 is the final gas phase product, neutralization taking place on the walls, the rate of synthesis will be practically zero when the outer electrode is positive and rapid when negative. On the other hand, if the formation of ammonia around a N^+_2 ion, say, goes to completion in the gas phase, a lower yield will be expected when the outer electrode is negative, since the larger surface and lower space charge will increase the possibility for removal of positive ions before they have had the chance to react.

The results obtained with the cylindrical electrode tube are shown in Table II.

From the data it will be seen that the rate of synthesis was exceedingly slow when the outer electrode was negative. A positive potential, however, increased the current efficiency some 600%, and the power efficiency about 30%. The intermediate values obtained with the A.C. current indicate that

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[1] Phys. Rev., (2), 31, 307 (1928); J. Chem. Education, (in press).

[2] J. Am. Chem. Soc., 45, 1605 (1923).

[3] J. Am. Chem. Soc., 50, 27 (1928).

TABLE II

Aluminum Cylinder— Current = 40 m.a.
Pressure = 3 mm.

Polarity of Cylinder	Magnetic Field	Voltage at 3 mm.	Rate mm. per min.	Mol. per electron	Grams per kwh.
−	0	85	.021	.093	2.71
+	0	425	.136	.596	3.52
−	on	175	.036	.159	2.27
+	on	385	.123	.544	3.52
A.C.	0	210	.058	.256	3.03

an appreciable synthesis took place only on the half cycle, in which the outer electrode was positive. These facts show in a most conclusive manner that NH_3 neutral, and not NH^+_3, is the final gas phase product.

The low current efficiency obtained with the outer electrode negative indicates that any type of discharge tube which facilitates the escape of positive ions to the walls, thus decreasing the active ingredient in the gas, decreases the rate of reaction. The concentration of the discharge by the magnetic field, therefore, would be expected to increase the current efficiency.

The results tabulated in Tables I and II furnish a comparison of the current and power efficiencies. If, as the data indicate, the formation of N^+_2 or H^+_2 is the initial step in the reaction, the significance of these two efficiencies at once becomes evident. The current efficiency is dependent on two things, the number of positive ions formed by each electron in passing through the tube, and the ratio of the number of positive ions reacting to form ammonia to those becoming neutralized without initiating chemical action. The power efficiency, on the other hand, is determined by the watts required to maintain a unit rate of synthesis, or the voltage necessary to maintain such a current through the discharge that the resulting effective positive ion concentration yields a unit of ammonia synthesized per unit time.

The fact that the formation of ammonia is a gas phase reaction introduces the possibility that an appreciable decomposition of the ammonia thus formed will take place before it has a chance to freeze out on the walls. The proportionality between current and rate shows such a decomposition to be extremely small. On the basis of probability, the quantity of ammonia decomposed, per unit time per unit volume of the gas phase, is a function of the product of the concentration of ammonia and of the concentration of electrons having a velocity component sufficient to decompose the ammonia; a two-fold increase in current, therefore, will give as a minimum a four-fold increase in the amount of ammonia decomposed. Since the observed rate of formation was found to be proportional to the current, it follows that the gas phase decomposition at liquid air temperatures is negligible. This is to be expected for these low concentrations, when one considers the possibility of a collision between an ammonia molecule and a high speed electron.

The fact that a straight line relationship exists between time and rate of synthesis for any given ionization current is of fundamental importance in the consideration of the mechanism involved. Since the rate of formation is completely independent of pressure even under the most widely varying conditions, it must be concluded, on the basis of probability, that the observed rate of synthesis is not the result of any complex system of formation and dissociation, but must be due to one single mechanism of synthesis operative under all conditions. The chance is exceedingly small indeed that any equilibrium ratio between different mechanisms for synthesis and decomposition could be the same for all current densities, diameters of discharge tubes, pressures and temperatures of the discharge,[1] positions in the discharge wherein synthesis takes place, and for the different magnetic and electrostatic fields.

From the above considerations, as well as those preceding the obvious conclusion to be drawn is that chemical action is initiated by positive ions formed in the discharge, and that the rate of synthesis is proportional to the rate of formation of positive ions, which, in turn, is proportional to the current. It is possible, therefore, that this represents a chemical equivalence law for discharge tubes which is analogous to Faraday's law for electrolytes.

The writers wish to express their appreciation to Dr. R. W. Harkness and to Mr. Leonardo Testa, glassblower, for the valuable suggestions and assistance so cheerfully given.

Summary

The synthesis of ammonia in the glow discharge has been investigated from 4 mm. to 0.1 mm. pressure of a 3-1 mixture of hydrogen and nitrogen. For any particular discharge tube the rate of synthesis is proportional to the current passing through the discharge and is independent of the pressure and potential gradient. The rate of synthesis per unit of current and per unit of power is discussed for discharge tubes of various types. The current efficiency varies directly with the length of column immersed and the power efficiency increases with the bore of the tube. The presence of a magnetic field at right angles to the electric field materially increases the rate of synthesis while a parallel field has no effect. The synthesis is shown to be a pure gas reaction. The data is interpreted as indicating that the reaction is initiated by the positive ions formed in the discharge, the rate of synthesis being proportional to the rate of formation of ions present, hence to the current. A new electrochemical equivalence law for discharge tubes is suggested.

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[1] The effective temperature of the gas in the discharge and of the electrodes varies considerably with the design of the tube, the current density and the gas pressure even though the walls of the tube may remain at liquid air temperatures.

OSMOTIC PRESSURES OF ACETONE SOLUTIONS*

BY M. J. MURRAY

The volume which results from mixing two components is equal to the sum of the volumes of the components only in the case of ideal solutions. Sometimes the volume after mixing is larger and sometimes smaller than the sum and in a few cases the total volume is less than that of the solvent. The latter is the case when 4 grams of sodium hydroxide are dissolved in 96 grams of water at 0°. The total volume of the solution is 95.4 cc.[1]

Bancroft has suggested that the volume occupied by the solvent in the solution may be calculated by use of the formula

$$PVg = \frac{RT}{M_2} \ln p_0/p_1$$

in which P is the osmotic pressure of the solution, Vg the volume occupied by one gram of the solvent in the solution, R the usual gas constant, T the absolute temperature, M_2 the molecular weight of the solvent in the vapor phase, p_0 the vapor pressure of the pure solvent and p_1 the partial pressure of the solvent over the solution.

Thus every term is either known or can be experimentally determined except Vg. Using this formula and the data for the osmotic pressures and vapor pressures of sucrose solutions, Bancroft and Davis[2] made calculations for the volume occupied by one gram of water in solution as well as for the density of the dissolved sugar. In this case the osmotic and vapor pressures have been painstakingly determined but the change in volume on mixing is not large enough to make the calculations exceedingly striking.

It is desirable then to find, if possible, components which mixed give marked volume changes and to measure the osmotic and vapor pressures of these solutions. Since vapor pressures can be determined for almost any solution whereas osmotic pressure cannot be, the point of attack is through measurements of the latter.

In measurements of osmotic pressures the question of the membrane is first to be considered. Copper ferrocyanide membranes have been the favorites throughout the years and much can be said in their favor. The disadvantages lie in the difficulties which have to be met in preparing really good membranes and in the fact that they are suitable for measuring the osmotic pressures of only a few solutions in water,—sucrose, glucose, calcium ferrocyanide, etc. They are not suitable for non-aqueous solutions nor for most electrolytes in water. The same general criticism holds for other precipitation membranes.

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* This work is part of the programme now being carried out at Cornell University under a grant to Professor Bancroft from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] Bousfield: Trans. Faraday Soc., 13, 141 (1917).

[2] J. Phys. Chem., 32, 1 (1928).

Of the other membranes proposed for use the one approaching nearest to semipermeability and utility is rubber. Raoult[1] made some qualitative experiments separating solutions of ether and methyl alcohol by vulcanized caoutchouc. The flow was from pure ether to the solution of alcohol in ether and the pressures developed were large but no quantitative work was reported. Flusin,[2] at Raoult's suggestion, a little later began measurements but ran into difficulties and finished by noting the rate of flow of liquids through the rubber. Kahlenberg[3] showed how vulcanized rubber could be employed but the results obtained were discordant both among themselves and with the van't Hoff theory of solutions. Cohen and Commelin[4] repeated Kahlenberg's work with a modified apparatus but with little or no better agreement in the results. Barlow[5] made some experiments with gutta-percha membranes and found that when water and alcohol were separated by such a septum the flow was slow and toward the water. Wilcox,[6] repeating some of Kahlenberg's work on pyridine solutions, maintained that the gas laws do not hold at all. Koenig[7] using pyridine as solvent and sugar as solute found that the gas laws did hold fairly well but that if silver nitrate or lithium chloride were the solute the pressures developed were far below the theoretical ones.

In the face of these results the immediate aim of this research became to discover wherein the trouble lies in the measurements of the osmotic pressures of solutions using rubber as a diaphragm, and to show that the gas laws do hold for non-aqueous solutions.

Since rubber is to be the septum we have a number of solvents which might prove worthy of trial. The first of these is pyridine which has already been the subject of a number of investigations. It has the advantage of being a very good solvent, dissolving electrolytes and water as well as many organic substances. It swells rubber somewhat but does not appreciably disintegrate it. Koenig reports that it has a deleterious effect on the membrane since the osmotic pressure developed with a given membrane drops off with use. Pyridine is disadvantageous not only because of its odor and physiological effects but also because it is extremely hygroscopic; this, Cohen and Commelin tell us, may be the cause of irregularities in its behavior.

Raoult suggested the use of ether. However, it swells rubber considerably and after a time the membrane loses its strength. Besides, compounds toward which the rubber should be impermeable are only slightly soluble in it. Barlow employed alcohol as solvent but the flow was very slow. On the other hand solvents like benzene, toluene, chloroform, carbon tetrachloride, etc., dissolve the rubber too easily.

Acetone, however, has a number of advantages. Its odor is not objectionable nor its vapor pressure extremely high at room temperature. It is a

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[1] Compt. rend., **121**, 187; Z. physik. Chem., **17**, 737 (1895).
[2] Compt. rend., **126**, 1497 (1898).
[3] J. Phys. Chem., **10**, 141 (1906).
[4] Z. physik. Chem., **64**, 1 (1908).
[5] Phil. Mag., (6) **10**, 1; J. Chem. Soc., **89**, 165 (1906).
[6] J. Phys. Cm., **14**, 576 (1910).
[7] J. Phys. Chem., **22**, 461 (1918).

very good solvent for a number of substances toward which rubber is most likely to be impermeable although not dissolving the wide variety of things soluble in pyridine. It swells rubber only slightly and after long periods a sheet of vulcanized rubber submerged in acetone does not appreciably change in strength; a sheet of unvulcanized rubber, however, rapidly disintegrates when in contact with acetone. The chief disadvantage of this solvent is its rather low rate of passage through rubber especially when near the equilibrium pressure. Experiments conducted in this laboratory by Nugent[1] suggested the use of acetone as solvent as well as the use of water as solute. Pure acetone could be forced through rubber with very little pressure applied but to force acetone containing dissolved water was another matter. The pressure applied had to exceed the osmotic pressure of the solution.

It was expected that rubber would be almost impermeable to the dissolved water and that true osmotic pressures could be measured. This then would give direct evidence of the molecular weight of water in acetone.

The acetone used in these experiments was that from Kahlbaum, from bisulphite compound, and Baker's "purified." Aside from the water contained there was no objectionable impurity. The water was removed by shaking with anhydrous calcium chloride. A number of treatments were necessary and several days were required to remove the water. The resulting dry acetone was distilled through a Hempel distilling column, the first and last portions being rejected.

Each of the investigators above mentioned as having worked with rubber membranes has described an apparatus for the measurement of osmotic pressure; but the one by Raoult seems to be most suitable for use when working with high pressures and a substance of high coefficient of expansion and volatility such as acetone. Since the rate of flow of this solvent through rubber is not great and since the area of the membrane itself is small (as compared to those of copper ferrocyanide membranes in the porous cups) modifications were necessary. It seemed desirable to apply pressure to the solution side of the osmometer to balance the osmotic flow. This method was first suggested by Tammann[2] and used successfully by the Earl of Berkeley and E. G. J. Hartley[3] in measuring the osmotic pressures of sucrose solutions with copper ferrocyanide membranes.

Apparatus

The apparatus used in the measurements of the osmotic pressures of acetone solutions is illustrated diagramatically in Fig. 1. The osmometer itself consists of two flanged halves, each having a capacity of approximately 100 cc. These were turned from a bar of monel metal, 15 cm. in diameter, which the International Nickel Company kindly furnished, and to whom our thanks are given. The flanges are each provided with six holes through which bolts may be inserted to hold the halves firmly together. Each half of the

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[1] Colloid Symposium Monograph, 5, 149 (1927).

[2] Z. physik. Chem., 9, 97 (1892).

[3] Phil. Trans., 206A, 486 (1906).

bomb is recessed to accommodate a 3/16 inch plate of monel metal. Both plates are drilled as full of holes as possible, those in plate P_1 being about 1 mm. in diameter and those in P_2 about 2 mm. The holes in P_2 are countersunk away from the membrane. Between plate P_1 and the membrane is placed a piece of strong muslin for additional support.

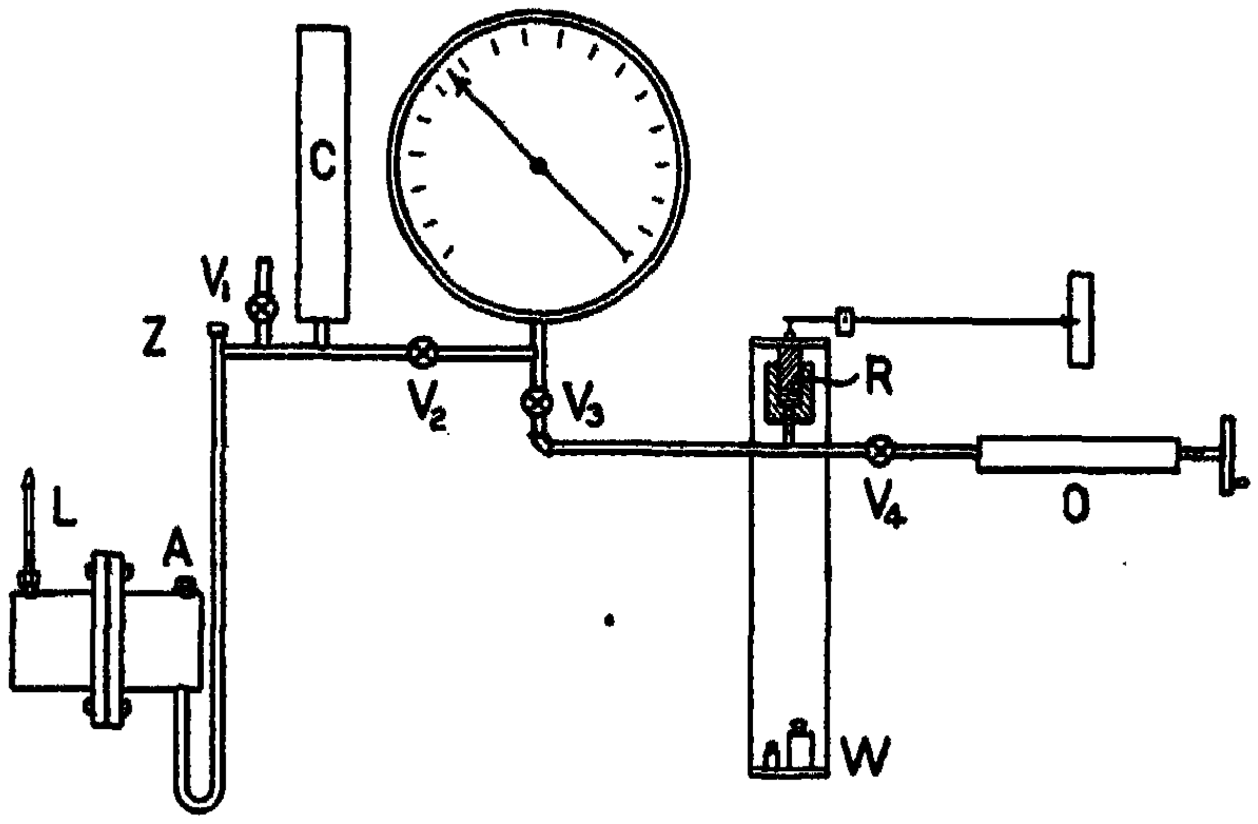

Fig. 1

When the two halves are placed together and fastened by the bolts the rubber membrane is pressed tightly between the plates and thus wrinkling is largely inhibited. The connections between the flanges and the membrane are made sure by a rubber gasket and rubber cement.

The side of the bomb which is to contain the pure solvent, otherwise to be designated as the "non-pressure" side, is provided with a hole for a 1/4 inch compression coupling by which the indicator tube L is attached. In order to observe the meniscus in this tube the upper part at least must be of glass. Pyrex tubing could be used directly in the compression coupling provided that instead of the regular brass ferrule one of rubber, whittled from a small one-hole rubber stopper, were used. Another method consisted of making the indicator tube in two parts, the lower of copper tubing and the upper of

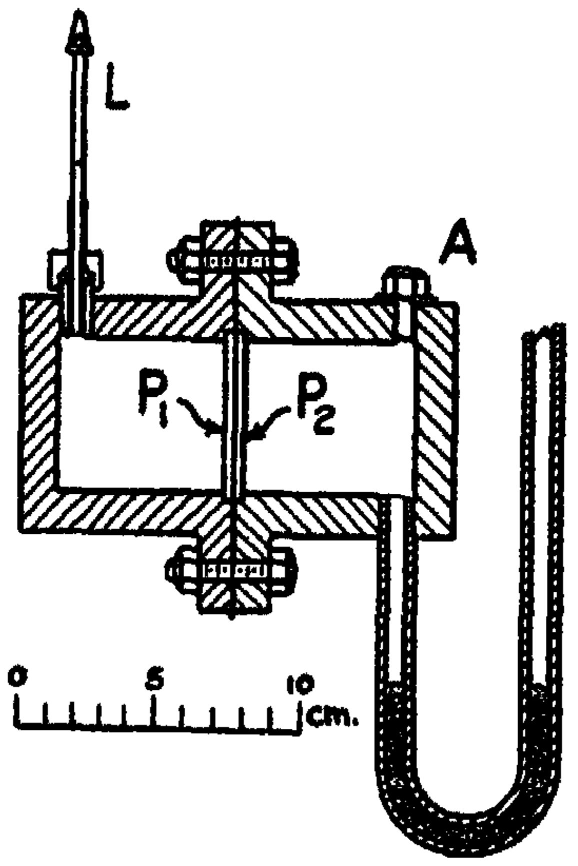

Fig. 1a

glass with a glass to copper seal. The copper tube was then used in the coupling with the ordinary ferrule. In either case evaporation from the top of the tube was prevented by a ground glass-cap.

The other side, to be designated as the "pressure side" is provided with two holes placed diametrically opposite. The one at the top is for emptying and filling, and during a run is closed by a plug A made secure by a hard rubber gasket. The second hole connects the bomb to the gauges by means of the nickel U-tube and is made tight by brazing. The U-tube which contains mercury during an experiment is made of 1/2 inch nickel pipe and L's.

The gauges used in the present work were assembled by Dr. H. L. Davis for investigation of the boiling points of solutions under high pressures. A detailed description of them will be found in his article.[1]

A Bourdon spring gauge is used to measure pressures directly, and this was checked continually against the dead-weight or "absolute" gauge. The pressure is applied through the valve V_1 to the mercury in the U-tube and to the Bourdon from a cylinder of compressed air.

The absolute gauge consists of a piston R the under side of which can be subjected to the pressure within the apparatus by opening the valve V_3. The upward movement of this piston is balanced by weights placed on the platform W. An electric motor attached by a worm gear and cam keeps the piston moving in a semirotational fashion, thus allowing true balance to be read more accurately by preventing the piston's adhering to the sides of the cylinder. Oil is used as a medium through which pressure is applied to the bottom of the piston. It is forced into the gauge by means of the screw pump O and through the valve V_4. After enough oil has been driven in to start the movement of the piston upward, V_4 is closed and V_3 opened and a comparison of the two gauges made. There was no attempt to keep the absolute gauge under the pressure within the apparatus during the entire determination—it was used only as a check on the Bourdon. To prevent oil from the absolute gauge from flowing over onto the mercury in the U-tube a vertical piece of tubing was inserted in the line directly under the Bourdon.

Since the piston has a rather large displacement and the total volume of the Bourdon and pipes is limited a movement of the piston causes a considerable change in the pressure within the apparatus. This was remedied by inserting a capacity chamber C.

The osmometer itself is immersed in a thermostat the temperature of which over long periods of time does not vary more than 0.02°.

Manipulation

The pressure side of the bomb contains the solution the osmotic pressure of which is to be measured. This side is filled through the opening A. Air bubbles are thus entrapped in the holes of plate P_2 and have to be removed, else, when pressure is applied, they will be forced through the membrane and invalidate the reading of the meniscus in the indicator tube. The removal

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[1] J. Phys. Chem., 33, 600 (1929).

is accomplished by simultaneously applying reduced pressure to the openings A and Z. (Valve V_2 is closed during the operation). This not only removes the air bubbles but also prevents the mercury in the U-tube from being displaced. A few applications and releasings of suction serve to remove the bubbles completely. After this is done the plugs are inserted at A and Z, valve V_2 opened and pressure applied from the cylinder of compressed air through the needle valve V_1.

The non-pressure side, or side containing the pure solvent, is filled quickly by inserting through the indicator tube L a small glass tube one end of which is drawn out into a funnel. However, in order to prevent the solvent from coming in contact for long with the air and thus absorbing moisture it is better to employ the device which is used to empty this side of the bomb. This consists of an Erlenmeyer flask fitted with a two-hole rubber stopper. Through one hole pressure for forcing the solution out or suction for filling the flask may be applied. Through the other, leading to the bottom of the flask, is inserted one arm of a glass U-tube made small enough to fit inside the indicator tube. Air bubbles entrapped in the holes of plate P_1 may be removed by alternately applying and releasing suction to the indicator tube.

When the osmometer and contents have come to the temperature of the bath the level is marked on the indicator tube. Usually when pressure is first applied or increased the level of the meniscus shows a slight rise, 1-2 mm., during the first hour. This is probably because the added pressure squeezes out some acetone from the membrane and in spite of the supporting plate the membrane is not quite rigid. After this preliminary rise the changes in level are reliable.

The first method used in an attempt to find the correct pressure to balance the osmotic pressure of water dissolved in acetone was to try a pressure somewhat too low and another too high (as shown by the movement of the meniscus in the indicator tube), and then to approach from both sides the point where no liquid flowed. It was thought that the level of the meniscus would remain stationary and that this method would give the correct osmotic pressure of the solution. Actually, however, the point of "no flow" dropped continuously, that is, the longer pressure was applied to a given solution the less was the pressure required to balance the osmotic flow. It was then found that quite appreciable amounts of water passed through the rubber membrane. Consequently the maximum pressure for a given pair of solutions steadily decreased. Since the period required to ascertain a true flow, especially when near the balancing pressure, was rather long (sometimes ten to twelve hours), there was opportunity for a good deal of water to go through the membrane.

It is easy to see that if water does go through in appreciable amounts one cannot expect to prepare solutions of given concentrations and measure the maximum pressure. If one did happen to set the pressure on the acetone-water side at the maximum pressure for a given concentration, a movement upward in the indicator tube would be observed; for as soon as a small amount of water had passed through, the pressure applied would be greater than the difference in osmotic pressures of the new pair of solutions.

If on the other hand one takes advantage of this and applies a pressure that is somewhat lower than the osmotic pressure (as determined by previous experiment), the level in the indicator tube will at first drop. As the water goes through the membrane and makes the difference in concentration less and less there will come a point at which the level ceases falling and begins to rise. If the solutions are removed and analyzed at the point of reversal of flow one can check results very well with a given membrane. With practice this point of no-flow can be readily determined to within two-tenths of an atmosphere.

This method demanded that the analysis for water in acetone or rather the difference in water content of two solutions be made accurately and quickly. Frankforter and Cohen[1] suggest such a method by determining the specific gravities of the solutions. There are some data in the literature on the specific gravity of acetone-water solutions but they are somewhat discordant and usually the first value given is for a ten percent solution. The concentrations with which I worked were all less than four percent. So solutions of known concentrations of water in acetone were carefully weighed out. In every case the same modified Sprengel pycnometer and the same temperature, 20°, were employed. The weight of the pycnometer full of acetone was determined and in turn the weight of the same pycnometer filled with the different known solutions.

In a number of determinations it was found that for each percent of water added, the increase in weight of the pycnometer full of the solution over the same pycnometer full of pure acetone was 0.1796 gram. Thus the difference in weight between the pycnometer filled with 3 percent water in acetone and pure acetone was 3×0.1796 or 0.5388 gram. Conversely, if the pycnometer containing the solution from the pressure side of the bomb weighed 0.5388 gram more than the same pycnometer filled with the solution from the non-pressure side, the difference in water content of the two solutions would be 3%.

The density of the acetone solutions up to 4% water is so nearly a linear function of the concentration as to be within the experimental error. The accuracy with which the determinations were made was such that the difference in water content of two solutions could be ascertained to within ±0.02%.

As soon as it was found that water passed through the ordinary vulcanized membranes a search was made for some preparation which would be impermeable to the water. It was thought that if rubber were first extracted with acetone before vulcanization it would prove impermeable. Such was not the case as will be seen later. Membranes so treated were furnished by the Goodrich Rubber Company. Some other preparations were tried, varying the amount of combined sulfur but with unsatisfactory results. The membranes which proved most useful were of ordinary commercial

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[1] J. Am. Chem. Soc., 36, 1103 (1914).

sheet sent by the United States Rubber Company. One of these was 0.024 inch thick while the other was 0.064 inch. Before using in the osmometer they were always extracted for a day in cold acetone.

The United States Rubber Company also sent some sheet gutta-percha. It was hoped that this would be impermeable to water since it is more satisfactory in submarine insulation than caoutchouc. This expectation was not realized. Actually gutta-percha does take up some water[1] and, besides, a large portion of it is soluble in acetone.

More experiments are being conducted in an effort to find a membrane which will be impermeable toward the dissolved water.

Results

In every case with each rubber diaphragm employed water was found to go through from the solution side to the solvent side, thereby not only decreasing the concentration on one side but also contaminating the pure solvent—both effects lowering considerably the osmotic pressure which could be developed.

Table I gives the results of a number of experiments using the same rubber membrane. Column 1 gives the composition of the solution (the osmotic pressure of which is to be measured), in percent by weight of water, before placing in the bomb. The non-pressure side was filled with pure, dried acetone.

Column 2 represents the percentage difference in water content between the solutions in the two halves of the bomb, which was determined by analysis at the end of the run. The concentration is calculated in molality in column 3 (molecular weight of water 18). Column 4 gives the osmotic pressures in atmospheres which were found. Column 5 gives those calculated from the formula

$$PV_1 = RT$$

Column 6 gives the pressures calculated from the formula

$$PV_m = RT \ln p_0/p_1$$

in which the values of p_1 for the various concentrations were taken from the graph of Makowiecki's data (Fig. 2),[2] on the partial pressures of acetone over solutions of water in acetone.

Thus in the first determination given in the table, a solution containing 1.50% by weight of water in acetone was placed in the pressure side of the bomb. The pressure was set at 8.2 atmospheres and in two or three days the point of reversal of flow, as previously described, was reached. Then the solutions were removed and analyzed. An absolute analysis would perhaps show that the pressure side now contained 1.45% water and the non-pressure side 0.05%. The difference, 1.40% is the value recorded in column 2; this is a 0.615 molal solution (column 3). From the formula $PV_1 = RT$ the pressure which should be developed for a 1.40 % solution, assuming that water has a

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[1] Lowry and Kohman: J. Phys. Chem., 31, 23 (1927).

[2] Chem. Zentr., (V) 2, 392 (1908).

TABLE I

Osmotic pressures of solutions of water in acetone at 30° using for membrane a commercial sheet of vulcanized rubber. Thickness 0.064 inch. Membrane number 1

% by weight water		Molality	Osmotic press. in atmospheres			Molecular Weight
Start	Finish		Found	Calculated $PV_1 = RT$	Calculated Makowiecki	Makowiecki
1.50	1.40	0.615	8.2	15.3	11.4	24.1
1.78	1.64	0.722	9.3	17.9	13.3	24.3
2.18	2.00	0.882	10.9	21.9	15.9	24.9
2.25	2.18	0.966	11.6	24.0	17.2	25.2
2.50	2.35	1.04	13.0	25.9	18.3	25.5
2.75	2.65	1.18	14.7	29.3	20.4	25.9
3.00	2.87	1.28	15.5	31.9	21.9	26.2
	5.2	2.375	—	59.1	37.4	28.4

molecular weight of 18 in the acetone, is 15.3 atmospheres (column 5). If the value for the partial pressure of acetone over a 1.40% solution is taken from the graph of Makowiecki's data, Fig. 2, and the osmotic pressure calculated we find the value of 11.4 atmospheres as recorded in column 6.

From the formula

$$PV_m = RT \ln p_o/p_1$$

if we assume an ideal solution in which

$$p_o/p_1 = \frac{N + n}{N}$$

we get

$$PV_m = RT \ln \frac{N + n}{N} = RT \ln \frac{N + g/M_1}{N}$$

where N is the number of moles of solvent, g the grams of solute and M_1 the molecular weight of the solute water in the solution. If we take the values of P found in the measurements, every other term is at least approximately known except M_1. This can then be calculated. In the third determination in Table I the final concentration difference in water content was 2%. Substituting 10.9 for P, 303 for T, 98/58 for N, and 2 for g and solving for M_1 we get 36 for the molecular weight of water. This gives the upper limit for the molecular weight at this concentration.

The molecular weight of water in acetone can also be calculated from another source—namely, from the partial pressures.[1] If in the formula

$$PV_1 = RT\frac{N}{n} \ln p_o/p_1,$$

where V_1 is the volume of the solvent containing one molecular weight of the solute, we assume that

$$PV_1 = RT$$

we get

$$n/N = \ln p_o/p_1 = \frac{g/M_1}{N}$$

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[1] Bancroft and Davis: J. Phys. Chem., 32, 1 (1928).

where the symbols have the same meaning as stated before. The molecular weights thus calculated are listed in column 7 and are probably the lower limit for the molecular weight of water in solutions of the concentrations represented. This distinctly shows that the molecular weight of water is increasing with increasing concentration.

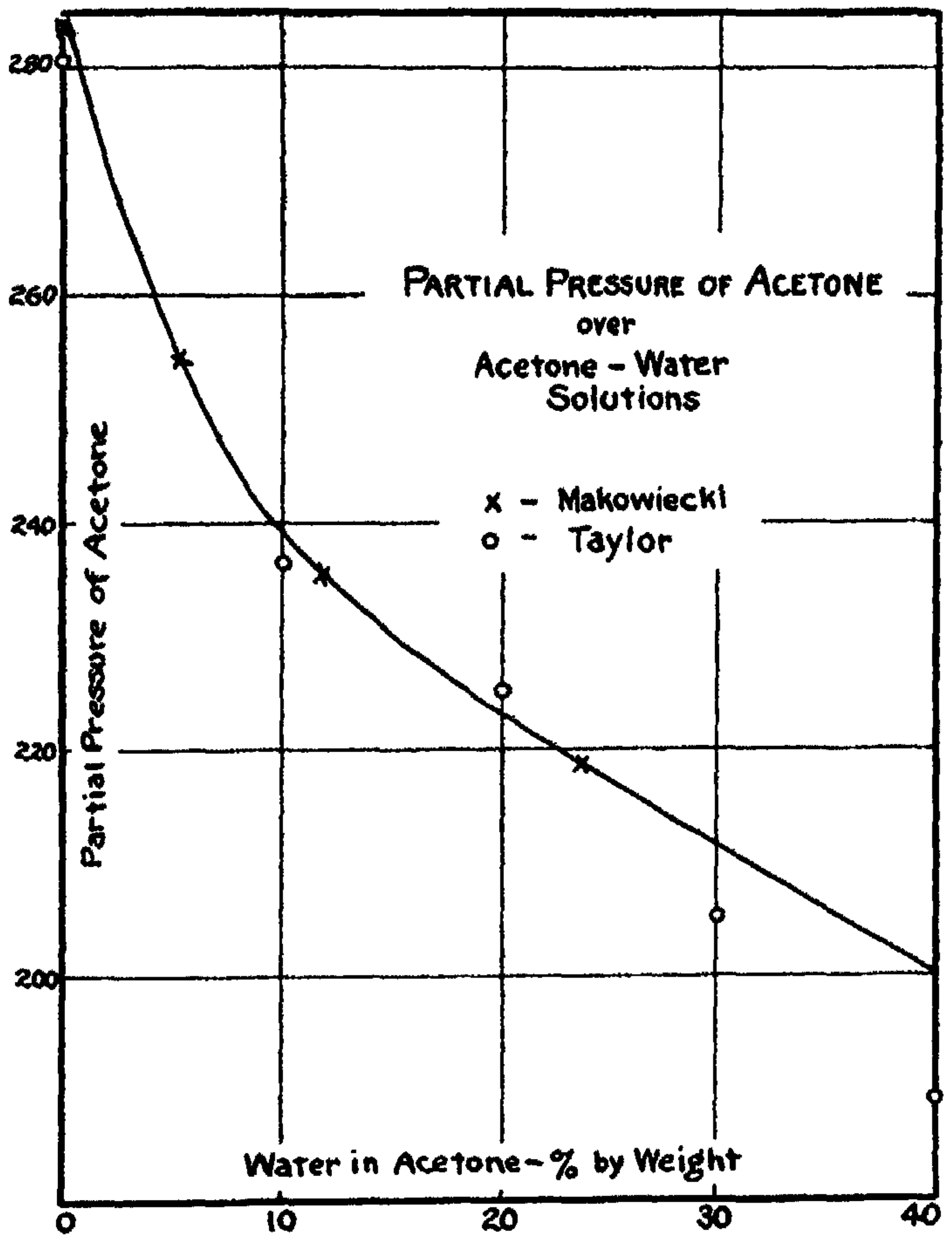

Fig. 2

Makowiecki claims reasonable accuracy for his work and it would have to be quite accurate in order to give such a smooth curve. The only thing which casts doubt is the high value for the vapor pressure of acetone at 30°. He reports 284.5 mm. whereas other investigators give 281 mm. or lower. Taylor[1] has also determined partial pressures of acetone over acetone-water solutions, but one glance at the graph of his data, Fig. 2, shows it to be of

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[1] J. Phys. Chem., 4, 683 (1900).

little use in the range here employed. However, for the sake of comparison, a straight line relationship for p_1 was assumed between zero percent water and the ten percent solution, and a calculation made for the osmotic pressures, again using

$$PV_m = RT \ln p_0/p_1$$

This gave values for P falling almost exactly on the curve for membrane number 1.

Other membranes were used but lower values were obtained for the osmotic pressures than with membrane number 1. Inasmuch as the higher pressures are more nearly correct, they alone are of use in making calculations. The results of the experiments with membranes other than number one are listed in Table II.

Here again column 1 gives the percent water in the solution before placing in the bomb, the non-pressure side being filled with pure, dried acetone. Column 2 gives the percentage difference in water content of the two solutions at the end of the run. Column 3 lists the measured osmotic pressures and column 4 the number of the membrane employed.

TABLE II

% by weight water		Osmotic press. in Atmospheres	Membrane Number
Start	Finish		
2.25	2.14	10.3	2
2.27	——	10.7	2(25°)
——	1.93	8.3	3
——	2.94	12.7	3
2.45	2.21	9.5	4
1.36	1.26	4.5	5
1.73	1.56	5.6	5
2.45	2.02	7.75	5
2.73	2.42	9.3	5
2.09	1.79	7.2	6
2.40	2.13	8.6	6
3.18	2.58	10.5	6
3.35	3.00	12.3	6
4.00 (?)	3.30	14.1	6
3.09	2.50	11.2	6
2.27	1.88	8.7	6

Membrane number 2 like number 1 (see Table I), was of commercial sheet rubber 0.064 inch thick. Numbers 3,5, and 6 were also commercial sheet but were only 0.024 inch in thickness. Membrane number 4 was made from acetone-extracted rubber.

The experimental values for all six membranes as well as the theoretically calculated ones are plotted in Fig. 3, as percent water against osmotic pressure in atmospheres. Instead of one curve for all membranes which would be the case if the membranes acted efficiently (as a copper ferrocyanide membrane does toward sucrose solutions), there is a curve for each one. With the exception of the last two readings with membrane number 6, which are probably erroneous, each of the membranes gives a good curve, the pressure being nearly a linear function (in the range studied) of the percentage water. The distance between the curve and the x axis is roughly dependent on how little water goes through the membrane. Although the analyses are not perfect they do show that water passes through a thin membrane more readily than

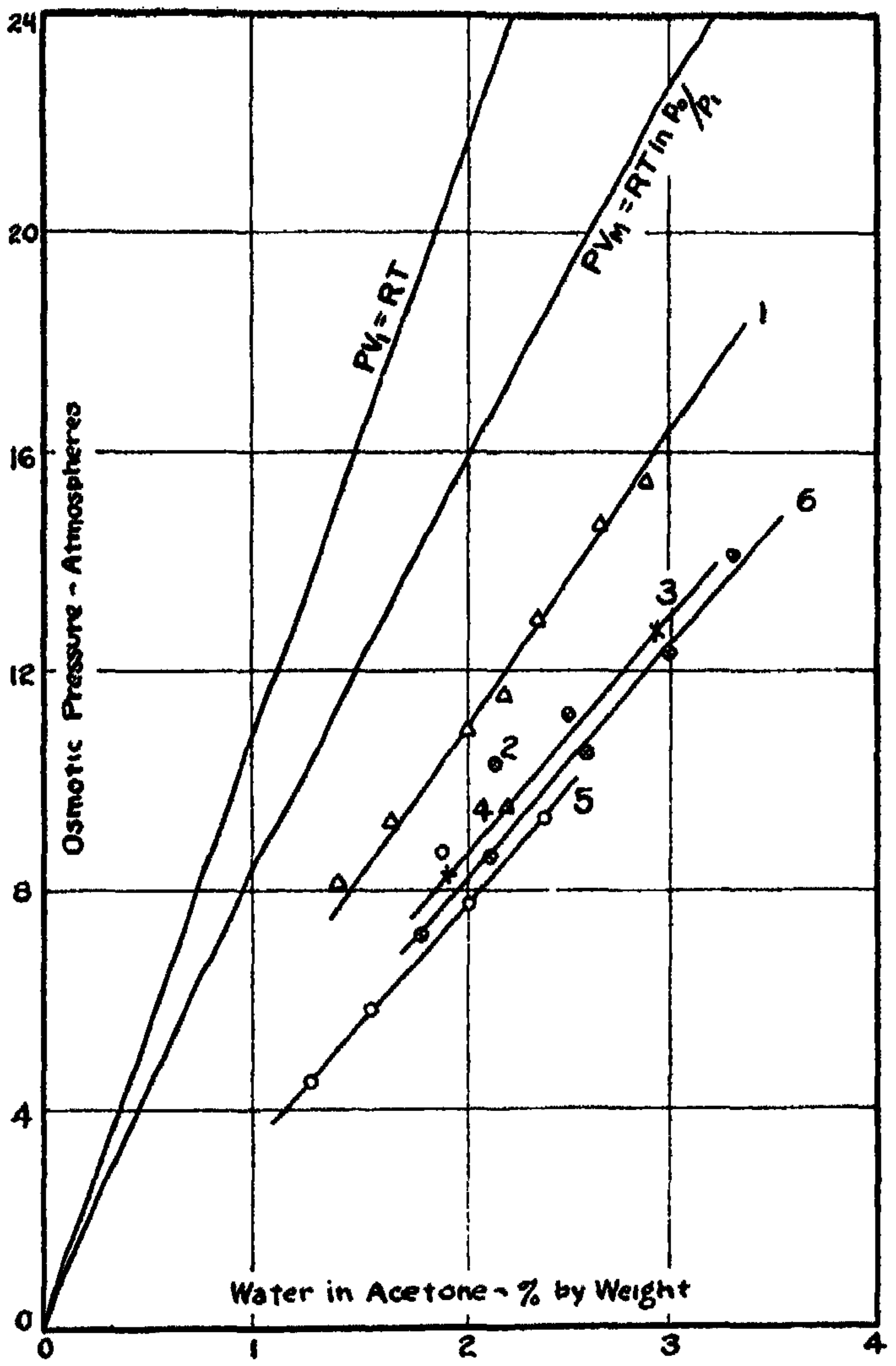

FIG. 3

through a thick one, and that higher pressures are given when less water passes through. The probable reason why membranes of the same kind do not give identical readings is that there are slight variations in the thickness caused by stretching in the bomb. Small inequalities of composition may be another cause of difference.

It would seem possible from the above considerations to increase the thickness of the sheet until a maximum osmotic pressure was developed. Through such a sheet little or no water would find its way. Actually this is not practicable because of the slow rate at which the solvent moves through the thicker membranes.

The question will be asked, "Why were the solutions in the bomb not stirred?" An internal stirrer operated by a solenoid through which an electric current could be passed at intervals was arranged for the pressure side of the osmometer and was run for some time. However, the non-pressure side is the one so constructed as to require stirring because the holes in its supporting plate are not only small but the plate is covered with a piece of muslin. On the pressure side of the apparatus the holes in the plate are much larger and are countersunk. By the application of nearly sufficient pressure to balance the osmotic flow the amount of solvent entering that side of the bomb is almost negligible. Certainly not more than two or three drops would pass through in half a day. On the non-pressure side a film of solute which has leaked through the membrane might easily be conceived of as in contact with it, and retained in the muslin and the small holes of the plate.

To be effective the stirring should be continual, and so agitate the liquid that if a film should concentrate next to the membrane it will be swept off as fast as formed. The device should not interfere with the reading of the meniscus in the indicator tube and should be tight so that none of the acetone may either leak out or evaporate. The bore of the indicator tube is too small to make a solenoid arrangement practicable. Possibly some device could be contrived for stirring in this side of the bomb but I have not been able to think of one which would be properly effective.

If the low pressures measured are caused by the slow diffusion of the solute which passes through the membrane, then anything which would aid diffusion, whether stirring or some other method should increase the measurable osmotic pressure of a given water solution. The first condition favorable to diffusion is a higher temperature. The runs were made at 30°, so it is not advisable to make a determination at higher temperatures. One experiment was made at 25° and another at 30° using the same membrane and the same concentration, as recorded in Table II under membrane 2. The lower temperature actually gave a little higher pressure which no doubt was due to experimental error, but even so diffusion did not change enough to markedly alter the osmotic pressure developed.

Another method for increasing diffusion is by changing the design of the apparatus. Plate P_2 was removed so that there was nothing between the membrane and the solution in the pressure side of the osmometer. In addition the position of the membrane is vertical and gravity should take care of all concentration changes in a very short time. Morse[1] believes that stirring within a cell is unnecessary. On the non-pressure side the process of diffusion should be aided if, instead of the plate with the small holes, we substitute one with larger holes and these countersunk away from the membrane. This necessitates the use of a piece of wire gauze as support in place of muslin.

A determination was made with the changed design. The membrane was of the commercial sheet, 0.064 inch, and the solution put in the pressure side was 1.7% water. The pressure measured was somewhat lower than that with membrane number 1 in spite of the increased possibilities for diffusion. The flow of solvent was greater through the membrane thus supported which may account for the pressure not being higher, as greater flow of solvent would probably carry through a larger amount of water. That this membrane was not defective is shown by the fact that it was used satisfactorily to determine the osmotic pressures of citric acid solutions, where it checked admirably with other membranes.

This modified arrangement of the supports for the membrane is that used later for the citric, malic, and tartaric acid solutions.

Rubber diaphragms are thus found to be somewhat permeable toward water in acetone, so that the maximum osmotic pressure cannot be measured. This could have been predicted, for it is well known that rubber absorbs water and that the amount taken up over long periods of time is considerable. Lowry and Kohman[2] give a number of references on the work done in this line. Professor Bancroft suggested that if a rubber membrane separated water from a salt solution, osmotic flow toward the solution should result. Qualitative experiments were conducted to show this to be true.

Rubber membranes were attached to thistle tubes in much the same way as that used by Kahlenberg[3] in his work. Over the rubber was securely tied a piece of muslin. A Witt plate served as additional support and was held in place by a second piece of muslin. A 4N NaCl solution was placed inside the bulb which was surrounded by distilled water. The rise of liquid in the stem served to indicate the direction and magnitude of the flow. The stem was stoppered with a small cork to prevent evaporation of the solution.

Several different membranes were employed and the result was the same in each case. Up to the time when the rubber disintegrated there was no doubt of the flow through the membrane toward the salt solution. Unvulcanized sheets were made by dissolving crepe rubber in benzene, pouring out the resulting solution on a glazed plate, and allowing the benzene to evaporate. The membranes so formed could with care be attached to the thistle tube without being damaged. Vulcanized membranes of dental rubber were also used. These lasted longer and in one case a rise of 21 cm. was noted in 600 days. This corresponds to about 4 cubic centimeters, the amount of water which passed through the membrane.

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[1] Am. Chem. J., 45, 519 (1911).

[2] J. Phys. Chem., 31, 23 (1927).

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

The unvulcanized membranes usually showed a more rapid flow at first but began to disintegrate rapidly after 50 to 75 days and to allow salt to pass into the outer solution. The average rate of flow for these membranes was about 0.5 cm. per week, making the passage of water through the membrane about 0.1 cc. per week.

Attention is called to the fact that these experiments were made to show only the presence of osmotic flow, and that rubber is much more permeable to water than to salt. Of course the rate of flow is too small to allow for quantitative measurements.

The use of sodium chloride suggests the possibility of inorganic salts as solutes in acetone, as they should tend much less than water to pass through the rubber.

Sodium Iodide as Solute

The common inorganic salt most soluble in acetone and most likely to be of use is sodium iodide. At 25° 41 grams of the salt dissolve in 100 grams of solvent which allows a wide range of concentrations over which to work. The rubber membranes should be much less permeable to this solute than to water and consequently osmotic pressures nearer the maximum should be measured. Furthermore these measurements should throw an interesting light on the theory of solutions of sodium iodide in acetone. Conductivity measurements show a certain amount of dissociation while the rise of boiling point seems to indicate a normal molecular weight.[1]

The procedure and apparatus for measuring osmotic pressures of solutions of sodium iodide in acetone were the same, with the following exceptions, as that used for acetone-water mixtures. Sodium iodide was found by experiment to go through the membrane very slightly so that with time the marked change of composition is not noticed as it was with the water as solute. So attempts were made to reach the maximum pressure which could be developed by applying pressures too high and too low. By noting the direction and rate of rise or fall of the meniscus in the indicator tube the equilibrium pressure could be ascertained. In each case an attempt was made to find the point where there was no flow of liquid as shown by the constancy of the level in the indicator tube. As a rule this pressure was maintained for a day to determine whether a further change would ensue.

The apparatus was modified by removing plate P_2. It was found that if the membrane were put in place between the two halves of the bomb immediately after removal from the extracting acetone there was very little wrinkling of the rubber.

Difficulties were encountered at once in attempting to measure the osmotic pressures of these solutions. This will perhaps best be shown by an example. A 3.6% solution of anhydrous sodium iodide in acetone was put in the pressure side of the osmometer and pure acetone in the other. From measurements of other and more concentrated solutions it was expected that the pressure of this solution would be somewhat greater than 8 atmospheres. This amount

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[1] McBain and Coleman: Trans. Faraday Soc., 15, 27 (1919).

was applied for a trial. Over night the level in the indicator tube rose several millimeters, showing that the pressure was too great. So it was released to 7 atmospheres. By the next morning the level was still rising, so the pressure was reduced to 5.5 atmospheres. Over night the level dropped seven millimeters giving evidence that the applied pressure was too low. Consequently it was raised to 7.2 atmospheres. Over night a decline in the level of 2 mm. occurred. Pressures of 8.0 and 8.5 showed a drop in the level while 9.0 gave rise and at 8.75 there was no appreciable flow in either direction.

The process was somewhat the same in nearly every measurement. The rate of flow was small even with the thinner vulcanized membrane (0.024 inch thick). The results follow in the order of their being run.

Experiment			
No. 1	8.5% NaI	Higher than	17.6 atmos.
" 2	4.4 "		11.6 "
" 3	4.4 "		7.15 "
" 4	6.5 "	Higher than	13.0 "
" 5	4.4 "		7.3 "
" 6	6.1 "		14.4 "
" 7	5.3 "		13.9 "
" 8	4.4 "		11.5 "
" 9	3.6 "		8.75 "

With the exceptions of numbers 3 and 5 the agreement is fair.

A check up on the results using the lowering of the vapor pressure to calculate the osmotic pressure was made. A 4.8% solution gave a lowering of 4.9 mm.; or P, the osmotic pressure when calculated from the formula

$$PV_m = RT \ln p_0/p_1$$

gives the value 7.2 atmospheres, which, of course, is as low as that found for even a 4.4% solution (Nos. 3 and 5)

Next after removing the solutions from the bomb, the vapor pressure lowerings of numbers 7 and 9 were determined. The solution taken from the pressure side of number 7 showed a vapor pressure lowering of 17.8 mm., as compared to pure acetone. This corresponds to an osmotic pressure of about 27 atmospheres. 13.9 atmospheres was the pressure found and 7.1 is that calculated from $PV_1 = RT$. Number 9 gave a lowering of 15.4 mm. corresponding to an osmotic pressure of about 23 atmospheres whereas 8.75 was the value found.

One glance of comparison at these solutions and the freshly prepared 4.8% solution shows that something in the former has undergone a decided change. The 4.8% solution was found to give a lowering of the vapor pressure of 4.9 mm. while that of the 3.6% solution on removal from the bomb was 15.4 mm.

The method for the determination of the vapor pressure lowerings required that the solutions be cooled in a carbon dioxide-ether bath. The solutions which were made up and directly cooled yielded a white crystalline precipitate while these which had remained in the bomb for some time showed no such precipitate even with more concentrated solutions.

To test whether traces of water would cause these solutions to have such abnormally large vapor pressure lowerings, 0.25 cc. of water was added to 25 cc. of a 4.8% solution of sodium iodide in acetone. This concentration of water was far more than that which the solution removed from the osmometer could have contained in the most extreme case, since the solutions were in contact with the air as little as possible during the filling and emptying of the bomb.

The vapor pressure lowering of this solution was greater than the pure 4.8% solution but by no means as great as, for example, the 3.6% solution removed from the bomb in number 9.

It had been noticed that the mercury and iodide solution formed a precipitate when stirred up together. When the bomb was taken apart its inner surface was discolored and showed a superficial attack. The brass plug A had become greenish black in contact with the solution.

Sodium iodide then appears to act on the metals when only slight traces of moisture are present and liberates oxides which react with the acetone to form condensation products. Whatever happens, the vapor pressure of the solution is distinctly lowered. This affects the osmotic pressure of the solutions more or less, as the case may be, as to whether or not the products which are formed are able to pass through the membrane. It is my belief that they go through to some extent because the vapor pressure of the non-pressure (solvent) side which was used opposite the 3.6% solution was determined and found to be 2.3 mm. lower than the pure solvent. This decrease could hardly be due to the trace of iodide which was found in the solution and which had passed through the membrane.

So the attempt to measure the osmotic pressures of sodium iodide solutions in acetone by means of the large apparatus was abandoned and trials were made with a modified Kahlenberg apparatus. This simple type of osmometer has the advantage that the solution is in contact with metal only at the surface of the mercury in the manometer. The diameter of the tube at this place is about 6 mm. and the point of contact is well removed from the main part of the solution. This modification of Kahlenberg's apparatus is superior in that pressure may be applied to the solution within the osmometer through the stopcock H by raising the mercury leveling bulb, Fig. 4. Thus pressure on the solution may be varied at will. This is advantageous in point of time and because so little solvent has to flow through the membrane before equilibrium is reached. As with the large apparatus, the pressure is set at different values and then note is taken as to whether the level of the mercury rises or falls. When a pressure is reached at which the level in the manometer remains constant that pressure is taken to be the equilibrium pressure. Care must be taken that the temperature of the bath be well regulated as acetone has a high coefficient of expansion.

The flanged end of the thistle tube was covered in the usual way (see Kahlenberg: loc. cit.) with the exception that the rubber used was that from toy balloons and was somewhat thicker than dental rubber. The bulb was filled and sealed as by Kahlenberg. The outer solution, acetone, was contained in a 500 cc. wide-mouth bottle provided with a one-hole stopper through which was inserted the stem of the thistle tube below the side arm. After the bulb was filled and sealed, acetone was put in the bottle and the stopper was loosely inserted. Then the bottle and contents were brought to the temperature of the thermostat, 25°. After the excess air had escaped, the stopper was pushed in securely and made air-tight and water-proof by means of a coating of paraffin. The whole apparatus except the capillary manometer and leveling bulb was immersed in the bath.

Always after raising the pressure the level in the manometer showed a rapid decline, varying in amount according to the magnitude of the pressure increase. This was followed with a slow rise whenever the osmotic pressure of the solution had not yet been reached. The process of reaching equilibrium was rather tedious and inaccurate because of this preliminary decline of the mercury level in the capillary and also because the acetone's rate of flow through the membrane is slow especially when the applied pressure is near the equilibrium pressure.

However, experiments using this apparatus with two different membranes were run. In each case the inner solution was 1% by weight of sodium iodide in acetone and the solution in the bottle was pure acetone. The first experiment after about a week of trial gave a pressure of 105 cm. while the second gave a pressure of somewhat over 100 cm. In neither case was there more than a slight trace of iodide in the outer solution.

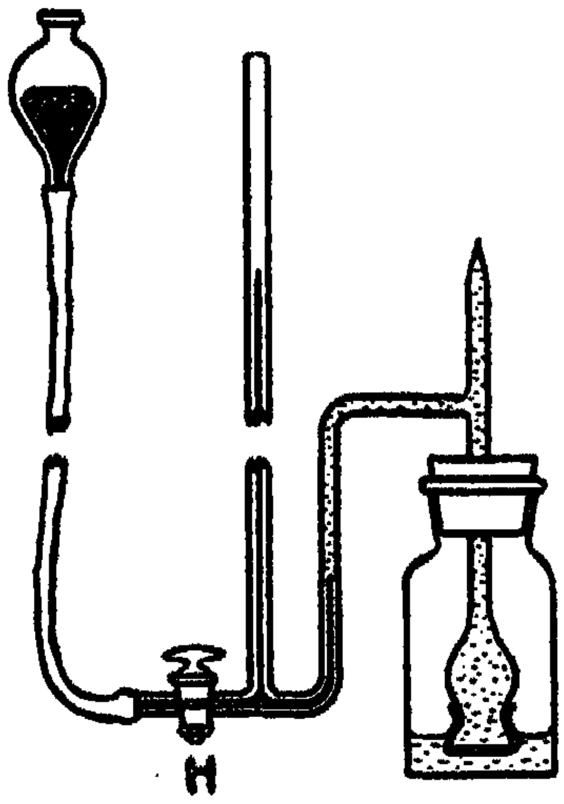

FIG. 4

In both experiments the determination of the equilibrium pressure was accomplished with great difficulty. The preliminary change after adjustment of the height of the mercury column was very bothersome. The cause of this change is thought to be as follows: The membrane in spite of its support of muslin and plate readjusts itself a small amount when additional pressure is applied. Because of the small diameter of the capillary a slight change in the position of the membrane results in a relatively large change in level in the manometer.

If the values for P of these solutions are calculated from $PV_1 = RT$ we find that the pressure should be about 98 cm. This of course assumes no dissociation. The values of 105 and 100 cm. which were found compare very favorably with the theoretical value, and possibly show some dissociation, although the determinations are not accurate enough to demonstrate it plainly.

Thus sodium iodide has proved itself to be unsuitable for use in the metal apparatus but would probably be all right in a non-metal one. The operation of the Kahlenberg apparatus is too slow and accompanied by too many obstacles to make the further use of this type advisable. The membranes of vulcanized rubber were almost impermeable toward the salt and the difficulties were not of the same kind as those encountered with the solutions of water in acetone.

Organic Acids as Solutes

Sodium iodide having been found unsatisfactory for use in the large apparatus it becomes necessary to search for other solutes. Since rubber itself is mostly hydrocarbon, something which would be as little soluble in other hydrocarbons as possible ought to be a suitable solute. Most inorganic salts meet this requirement but they are sparingly soluble in the solvent which we have chosen. Besides they might act in the bomb very much as did the sodium iodide. So attention was turned to organic compounds. A high oxygen content would seem to be most desirable, but such compounds are usually insoluble or only slightly soluble in acetone, as for example the sugars.

Succinic, malic, tartaric and citric acids all have a high oxygen content and a fair solubility in acetone. Of these four succinic acid is the least soluble and has the lowest percent of oxygen. However, two measurements were made with it. A 3.76% solution was put in the bomb and a balance of pressure attained. This pressure was found to be 4.0 atmospheres in each of the two solutions determined. Each run required about a week as the flow of acetone was very slow, even though the membrane used was the thinner vulcanized commercial sheet, (0.024 inch). At the end of the second run the solutions were on removal analyzed by titration with NaOH using phenolphthalein as indicator. The solution from the non-pressure side contained about 0.12% acid showing that about one thirtieth of the original acid had passed through the membrane.

Assuming no association and calculating the pressure which should be developed from the formula

$$PV_m = RT \ln \frac{N + n}{N}$$

we find P should be approximately 5.9 atmospheres, whereas 4.0 was the value found. Thus, like water, succinic acid does not give the maximum osmotic pressure as quite appreciable amounts go through the membrane.

The next experiments were with citric acid which not only contains three carboxyl groups but also one hydroxyl. The rubber should be pretty impermeable to this compound since the carbon residue within the molecule is well covered by the oxy groups. It has the further advantage of being much more soluble in acetone. The anhydrous acid was made by heating the crystalline acid at 70°.

Malic acid has a larger percent of oxygen than succinic acid and is much more soluble in acetone. Tartaric acid is not as soluble but the oxygen content is higher.

The apparatus was modified as previously mentioned under the determinations of the pressure of water in acetone solutions. Plate P_2 was omitted and plate P_1 was changed so that the holes were not only larger but were countersunk. This arrangement gives more chance for solvent to flow through the membrane. Instead of the muslin used in the earlier experiments as a support for the membrane a piece of fine wire gauze was employed.

The following table gives the data obtained with the organic acids as solutes.

TABLE III (Temp. 25°)

Membrane number	Solute (acid)	Molality	Osmotic pressure in atmospheres Found	Calculated $PV_m = RT\ln p_o/p_1$	 $PV_m = RT\ln\frac{N+n}{N}$
8	Citric	0.185	3.9	——	4.5
8	"	0.224	4.7	——	5.5
9	"	0.229	4.9	——	5.6
8	"	0.304	6.0	——	7.5
8	"	0.448	9.3	10.4	10.8
8	"	0.526	10.9	12.1	12.7
9	"	0.675	14.1	15.2	16.1
7	"	0.684	14.3	15.5	16.3
8	"	0.795	16.5	17.8	19.0
8	"	0.952	19.8	21.0	22.5
9	Malic	0.53	9.9	12.4	12.8
9	"	1.16	20.6	24.8	28.9
9	Tartaric	0.44	9.3	——	10.7
10	Succinic	0.24	4.0	——	5.9

Column one gives the number of the membrane used, and column two the solute. Column three gives the moles of acid dissolved in a liter of acetone. Column four gives the osmotic pressures in atmospheres which were found by direct measurement, and column five those which were calculated using the formula

$$PV_m = RT \ln p_o/p_1$$

in which p_o and p_1 were found by vapor pressure measurements. In column six are the values calculated assuming no association of the acid. The formula used was

$$PV_m = RT \ln \frac{N + n}{N}$$

In the experiment in which membrane number 7 (0.0064 inch commercial sheet) was employed the pressure was set first too low and then too high. The fall and rise of the meniscus in the indicator tube were compared and from this comparison the equilibrium pressure was presumed to be 14.3.

Such a pressure was maintained for four days during which time no change in the level in the indicator tube occurred. This demonstrates two things. First that the hastily found value, 14.3, is exceedingly close to the equilibrium pressure and second, that the measured osmotic pressure with a given membrane does not change appreciably with time. The membrane was so nearly impermeable to the solute that only one part in 7000 of the citric acid went through as shown by analysis of the solutions after removal from the bomb.

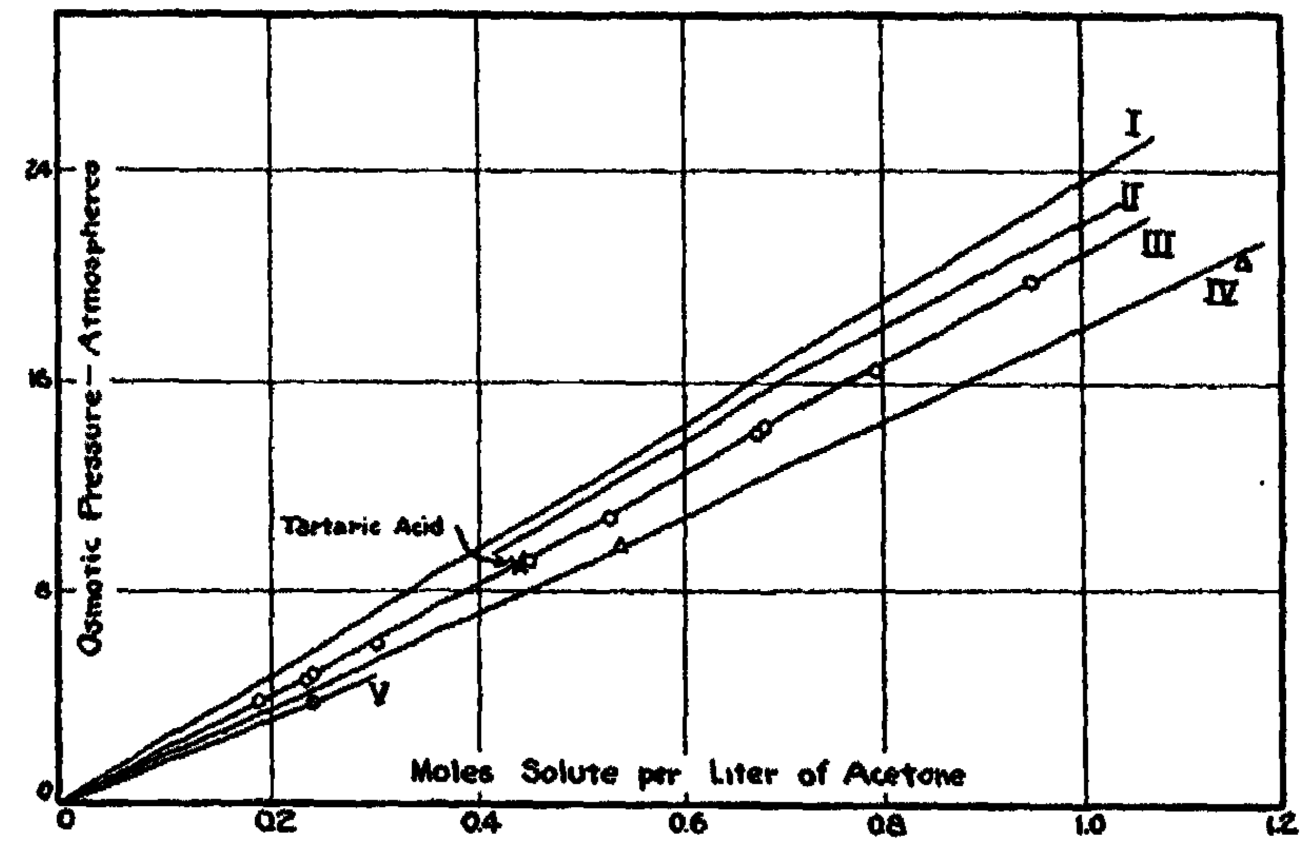

Fig. 5

Membrane number 8 was of 0.024 inch commercial sheet. Flow of solvent through this was considerably faster and it was possible to complete a determination in about two days. Analysis of the solutions showed that only about one part in 500 of the original citric acid passed through the membrane. This small change in composition could not be detected by a decreasing pressure.

Membrane number 9 was from a 0.14 inch thick toy balloon which had long been soaked in acetone to remove the dye. Acetone flowed through it more rapidly than through either of the others but it proved almost as impermeable toward citric acid as the thicker one. It was this membrane which was used to determine the pressures developed by the solutions of malic and tartaric acids. It proved almost equally impermeable to tartaric and citric acids while malic acid passed through in somewhat larger amounts.

The pressures of the citric acid solutions agree extremely well with each other even when membranes of different thickness are employed. They appear to be very nearly a linear function of the concentration and the variance from this line is remarkably small. While the pressure for a 0.95 molal solution is about 12% lower than the ideal it is only 6% less than that calculated from the vapor pressure lowering. This 6% error leaves a very narrow margin for those who declare that the gas laws do not hold at all.

In Fig. 5 the results with the different solutions are plotted as moles of solute per liter of acetone against the osmotic pressure. The highest curve, number 1, is that of the ideal solution with values of P calculated from

$$PV_m = RT \ln \frac{N + n}{N}$$

This formula being used rather than

$$PV_1 = RT$$

because as n becomes larger it cannot be neglected. In case one mole is dissolved in one liter of acetone the ratio of n to N is 1/13.5 and, as Bancroft and Davis have pointed out, this introduces quite a large error into the calculation.

Curve II is that for the pressures calculated from the vapor pressure lowering using the formula

$$PV_m = RT \ln p_o/p_1$$

Curve III is for the pressures found for citric acid solutions; curve IV for malic acid and curve V for succinic acid. The one point determined for tartaric acid lies almost on the curve for citric acid.

Disregarding any slight polymerization which enters in the case of acids dissolved in acetone we note the following: the less the solute passes through the membrane the nearer is the approach of the measured pressure to the ideal. Vulcanized rubber is almost impermeable toward citric and tartaric acids, and, contrary to the case with water as solute, a thick membrane gives no higher pressure than a thin one. Malic acid passes through a little faster than citric acid and its measured pressures are lower. Succinic acid goes through still more quickly and the pressures are lower. (We have seen earlier in this paper what difficulties were encountered with water passing through the membrane). No doubt the experiments could be carried further. Ethyl alcohol dissolved in acetone would probably give a curve lower than that for water and propyl alcohol one still lower. We should finally come to a substance toward which the rubber is exactly as permeable as to acteone. With this solute no pressure could be measured. We could even imagine a curve with a negative slope in which the acetone would be solute and another liquid the solvent. Such might be the case with ether-acetone mixtures or certainly with benzene-acetone solutions.

Bigelow, Bartell and their co-workers[1] have shown that the osmotic pressure developed by a solution separated from the pure solvent by inactive membranes (membranes of porous material with the pores clogged with finely divided substances such as lamp black, silica, etc.) is increased with the decrease in the size of the capillaries in the membrane. This means that the membrane is becoming more nearly semipermeable—or that not so much solute finds its way through the pores. Morse[2] has shown that a copper

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[1] Colloid Symposium Monograph, **4**, 234 (1926) and many previous papers.

[2] Am. Chem. J., **45**, 558 (1911).

ferrocyanide membrane is truly semipermeable to aqueous sucrose solutions. In sixty days an experiment showed that no leakage of sugar occurred. If on the other hand it was desirable to measure the osmotic pressure developed by other substances, especially those of lower molecular weight, the membrane had to be made thicker and more dense. Only when the membrane is really semipermeable, as is the case with copper ferrocyanide membranes toward sucrose solutions in water, is the true thermodynamic or the maximum osmotic pressure measurable. The preceding experiments on the osmotic pressure measurements of acetone solutions bring out this fact strikingly.

Criticism of Kahlenberg's Work

In Kahlenberg's paper (loc. cit.) an experiment is recorded wherein the osmotic pressure of a normal silver nitrate solution in pyridine at 20° was found to be about 15 atmospheres. In another experiment, the same concentration of silver nitrate, with the temperature at $-16°$ to $-15°$ there was very little flow of solute, only 15.6 cm. in 3 days; whence it was concluded that the osmotic pressure of the solution is negligible. This is of course a case of experimental error; but where the trouble lies is not easily seen. It is obvious, however, that time enough was not given for equilibrium to be reached. Furthermore, the 15.6 cm. represents the flow of solute and not osmotic pressure. Had a pressure sufficient to stop this small flow been applied it would doubtless have been very great. The cell used was not arranged for this and the membrane was not even supported.

We should expect pyridine to be less soluble in rubber at low temperatures and if this is true the rate of flow through the membrane might become so slow as to be mistaken for almost no flow. Rubber becomes almost impermeable to CO_2 at low temperatures.

Traxler[1] has measured the change in rate of flow of pyridine through rubber to pure water with change of temperature and found that the rate doubled from 5° to 15° and again doubled from 15° to 25°. With water it would not be possible to measure lower than zero but if the rate fell off as fast as that, by the time the temperature reached $-16°$ the rate of flow into a comparatively dilute solution of silter nitrate (dilute as compared to the concentration of pure water used by Traxler) might easily fall to a very small amount.

Traxler brings in the assumption that it is monohydrol which causes the pyridine to pass through the membrane into the water and since at lower temperatures there is less monohydrol the inducement for pyridine to permeate the rubber is less than at higher temperatures. Had he arranged his cell to measure the flow of pyridine through rubber into a sugar solution of pyridine, as I did, he would have had to offer an altogether different explanation. I found that the flow of pyridine through rubber to a 0.125 N sugar solution was roughly three times as large at 23° as at 3°. The rate was not great even at $+23°$ and it is reasonable to expect that at $-16°$ it would fall

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[1] J. Phys. Chem., **32**, 127 (1928).

to a very small value indeed—thus making measurement of osmotic pressures extremely difficult and possibly leading one to conclude that the pressure developed is almost zero. Three days are hardly long enough to wait to assume that the osmotic pressure is negligible. When an aqueous salt solution is separated from pure water by a rubber sheet, it is several days before osmotic flow becomes evident. It would be incorrect to say that such a solution can therefore develop no pressure. We have seen that in 600 days a height of 21 cm. of solution was reached, and had it been experimentally possible to determine what pressure would have been required to prevent that slow but certain flow, there can be no doubt that it would have been a large one.

Summary

1. A modification of Raoult's osmometer has been designed for measuring the osmotic pressures of non-aqueous solutions with vulcanized caoutchouc as the diaphragm.

2. Acetone was selected as the most suitable solvent.

3. With water as solute the membrane was so permeable as to necessitate a special method of procedure.

4. Different rubber membranes gave different values for the measured osmotic pressures of a definite concentration of water in acetone. The pressure developed depended on the thickness of the membrane and the ease with which water was prevented from passing through it.

5. The molecular weight of water as calculated from the lowering of the partial pressures of acetone, using the formula

$$n/N = \ln p_0/p_1 = \frac{g/M_1}{N}$$

was found to be approximately 25 at about 2% weight concentration. The value increases with increasing concentration.

6. The molecular weight of water as calculated from the best measurements of the osmotic pressures over the same range gives the value as about 36.

7. Osmotic flow of water through a rubber membrane resulted when concentrated sodium chloride solutions were separated from pure water by thin rubber sheets.

8. Measurements of the osmotic pressures of sodium iodide solutions in acetone proved unsuccessful because of a change in the solution when in contact with the metal of the osmometer. Rubber is, however, almost impermeable to sodium iodide dissolved in acetone.

9. A modification of Kahlenberg's osmometer was employed to measure the osmotic pressures of two solutions of sodium iodide in acetone. The results of these experiments show the pressures to be very near the theoretical ones, although the difficulties in measurements were such as to make the readings somewhat uncertain.

10. Measurements of the osmotic pressures of solutions of succinic, malic, tartaric, and citric acids in acetone were made.

11. An increase in the oxygen content as in the series succinic, malic, and tartaric acids decreased the permeability of the rubber toward the acid.

12. Tartaric acid, although having a smaller molecular weight than citric acid, is prevented from passing through the membrane just as efficiently as is the latter.

13. Measurements of citric acid solutions show the rubber to be only very slightly permeable to this compound. The pressures found with different membranes agree extremely well with each other.

14. The measured pressures are 12 to 15% lower than those calculated from the gas law but only 6 to 11% lower than the values calculated from the vapor pressure lowerings. Considering the difficulties of measurements and the fact that the membrane is not truly semipermeable, this error is hardly sufficient to say that the gas laws do not hold. It is rather to be said that when experimental difficulties are overcome, the measured osmotic pressures of non-aqueous solutions will be found to be those required by the gas laws.

Acknowledgment

This problem was suggested by Professor W. D. Bancroft and carried forward under his direction. To him I wish to express my thanks. I also wish to thank the United States Rubber Company, the B. F. Goodrich Rubber Company and Dr. W. C. Geer for kindly furnishing most of the membranes used in this work.

Cornell University.

SOME OBSERVATIONS UPON WETTING POWER*

BY E. L. GREEN**

Introduction

When an orchard is to be sprayed with a liquid insecticide the readiness of wetting becomes an important consideration. If the spray is intended to cover plant organs with poison and kill or repel insects seeking to bite them, the liquid must wet the plant. If the purpose is to place a toxic substance upon the insect's body, the insect itself must be wetted. This has been discussed at some length by English (1),*** Stellwaag (2), and others.

Since spraying operations are finished for a given area in an extremely short time, the spray liquid must wet its object rapidly. Insects will escape and do their customary mischief, if for any reason areas are not covered by the spray, even though the insecticide possesses satisfactory toxicity.

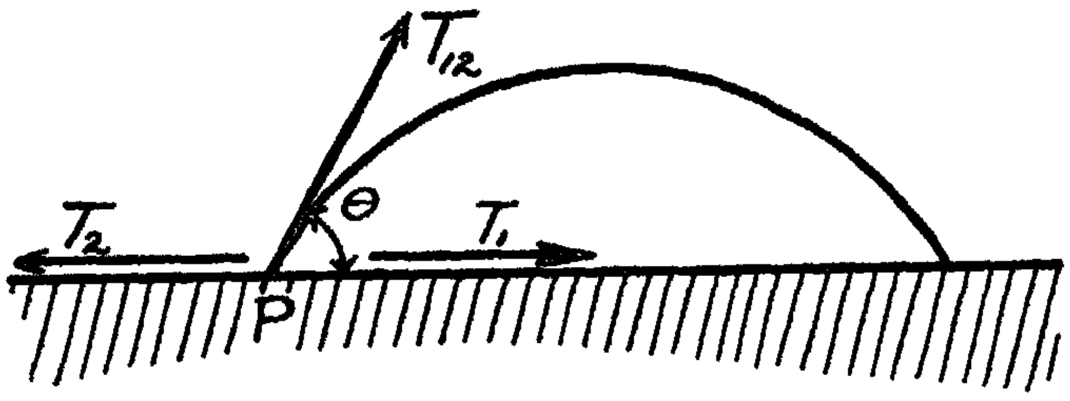

FIG. 1. Taken from Freundlich (11) among others.

In the studies on the chemistry of oil sprays carried on at the Washington Agricultural Experiment Station since 1923, the importance of wetting power has often recurred, but it was not thought possible to measure it. Within the present year, however, English (1) has published a description of a method, by which, with a simple apparatus, a measurement can be taken on a liquid and a solid which appears to define the intensity of wetting. The measurement is of the angle of contact.

A treatment of the theory of wetting and the angle of contact that has been used in various other texts is given by Freundlich (11, p. 157) and may be reviewed briefly. Fig. 1 illustrates a drop of liquid resting upon a solid. The edge of the drop may be considered a series of ultimate particles of liquid, as at P, which are subject to tension in three directions; due to the surface tension of the liquid, T_1, the surface tension of the solid, T_2, and the liquid-solid interfacial tension, T_{12}.

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** Assistant Chemist, Washington Agricultural Experiment Station, Pullman, Wash.

*** Numbers in the text refer to the bibliography at the end of the paper.

It is now to be assumed, or conditions so regulated that the position of P upon the surface of the solid is determined by these tensions and no others. Then for equilibrium:

$$T_2 = T_{12} + T_1 \cos \Theta$$

$$\text{or } \mathrm{Cos}\ \Theta = \frac{T_2 - T_{12}}{T_1}$$

Assuming, as do many authors, among whom Quincke (14) appears to have been the first, that these three tensions define the tendency of the drop to spread over the solid; the angle Θ may be used to measure that tendency. Θ may not be less than zero nor greater than π (180°), and over this range the wetting power is great for small angles, being greatest when Θ is zero; and small for large angles. It reaches a minimum when Θ is 180°, for which it has been said to be zero and theoretically to touch the solid at only one point. Many authors associate "perfect wetting" and a zero angle of contact, in which case the drop spreads out in a thin film over the solid surface.

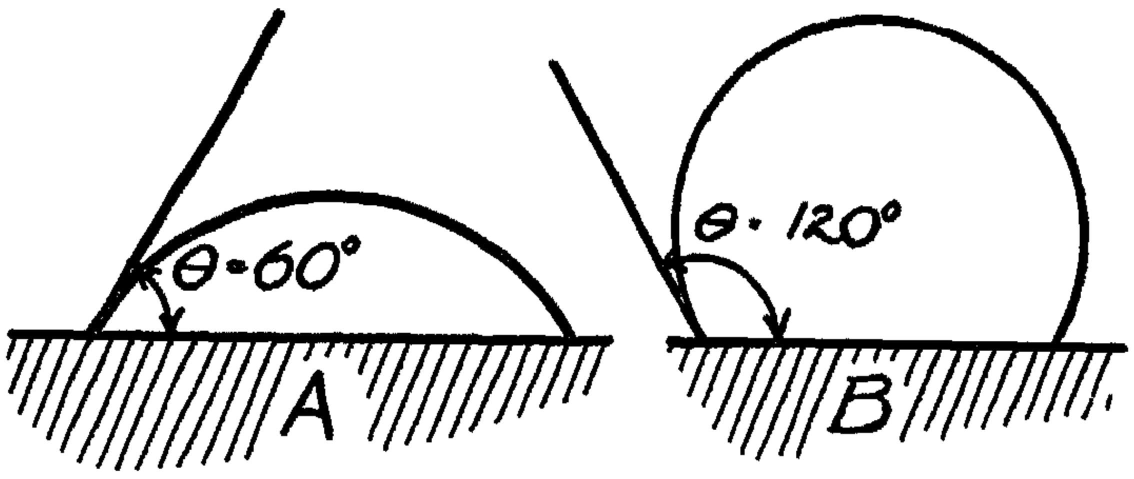


FIG. 2. (Taken from English)

Fig. 2 illustrates two hypothetical cases. The adherence of the drop to the solid is manifestly greater in A than in B.

To be valid for discussions based on this derivation the angle of contact must be measured when all other forces are prevented from affecting it. Also that portion of the liquid-air interface that is affected by no other forces in any case and displays the contact angle is extremely narrow. The rest of the surface of the drop is a smooth curve.

To avoid some of these difficulties the method of the rotable solid surface was devised (6). The apparatus includes a wide-mouthed container for the liquid; a means for holding, raising, immersing and turning a specimen of the solid; and a device for measuring the angle which the surface of the solid makes with the horizontal free surface of the liquid. A complete description of a suitable apparatus is given by Stellwaag (2) and by English (1).

For the purpose of the method, it is assumed that when a solid is partially immersed in a liquid, the free surface of the liquid always meets the surface of the solid in a definite angle of contact, fixed by the properties of the liquid and solid, no matter what angle the solid surface may make with the horizontal. Thus a portion of the surface of the liquid is generally compelled to incline itself to the horizontal, according to this relation; and the surface joining this portion to the horizontal free surface assumes a smooth curve. Then if the solid is turned an inclination of the solid can be found for which the portion of the liquid surface constrained to turn with it will be horizontal. No warping would occur in the surface of the liquid, since it is now horizontal throughout, and this condition discloses the endpoint. The inclination of the solid surface to the horizontal is now the angle of contact, and is to be measured by any convenient means.

The following diagram illustrates the operation.

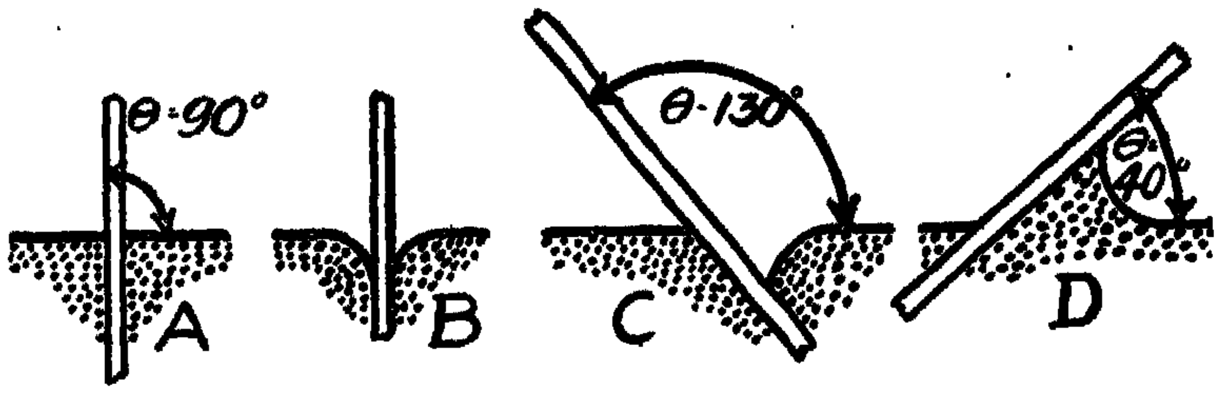
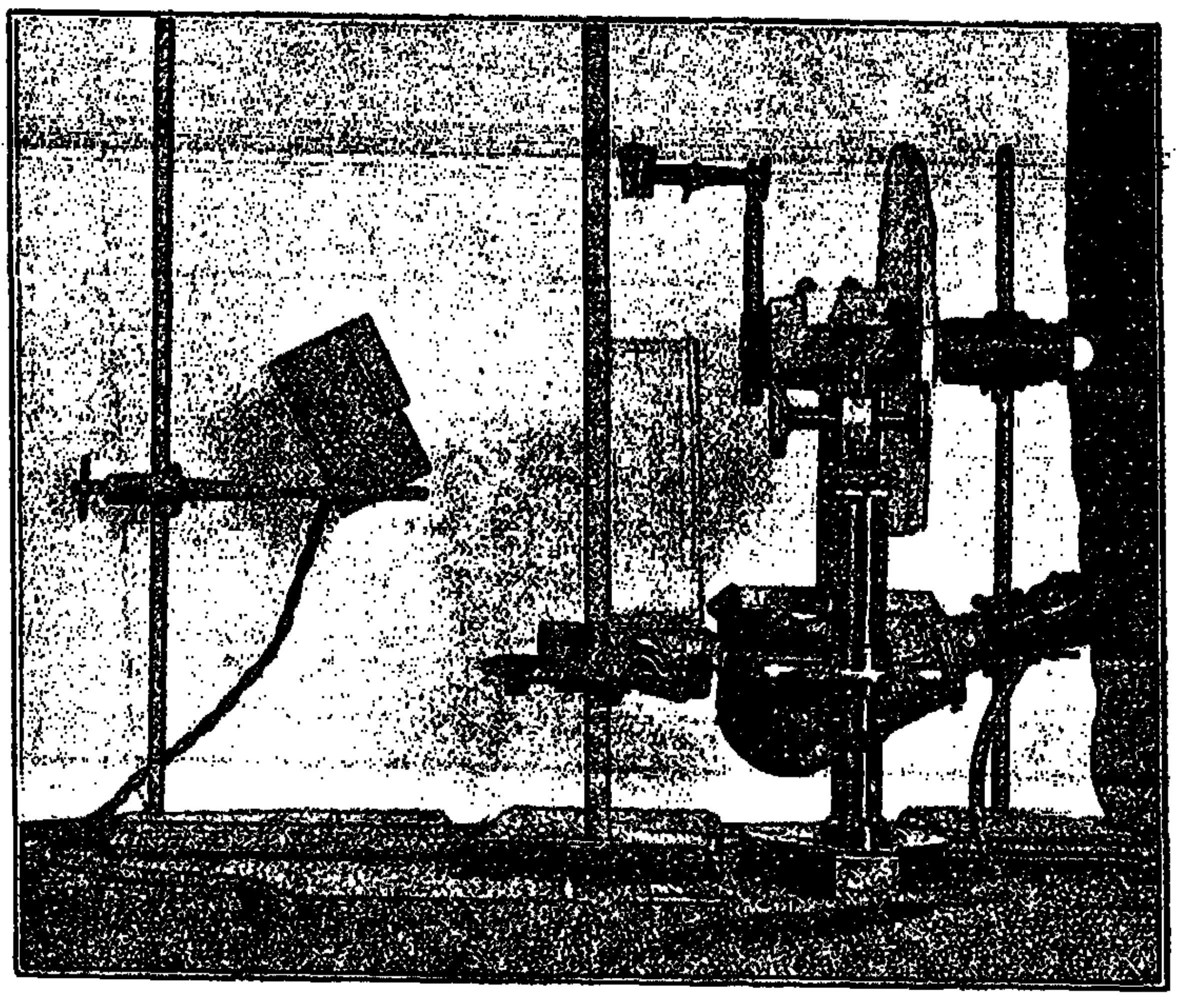


Fig. 3. (Taken from English) (1).

In A is shown the condition when the angle of contact is 90°. In B it is greater than 90° and for the measurement the solid must be rotated to a position such as is shown in C. In D is shown the endpoint for an angle of contact less than 90°. It is to be added that it is best to arrange the apparatus so that the axis of rotation coincides with the line of intersection of the solid surface and the horizontal plane determined by the free surface of the liquid

Experimental

As a part of the study of oil spray materials, an extension of the data and observations of English and Stellwaag to the materials used in Wenatchee was undertaken. An apparatus was constructed as illustrated in the accompanying photographs, after a study of the two reports available and of the experimental conditions. Some departures are evident, but the principle was carefully retained. The principal part of the apparatus is an axis long enough to turn steadily and without lateral motion. A handle by which to turn it was fastened at one end, and at the other was attached an arm by which an ordinary object clamp could be carried across the side of a vessel high enough to interfere with the axis itself. The axis itself was made hollow and cross-hairs were fixed in the object end. Thus with a mirror behind the jar the object could be shifted in the clamp and the height of the axis regulated with the rack and pinion of the microscope stand so that the line of sight, now also the axis of rotation, passed near the line of contact of the solid and liquid. This adjustment completed, the mirror was removed and a white background placed behind the jar for the observation. The liquid was illuminated by lamps so placed that the surface was thrown into sharp relief and the observation was made by means of a three times magnifying telescope. To measure



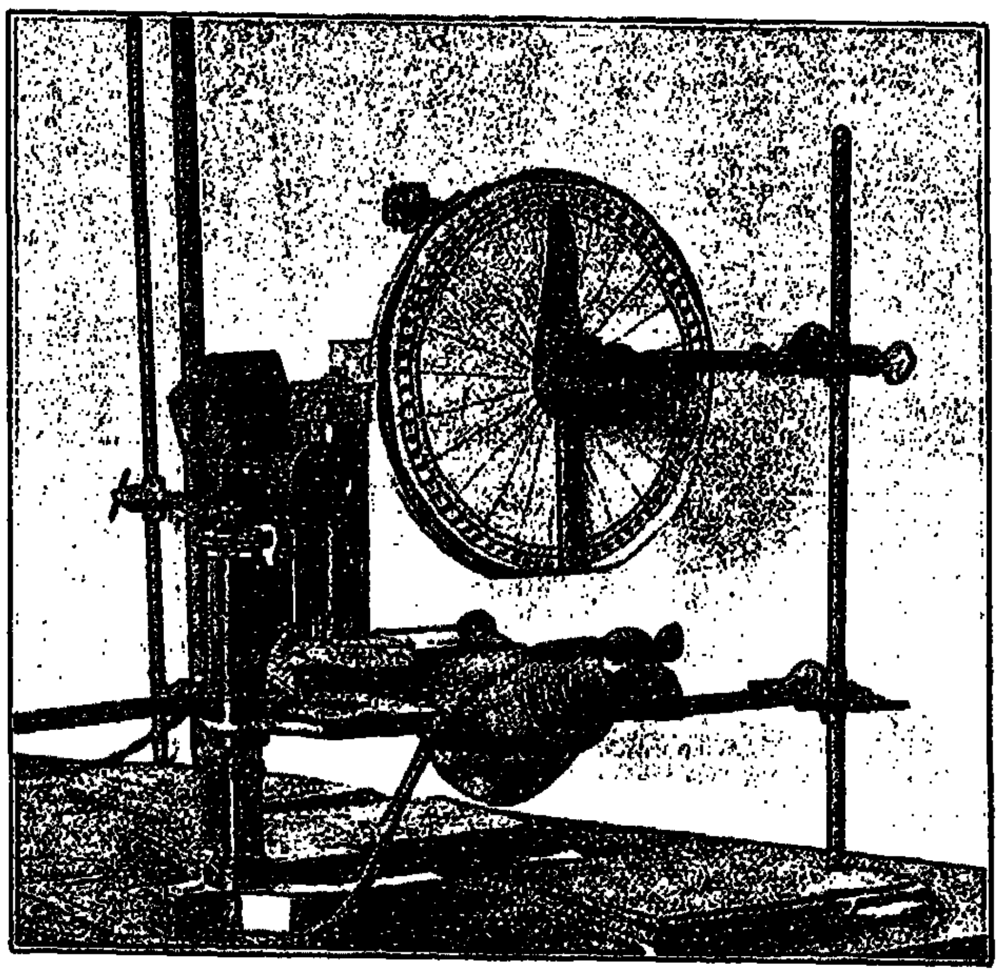


Plate I

the angles, a graduated circle was attached to the support and a pointer was fastened to the handle so as to travel over the circle as the object was turned.

These arrangements made the location of the end point possible to within a degree or so. There remained, however, some difficulty in the location of the beginning-point, namely, the reading of the protractor when the surface of the solid stands exactly vertical. Due to irregularities of the object this could not always be depended upon to be 90 degrees. The cross hairs and other arrangements mentioned were able to assure a minimum of displacement of the object during rotation, but could not fix its direction. Since it had already been decided to use apple twigs and glass rods for objects and these have approximately parallel sides, it seemed reasonable to simply read the end point first on one side and then on the other, and determine theta as half of 180 degrees minus the difference between these readings.

When the apparatus had been constructed it was turned over to Mr. James Marshall, a graduate student in entomology, to be used in the collection of data for comparison with field trials and with the surface tensions of the same solutions. The data remain in his hands and may be published later. From the first, however, he claimed that the end-point lacked definiteness. Improvements in the visibility and in the mechanical precision of the apparatus did not remove the objection. He finally stated that, although there appeared to be an end-point, he could still see a thin sheet of liquid above the line of contact on the object, whether glass or twig, and could do nothing to prevent its presence there. This is, of course, altogether contrary to the behavior required by the theory at the end point.

Review of Literature

This statement was found to be true and a study of the present state of the theory upon which this method is based was begun. A curious survival of the method in spite of very serious objections was disclosed. For example, the angle of contact of water with glass has been definitely decided to be zero and has hardly been a subject of controversy for several years. Yet this set-up indicates for it a value in the neighborhood of 30°. It was noticed, however, that whenever an end-point was established, examination of the water surface under still higher magnification would discover some curvature remaining in the water surface.

A brief review of the literature on the angle of contact and related discussions leads back to the classical discourses on surface energy and surfaces by Laplace, well over a hundred years ago. A review occurs in Poynting and Thomson (8 pp. 173 ff). As long as these treatments are found to be valid, a consideration of the surfaces that form the angle of contact would be incomplete without due regard for them. The experimental work on the angle of contact may be thought of as beginning with Quincke (14). He devised the method of measuring the angle of contact of liquids in drops and bubbles resting against solids, and it is believed that he originally published the derivation, sketched above, of the equation: $\text{Cos}\ \Theta = \frac{T_2 - T_{12}}{T_1}$.

His method, however, seems not to be altogether successful, as shown by Magie (15). In certain cases it has contributed to the misunderstandings as well as helped to dispel them, and it seems to require more study before it can become very useful.

Ramsay and Shields (16) and Lord Rayleigh (17) became interested in the angle of contact because it introduced an unknown into their determinations of surface tension by the capillary elevation method. Their work definitely indicated zero as the angle of contact of water with glass. But the work of Richards and Carver (9) in 1921 and that of Bosanquet and Hartley (13) in the same year has surely disposed of that question permanently. Taking precautions against evaporation, the one work describes the search for a break in the narrow beam of light reflected from the region about the line of contact. Bosanquet and Hartley allowed a little water to spread over a large glass plate and examined the edge of the sheet of water for a break in refraction. Had a real angle of contact occurred that was greater than 30 minutes of arc they believe they would have found it.

Some difficulty has been encountered in tracing the original authorship of the method of measuring angles of contact with the rotable solid surface. English (1) ascribes it to Stellwaag (2); Stellwaag credited it to Bosanquet and Hartley (13) or to Sulman (3). Bosanquet and Hartley are silent on this point, and Sulman states that it was devised by Dr. H. A. Wilson and was communicated by A. K. Huntington in the Faraday Society, 1905, under the title, "The Concentration of Metalliferous Sulfides". Up to the present I have not been able to read this article. But from the quotations it is evident that it led to disagreements with the more exact methods of the physicists and physical chemists. Instead of taking up the vagaries of the results on biological material like leaves and twigs, which introduce more complicating factors, it may be sufficient to point out that all users of the method find that it gives erroneous results with water and glass. Hence it can not be used in its present form for other liquids and other solids, where the results by this procedure can not be verified by recourse to other methods or previous work.

Discussion

It is self-evident that the finished spray must be capable of completely wetting the object sprayed, leaving no dry areas. Now wetting is said to occur when an object, on being dipped into a liquid, can not be completely separated from the liquid by the simple process of emergence, for a film of the liquid adheres to the solid. More rigorous definitions are difficult to set up. Wetting occurs, says Freundlich in "Colloid and Capillary Chemistry," (1922) when the surface tension of the solid is greater than the sum of the surface tension of the liquid and the tension of the liquid-solid interface. Returning to the diagram of Quincke (14), Fig. 1, the cosine of the angle of contact assumes its maximum value, one; the angle becomes zero, and yet the surface tension of the solid is greater than the sum of the tensions that oppose it. It is reasonable to expect, in general, that this indicates a value of the interfacial tension that is small in comparison with the surface tension of the solid. Millikan (7), twenty years earlier, said that if wetting occurred the angle of contact was zero. The fact that Freundlich used a zero angle of contact to define wetting and Millikan used the idea of wetting as a foundation for his approach to a zero contact angle shows that an intimate connection was a familiar idea. At any rate, the tendency of the liquid to spread over the solid has brought the angle of contact to an irreducible minimum, and its cosine to an ultimate maximum, but the tendency itself may not have reached a limit. The angle of contact is a bit of evidence over only a limited portion of the possible range of this tendency; which, according to Quincke's notation as adopted by Freundlich is from $T_2 - T_{12} = -T_1$ to $T_2 - T_{12} = +T_1$. Now from figures available today T_2 (the surface tension of the solid) may be a hundred times as great as T_1 (the surface tension of the liquid). When one of these terms is so large the total probable range must be very much larger than from minus T_1 to plus T_1.

The entomologist will probably never be content with wetting that remains within this range. In fact both physical chemists and physicists say, in effect, that where a finite contact angle is observed wetting does not occur. Therefore, nearly all of the spraying operations of today use wetting phenomena not characterized by contact angles. From this discussion, wetting power or wetability may be defined as the degree in which the surface tension of the solid exceeds the tension of the liquid solid interface. Following this concept there may be positive, negative, slight, or great wetting.

Returning to the needs of the entomologist, it will not suffice to supply him with a spray liquid that will eventually spread over the objects to which he seeks to apply it. He works in many cases out in the open orchard; if his liquid is slow in spreading it will drain off the tree and finally evaporate before it has attained complete coverage. He must have as much speed as possible without producing an excessively thin film of liquid; for then he will not be able to place upon the surface enough of the insecticide. Here, possibly, the mobility of the liquid plays a part. It is difficult to imagine good spraying being done with a viscous liquid. Yet it is also easy to imagine excessively low viscosity causing a troublesome run-off. The surface tension, also, from an inspection of Quincke's formula, must not be too high. However, since water is to used be for the dispersing medium, it is perhaps idle to speculate upon viscosity and surface tension, because from considerations of expedience and expense they cannot be greatly altered.

The remarks previously made about the magnitudes of Quincke's quantities T_1, T_2, and T_{12} are of importance in the case where the surface is contaminated with some other liquid or gas, as with air or grease. The surface and interfacial tensions of these materials are of the same low order as those of water, hence wetting is retarded unless the spray liquid displaces them rapidly. The force with which the spray is applied may be sufficient to take care of the air film. Its action resembles rubbing the liquid into the solid with the fingers.

But in the case of certain hairy insects and plant organs the difficulty has not been successfully met. In fact the factors operating to cause the difficult wetting have not been completely explained.

The velocity of wetting might be proposed as a definition of "spreading" as the word is used by practical sprayers.

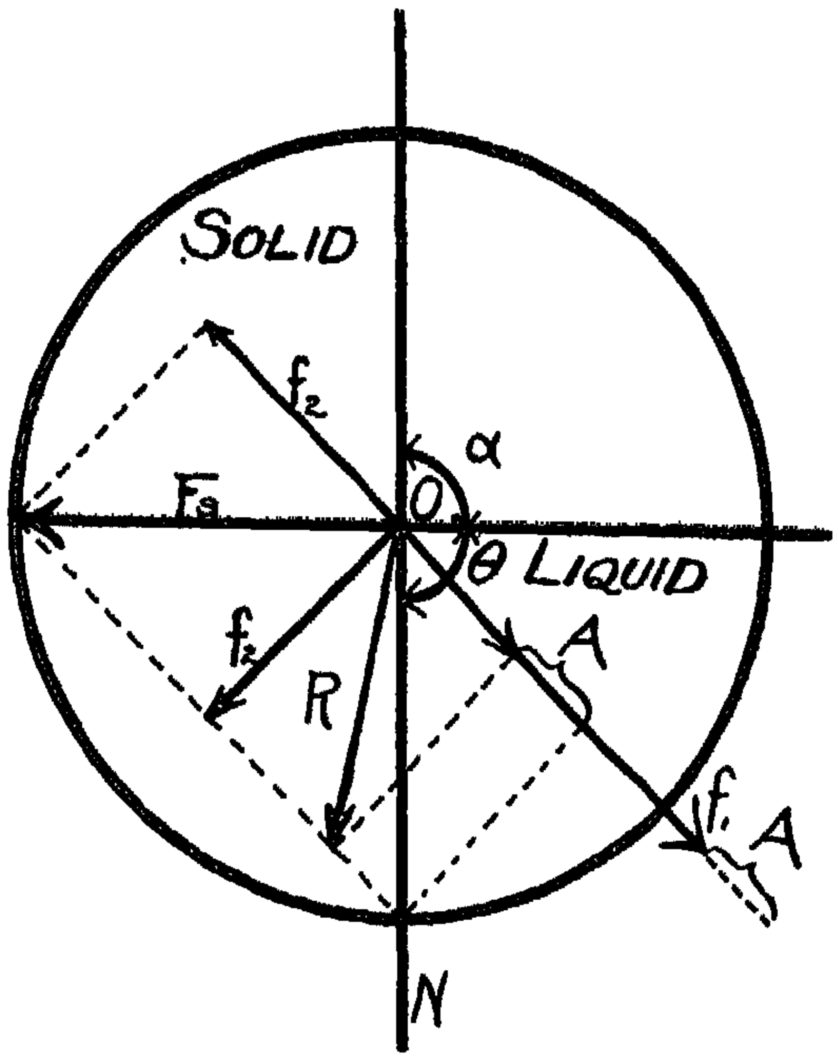


FIG. 4
(Taken from Millikan)

There is still a word to be said about the diagram of Quincke. It has been pointed out that surface tension is not in every sense a force, but may also be regarded as potential energy. It is true that a surface acts like a stretched flexible cord. Nevertheless, according to the physicists, all its manifestations are due to forces at right angles to the surfaces, and can be explained upon that basis. This aspect is neglected in the treatment by Quincke.

Also there is the matter of that resolution of the surface tension T_1; letting it be considered a force for the moment. What has become of $T_1 \sin \Theta$? Why does it not curl up the edge of the drop? It should; for it would appear that it is unopposed except by gravity, which is vanishingly small for the mass at O. Perhaps it is taken care of by an attraction of the solid. Then there should be a similar pull upon the adjacent liquid where the surface tension has no opposing effect. It would appear then that the drop is not in equilibrium and will spread over the solid, making the contact angle always smaller.

A rational consideration of the situation is possible when no forces are considered as capable of causing motion except those at right angles to the surfaces. For the fundamental theory, the following is taken from Millikan (7 p. 187):

"It only remains to show why a liquid in a capillary tube assumes a curved surface—a task of no difficulty when it is remembered that a liquid surface can be in equilibrium only when it is perpendicular to the resultant force acting upon its molecules. This fact follows simply from the fact of the mobility of the particles. For, if the force acting upon the surface molecules had any component parallel to the surface, the molecules would move over the surface in obedience to this component, i.e. equilibrium would not exist. If, then, O X (Fig. 4) represents the line of junction of a liquid with a solid wall; f_1 the resultant of all the forces exerted upon the molecules at o by such portion of the liquid as lies within the molecular range when the liquid surface is assumed horizontal and f_2 the resultant of forces exerted upon the same by the molecules of the wall which lie either above or below the horizontal line passing through O, then three cases may be distinguished:

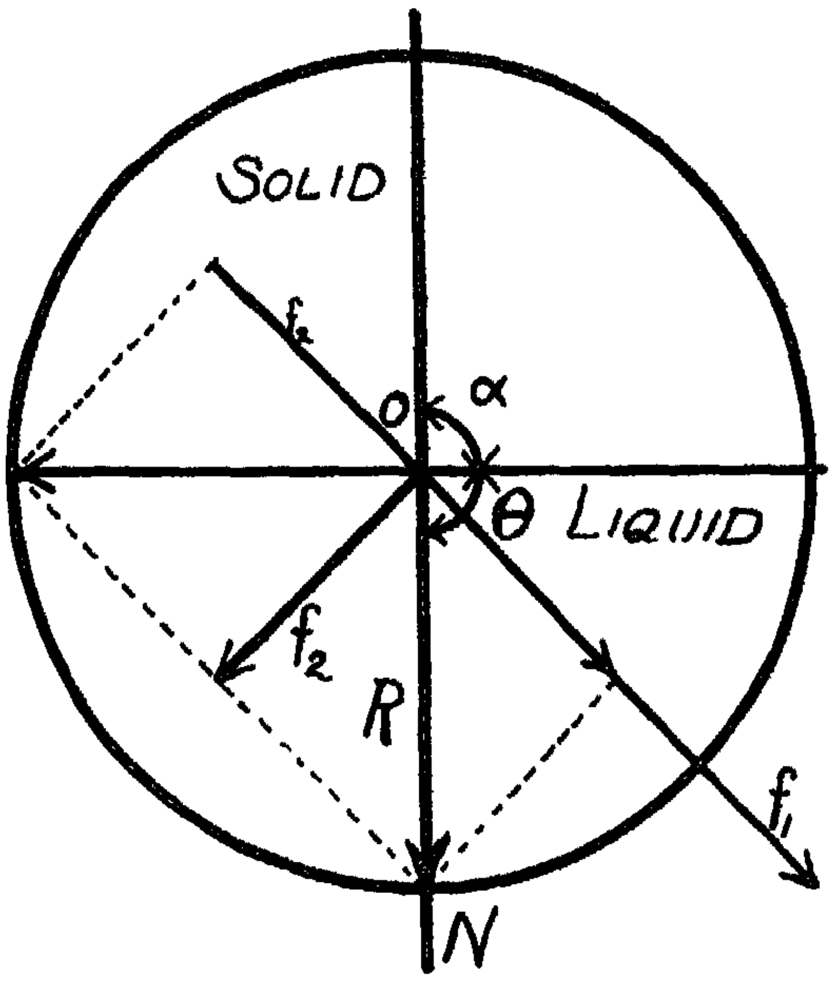


FIG. 5

"*1*. That in which $f_1 = 2\ f_2$. In this case, as appears from Fig. 4 the cohesion of the liquid is exactly equal to twice the adhesion of the solid and liquid and the final resultant R is parallel with the wall. Hence, equilibrium exists in the condition assumed, i.e., the angle of contact is 90°.

"*2*. That in which $f_1 > 2f_2$; the resultant R then falls to the right of O X — — — — — — — — — — — — —.

"3. That in which $f_1 < 2f_2$. The resultant R then falls to the left of O N. (See Fig. 5). Hence equilibrium can not exist until the surface near O has become concave and the angle of contact obtuse."

This is the case of greatest interest in this discussion and it seemed worth while to continue the examination of the resultants of the forces.

The angle which Millikan calls alpha is the supplement of the angle theta, and this is called the angle of contact by many writers, especially the physical chemists. It is within the liquid and approaches zero for liquids that wet well and 180° for liquids that wet poorly. The case of a liquid and a solid whose angle of contact Θ is less than 90° is illustrated in Fig. 5. For this case, Millikan has shown in the above citation that $f_1 < 2f_2$. This relation between the forces occurs at the instant when the solid has just been dipped into the liquid, the line of contact is beginning to rise with respect to the free liquid surface, and the angle Θ, changing to attain its equilibrium value, passes through 90° or $\pi/2$. It seems reasonable to suppose that, for the same liquid and solid, no matter what value Θ may have at a given instant, the force exerted upon the ultimate particle of liquid at O by the solid is constant. This assumption is made in what follows and this force is called F_S. It is the resultant of the two f_2's of Fig. 4, and is equal to $\sqrt{2}f_2$. The characteristic of the case under discussion is that $2f_2$ is quantitatively greater than f_1, the

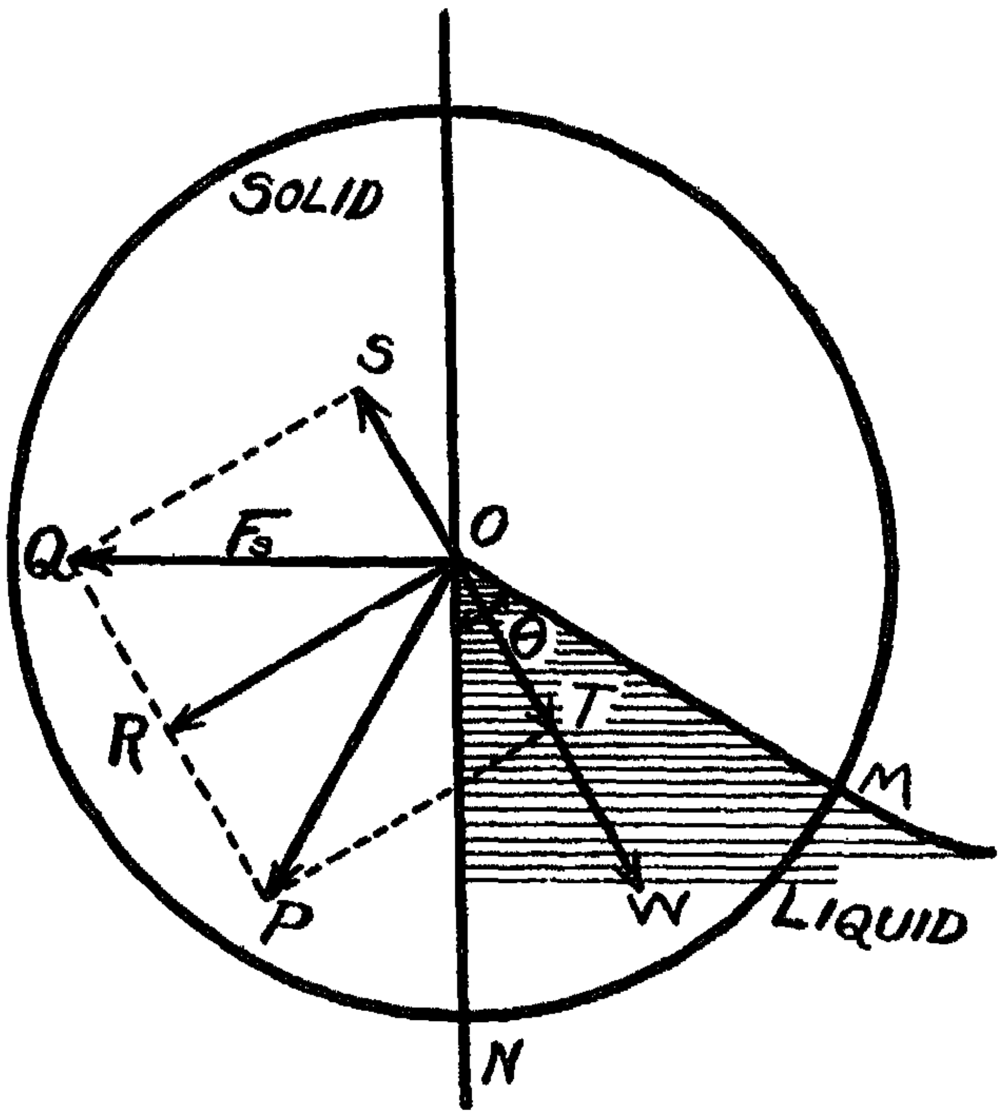


FIG. 6

force exerted upon the ultimate particle of liquid at O by all the other molecules of the liquid that are near enough to affect it at the instant when Θ passes through 90°. Let this difference be A.

Then $2f_2 = f_1 + A = \sqrt{2}F_S$

Now as theta varies the resultant of the forces exerted upon the ultimate particle of liquid at O by all the other molecules of liquid that are near enough to affect it may not be constant. The range beyond which these forces may be neglected is represented in the figures by the circle. It has been reported to be between a ten-thousandth and a millionth of a millimeter (5). If this variable force is called F_L, then only as Θ passes through and is momentarily equal to 90°; $F_L = f_1$.

New let Θ, the angle of contact, diminish by the climbing of the liquid, according to the conclusion for this case reached by Millikan. Fig. 6 represents a certain instant when it is less than 90° and greater than zero. The liquid within the molecular range of O is contained in the segment of the circular cylinder whose base is the segment of the circle cut out by the angle Θ and whose altitude is the unknown, but constant length of the line of contact. Therefore this volume is linearly proportional to Θ expressed in radians. And if the forces summed up in F_L are in proportion to the number of molecules exerting them, then F_L is likewise proportional to Θ. That is

$$F_L = C \text{ (an unknown constant) } \times \Theta \text{ and when}$$
$$\Theta = \pi/2,\ F_L = f_1 = C \times \pi/2$$

As Millikan has shown, F_L lies along the bisector of Θ. It is so represented in Fig. 6.

Now let F_L, which is assumed to be constant, be resolved into OS parallel to OW, the line of action of F_L, and OR perpendicular to it. OW represents F_L in magnitude and direction. From W lay off WT equal to OS. Then the resultant OP of OR and OT represents the resultant in magnitude and direction of those forces acting upon the ultimate particle of liquid at O that have been taken into account in this discussion. It makes an angle ROP with OR, whose magnitude is to be determined.

By various elementary propositions in geometry the angles MOW, WON, SQO and QOR are all equal to Θ/2.

Now let it be assumed that the liquid has attained equilibrium and has ceased climbing, and attempt to derive an expression for Θ in terms of the constants A and C. As has been quoted above from Millikan, who takes it originally from Laplace, at equilibrium the final resultant OP must be perpendicular to OM, the surface of the liquid; that is POM must be a right angle.

NOQ and QOR have been drawn to be right angles.

Then at equilibrium the angle ROP is equal to Θ/2.

Also OT = OS = TW
2 OS = OW

$$\text{Now OS} = \text{OQ} \sin\frac{\Theta}{2} = \text{F}_\text{S} \sin\frac{\Theta}{2}$$

$$= \frac{\text{f}_1 + \text{A}}{\sqrt{2}} \sin\frac{\Theta}{2}$$

$$= \frac{1}{\sqrt{2}} (\text{C} \times \frac{\pi}{2} + \text{A}) \sin\frac{\Theta}{2}$$

$$\text{And OS} = \frac{\text{OW}}{2} = \frac{\text{C} \times \Theta}{2}$$

Substituting and simplifying

$$\frac{\text{C} \times \Theta}{2} = \frac{1}{\sqrt{2}} (\text{C} \times \frac{\pi}{2} + \text{A}) \sin\frac{\Theta}{2}$$

$$\frac{\Theta}{\sin\Theta} = \frac{\pi}{\sqrt{2}} + \frac{2\,\text{A}}{\text{C}}$$

If the assumptions made may be justified, and if no other forces need to be taken into consideration, it may be stated that, for given values of A and C, equilibrium will not exist except for some value of the angle Θ that satisfies the equation:

$$\frac{\Theta}{\sin\Theta} = \frac{\pi}{\sqrt{2}} + \frac{\sqrt{2}\,\text{A}}{\text{C}}$$

Now the term $\frac{\Theta}{\sin \Theta/2}$ has the value π at $\Theta = \pi$ (180°); 2.220 at $\Theta = \pi/2$ (90°); and from this value it decreases slowly but steadily for decreasing values of Θ until, for such small angles that sin Θ/2 may be set equal to Θ/2, it becomes exactly 2. The right hand side of the equation has the value 2.2202 × 2A/C. Thus, if A were zero, Θ equal to π/2 would satisfy the equation, which is Millikan's case I quoted above, under Fig. 4.

But if A and C are real, positive quantities, as has been assumed, no value of Θ between O and π/2 will satisfy it. Thus the tendency of the liquid to climb will not be limited by reaching an equilibrium angle. The inference may be drawn that, as Millikan (7) shows for "perfect wetting", the liquid will continue to climb up the solid until it becomes a sheet so thin that F_L may be said to vanish. Then the resultant force upon the upper margin of this film of liquid is simply F_S, which is perpendicular to the surface of the solid and thus also to the surface of a thin sheet of liquid adhering to the solid. Then equilibrium, as far as these forces affect the orientation of the surface of the liquid will be established. The liquid may climb still higher than would be required to arrive at this condition, as may be observed with water upon glass. The solid, in such cases, seems to press the liquid against itself and causes a thin film to rise above the level of the main body of the liquid until it is halted by a combination of gravity and surface tension.

It is to be emphasized that these conclusions have been reached by considering only the magnitudes and presumable directions of the cohesive forces of the liquid and of the adhesive forces displayed between the liquid and solid. The employment of the terms "wetting" and "perfect wetting" has been successfully avoided. This is desirable because they have not been clearly defined and are not easy to define, and because different writers have not the same conception of them.

Conclusion

The data are not submitted for the reasons given above and further because it has been possible to show that the values obtained depend more on the characteristics of the apparatus than on the properties of the experimental materials.

The phrase "if no other forces enter," and their equivalents deserve some emphasis. It is known that with exact technique some angles less than 90° and greater than zero can be found; compare, for instance, Bosanquet and Hartley (13). The possibility of other forces must not be neglected, although for the purposes of this paper it is impossible to evaluate them. The profound modifications of surfaces by small amounts of contamination are well known (4, 10, 12) and for this reason the consideration of the wetting of solid surfaces by liquids such as mixtures, solutions, dispersions and emulsions must be approached with the utmost caution. One of the components may be selectively adsorbed, and thus phenomena observed and referred to one set of causes when an entirely different set are responsible.

Finally it must be considered that there must be another fluid already in contact with and perhaps very strongly adsorbed upon the surface of the solid. That fluid is the gases of the atmosphere, and the fact that it is gaseous and not liquid brings about quantitative rather than qualitative differences in its behavior toward surfaces.

Stellwaag (2) gave considerable thought to what appears to be a resistance of the air film to displacement. Thus he says "The bare spots upon leaves which wet can be made to disappear if the water is spread uniformly over the leaf or if it is applied to the surface with great pressure. It then penetrates into the interspaces between the outgrowths (of the leaf) and after that is carried along by capillarity." Now if the angle is changing, such as when the water is "carried along by capillarity" it can scarcely be accurately measured. If a steady state has not been reached when the angle of contact is measured the value obtained will be dependent upon many other factors. It would appear, upon reflection, that a steady state, or equilibrium, must be awaited, no matter how long that takes.

It would seem that emphasis upon the necessity of a plane surface as a foundation for angle of contact measurements is superfluous. Nevertheless, according to their own statements, several of the investigators have proceeded to determine the angle of contact of liquids with surfaces such that even remote accuracy in the orientation of the tangent that is to represent the solid plane surface is out of the question. Such are segmented and otherwise convoluted larvae, more mature insects, leaves with ribs, and stems with nodes and scars. Furthermore, they have not allowed for the effects of hairs and other outgrowths that still further modify these surfaces.

It was intended at the start to endeavor to relate these measurements to glass so that glass might be used as a reference surface if it could be shown that parallel variations occurred on tree tissue and glass. This has had to be abandoned for the reasons as summarized below:

1. The set-up as described permits the operator to deceive himself into the belief that the angle of contact is much larger than it is unless the observation is confined to an ultimate film of the liquid, no wider than the range of action of the molecular forces and above which is perfect dryness.

2. The question of the establishment of equilibrium enters too largely into the problem. If equilibrium is established when the measurement is taken no information is obtained regarding the ease of replacing the air film and other factors tending to retard spreading. The rapidity of spreading is of as great if not greater importance in spraying than the angle of contact where this is less than 90 degrees. With this method the measurement can not be taken accurately until equilibrium is established.

3. The materials that are to be wetted are not suitable to measurements of the angle of contact.

Acknowledgment is gratefully accorded to Dr. R. O. Hutchinson for suggestions and criticisms in the theoretical considerations.

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THE DECOMPOSITION OF MERCUROUS CHLORIDE IN CONCENTRATED SOLUTIONS OF OTHER CHLORIDES*

BY T. W. RICHARDS AND MARCEL FRANÇON**

I. Introduction

In 1885, Gockel[1] published a paper when he was studying cells for which there was a difference between the total chemical heat and the part of it which is transformable into electrical energy. Gibbs' work was not well known then and often it was asked what relation, if any, there was between heat of reaction and electrical energy. They spoke of "free" and "bound" energy. Today it seems clearer to us to use the functions of "heat content" and "free energy," which are well defined and which enable us to express the correct relations in a simple and accurate way, by the following formulae:

$$(\Delta F)_{P,T} = -E\,dq \qquad (1)$$

$$E\,dq + (\Delta H)_P = T\left(\frac{\delta E}{\delta T}\right)_P dq \qquad (2)$$

$$\left(\frac{\delta E}{\delta T}\right)_P dq = \int \Delta C_P\, d\ln T + K \qquad (3)$$

where F, E, H, dq, P, ΔC_P, T represent respectively the free energy, the electromotive force of the cell where the reaction considered takes place, the "heat content," the amount of electricity passing through the cell, the atmospheric pressure, the change of heat capacity at constant pressure, the temperature.

Gockel studied cells, the two ends of which were at different temperatures, so that he might get information on the temperature coefficient of the electrode potential. He found that for cells of the general type:

$$Hg/Hg_2Cl_2/MCl/Hg_2Cl_2/Hg$$

the electromotive force depended on the salt solution, and explained that phenomena by the decomposition of mercurous chloride into mercury and mercuric chloride,—decomposition which depended on the salt solution used. Richards[2] afterwards studied the same cells and found that the cation of the electrolyte influences the temperature coefficient of the potential of the calomel electrode, the disturbing influence being decreased very much by dilution. Attention was thus drawn upon the reaction:

$$Hg_2 \rightleftharpoons Hg + HgCl_2.$$

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* Contribution from the Chemical Laboratory of Harvard University.

** The research reported in this paper was undertaken under the direction of Professor T. W. Richards, at the Wolcott Gibbs Memorial Laboratory, and finished after Professor Richards' death, in 1928. The junior author is responsible for the form of the following article.

[1] Gockel: Wied. Ann., 24, 618 (1885).

[2] Richards: Proc. Am. Acad. Arts. Sci., 33, 3 (1897).

The action of common salt upon calomel seems to have been noticed by J. Capellina;[1] Proust,[2] then Miahle[3] studied it. A. Larocque[4] claimed that solutions of alkali chlorides dissolve calomel without changing it simultaneously into mercuric chloride and mercury, for, when the solution is agitated with ether, no mercuric chloride is extracted by that solvent. Ruyssen and Varenne[5] measured the solubility of mercurous chloride in different amounts of hydrochloric acid and found that the solubility increases as the proportion of acid increases. According to Ditte[6] calomel is feebly dissociated by cold water, but much more by hot water; in the presence of an alkali halide, a double salt is formed which disturbs the equilibrium of dissociation and more calomel is dissolved. This continues until the double salt is also in equilibrium with its components. For S. Hada,[7] dissociation fully accounts for the decomposition of mercurous chloride into mercuric chloride in aqueous solution, without any oxidizing effect of air. He made some quantitative measurements and found that potassium chloride has a much greater action than hydrochloric acid which, already, had a great action on the decomposition of mercurous chloride. Neither light nor oxygen are important causes in effecting the decomposition, but the reaction is much furthered by increase of temperature. Richards found also that light has no considerable effect on the reaction and that dissolved air is not the essential factor. Later, Richards and Archibald[8] found that the decomposition of mercurous chloride into mercuric chloride is more marked with sodium chloride than with hydrochloric acid, more marked with hydrochloric acid than with barium chloride, with barium chloride more than with calcium chloride, the action being scarcely perceptible with cadmium chloride.

Gewecke[9] also studied the phenomena which he explained by the formation of a double salt between mercuric chloride and the alkali chloride. Richards and Singer[10] found the action of strontium chloride less marked than the action of barium chloride, but more than the action of calcium chloride. The action of magnesium chloride at first more marked than the action of calcium chloride, became, when the concentration was increased, less important than the action of calcium chloride, and passed by a maximum at a concentration of four times normal. One determination showed that the action of zinc chloride is less marked than the action of magnesium chloride. It was pointed out that the great difference between the action of zinc chloride for instance, and that of potassium chloride could be found in the differences in tendency of the chlorides "to form a soluble double salt."

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[1] J. Capellina: Manuscript 58 de la Bibliotheca Madrid (1576); cf. J. W. Mellor: Comprehensive Treatise on Inorganic and Theoretical Chemistry.

[2] L. J. Proust: J. Phys., **81**, 321 (1815).

[3] M. Miahle: Ann. Chim. Phys., (3) **5**, 177 (1842).

[4] A. Larocque: J. Pharm. Chim. (3) **4**, 9 (1843).

[5] E. Ruyssen and E. Varenne: Compt. rend., **92**, 1161 (1881).

[6] A. Ditte: Ann. Chim. Phys., (5) **22**, 558 (1881).

[7] S. Hada: J. Chem. Soc., **69**, 1667 (1895).

[8] T. W. Richards and E. H. Archibald: Proc. Am. Acad., **37**, 13, 347 (1902).

[9] J. Gewecke: Z. physik. Chem., **45**, 684-696 (1903).

[10] This investigation has not been published, but use is made here of the qualitative results.

2. Object of the Present Investigation

Determinations of the action of concentrated solutions of potassium chloride, lithium chloride, caesium chloride, at 25°C. on mercurous chloride.

3. Method and Apparatus

Calomel was treated with solutions of alkali chlorides of various concentrations for six hours in a thermostat. The extent of the reaction was obtained by determining the amount of mercury dissolved.

The same details of procedure as those described by Richards and Archibald were made use of: large test tubes of 60 cc. capacity, corked with rubber stoppers (boiled with dilute alkali, rubbed and washed); into each tube, a large excess of calomel, about a decigram of mercury and about 50 cc. of one of the chloride solutions used. The test tubes were placed in a big thermostat, and continually rotated for six hours at 25° C ± 0.02. It was found that after six hours, the equilibrium had been reached.

The mercury in solution was determined by precipitation with hydrogen sulfide, collected on a Munroe-Gooch crucible, washed with alcohol, carbon disulphide, again with alcohol, and finally dried at 100°. Analyses were always made in duplicate. In all cases, except one with caesium chloride, the concentrations of the chloride solutions were determined by analysis; the silver chloride formed by precipitation was weighed in Munroe-Gooch crucibles.

The densities of the solutions of lithium chloride and caesium chloride were determined with a pycnometer; ordinary corrections for the buoyancy of air were made. The densities of potassium chloride were obtained from a diagram constructed by means of the figures of Wagner.[1]

It ought to be rememberd, as Richards had stated about his work with Archibald, that : "In this paper, no evidence is given concerning the size of the grains of calomel. Ostwald. . . . has shown that this may be an important factor in determining the concentration of a saturated solution, and hence in fixing the basis of the present equilibrium. Concerning this point, it need only be said that while the *absolute* extent of solubility may vary with the size of the grains, the *relative results* upon which alone the conclusions of this paper are founded, are not affected. This is the case because the same preparation of calomel was used in every instance."

The chloride solutions, before and after reaction with mercurous chloride, were tested with phenol-phthalein and methyl red; the p_H was between 6 and 9. That the mercury in solution was, in part at least, in the mercuric state was made sure of: a solution of permanganate never suffered an appreciable trace of reduction; stannous chloride gave a definite white precipitate of calomel (the last test could not be used with caesium chloride because of the insoluble double salt formed with stannous chloride).

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[1] Wagner: Z. physik. Chem., 5, 36 (1890).

4. Preparation of Material

The mercurous chloride used was Baker's mercurous chloride; its analysis was N.V.M.: 0.002%. Potassium chloride was purified by two recrystallizations of Baker's analysed potassium chloride, C. P. Strontium chloride was purified by two recrystallizations of Baker's chemicals, C. P. Lithium chloride was obtained from lithium nitrate prepared in connection with the atomic weight of lithium, and very pure. The nitrate was transformed into chloride by several evaporations of its solution with hydrochloric acid (purified by distillation) until no vapours of chlorine appeared, then crystallized.

Caesium chloride was prepared from pollucite which was attacked by hydrochloric acid as shown for the determination of atomic weight of caesium,[1] then the chloride solution was precipitated by perchloric acid, the perchlorates were recrystallized three times; the perchlorate was transformed into chloride by heating, and the chloride crystallized twice.

One solution of caesium chloride was made with pure and dry caesium chloride prepared by Mr. Root. The dry salt was weighed and the solution weighed, and the density was determined with a pycnometer. In the experiments with lithium chloride the solution containing mercury was analyzed by taking a known volume of the solution (measured with a calibrated burette).

The results are given in the following tables and represented in the accompanying diagram, as well as the data of Richards and Archibald.

TABLE I

Mercuric Chloride found in Solutions of Potassium Chloride

Weight of Solution	Weight of HgS	$HgCl_2$ per 1000 cc. of Solution	Average	KCl in weight %	Density of the Chloride Solution	Normality of the Chloride Solution
81.36	0.0024	0.035	0.035	53.94	1.033	0.75
80.77	0.0023	0.034				
82.63	0.0024	0.035				
82.69	0.0110	0.165	0.166	11.23	1.074	1.62
84.41	0.0111	0.167				
46.39	0.0208	0.592	0.590	18.03	1.131	2.73
82.02	0.0375	0.589				
48.843	0.0449	1.258	1.256	23.67	1.167	3.70
45.463	0.0420	1.252				
44.87	0.0504	1.548	1.570	25.50	1.181	4.05
57.75	0.0666	1.592				
55.92*	0.0669	1.659	1.666	26.2	1.188	4.17
56.20*	0.0678	1.673				

* These last data were found by Mr. S. K. Singer. They have been corrected for a slight error in calculation.

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[1] Cf. T. W. Richards and Marcel Françon: J. Am. Chem. Soc., 50, 2162 (1928).

Mercuric Chloride found in Solutions of Lithium Chloride

Weight of Solution	Weight of HgS	$HgCl_2$ in grams per liter of Solution		Density of LiCl Solutions	LiCl % in grams	Normality of the LiCl Solution
88.80	0.0038	0.050	0.049	1.0277	5.26	1.27
99.86	0.0040	0.047				
44.01	0.00565	0.153	0.160	1.0619	11.37	2.87
38.48	0.0054	0.168				
38.97	0.0099	0.296	0.294	1.1001	17.89	4.64
35.01	0.0088	0.292				
26.90	0.0075	0.325	0.325	1.1138	21.07	5.56
25.15	0.0070	0.325				
26.00	0.0086	0.386	0.386	1.1578	26.9	7.34
23.93	0.0079	0.385				

Mercuric Chloride found in Solutions of Caesium Chloride at 25°C

Weight of Solution	Weight of HgS	$HgCl_2$ per 1000 cc. of Solution	Average	Density of the Solution	Normality
57.7437	0.0513	1.355	1.35	1.307	2.45
50.5039	0.04465	1.346			
86.7684	0.0203	0.3246	0.324	1.188	1.51
75.840	0.01765	0.3228			
25.410	0.00070	0.0349	0.0344	1.0577	0.476
27.148	0.00075	0.0339			

Mercuric Chloride in Solutions of Strontium Chloride at 25°C

Density of Strontium chloride solution	normality	Weight of Solution	Weight of HgS in gr.	$HgCl_2$ in one liter of solution	
1.240	3.59	36.3825	0.0072	0.286	0.283
		75.1814	0.0142	0.279	

The interesting outcome of this investigation is that lithium chloride is the salt of the alkali and alkaline-earth metals which affects mercurous chloride the least, while caesium chloride is the salt which affects mercurous chloride the most.

The diagram enables us to compare the action of a twice-normal solution of each chloride on mercurous chloride.

Twice Normal Solutions	Weight of $HgCl_2$ in grams per liter of solution	Twice Normal Solutions	Weight of $HgCl_2$ in grams per liter of solution
LiCl	0.09	HCl	0.15
$CaCl_2$	0.08	KCl	0.28
$BaCl_2$	0.11	CsCl	0.70
NaCl	0.14		

These figures show the respective positions of the curves. It is to be noticed that at higher concentrations LiCl is less active than $CaCl_2$, and HCl less active than NaCl, so that the order given above must be changed somewhat; but there are certain regularities which must be pointed out:

The greater the molecular volume of the elements of the same valence, the more important the action of the chlorides is. Manifestly, each chloride acts in a specific way.

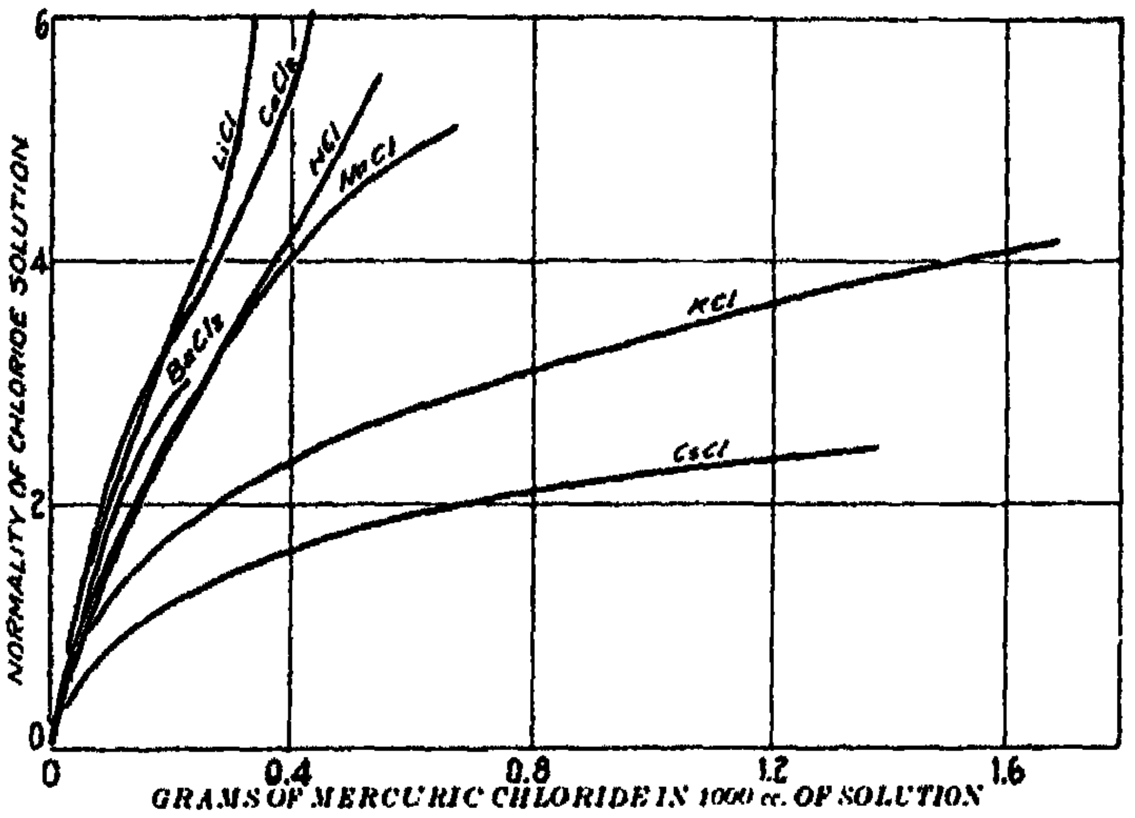

FIG. 1

5. Interpretation of the Results

The results obtained by all the workers who have studied the action of concentrated chloride solutions on mercurous chloride point out that the reaction at the basis of the phenomena is the decomposition of mercurous chloride into mercury and mercuric chloride. It is probable also that the equilibrium is disturbed by the nature of the solution; and that a complex compound is formed.

At first it seemed that the decomposition of mercurous chloride might be explained by the formation of a complex ion made up of mercuric chloride and chlorine ion. The specific action of the chlorides on the decomposition of mercurous chloride has been explained thus, for it was believed that the different alkali chlorides had different degrees of dissociation, furnishing therefore solutions of different concentrations in chlorine ions, for the same total molality. But that position is hardly tenable nowadays. The degrees of dissociation of the halides of the alkali metals as well as of hydrochloric acid are not considered now as being very different. Indeed they claim sometimes that the chlorides are completely dissociated although the ratio of the electrical conductivities λ/λ_∞ for a given solution referred to an infinitely diluted solution of the same salt vary from 0.83 to 0.93. But Kohlrausch's law of the constancy of the mobilities is not considered to hold, and Lewis calculated the degrees of dissociation in taking the variations of the mobility with concentration into account. By calculating the ratio of the degree of dissociation α of a number of electrolytes in tenths molal solution to that α' of KCl, Lewis found that for all the halides of the alkali metals and HCl, KOH, NaOH, the ratio α/α' lies between 0.99 and 1.02. At higher concentrations, of course, there would be much greater differences between the different halides; but, as Lewis points out, what is exactly the meaning of "degree of dissociation?" According to the modern theories of matter, polar compounds are formed of ions held to one another by electrostatic forces; whether those ions are "free" or not is therefore only a matter of definition, and it seems that the "concentration" of an ion has little significance, and may not be defined without some arbitrariness.

In fine, it is hardly possible to explain the differences in the actions of the alkali chlorides on mercurous chloride by the "concentration" of the chlorine ion. Two methods of attack seem to offer themselves for the study undertaken: a purely thermodynamic one based on the general principles derived from experience itself, and a treatment of the phenomena based on various mechanisms.

It is assumed, however, in both cases that the mass action law applies to solutions.

In a strictly correct thermodynamic treatment for solutions which are not dilute, the so-called mass action law holds good not for the "concentrations" but for the "activities" of the substances involved. The ratio of the activity to the molality of the substance concerned, $f = a/m$, is the activity coefficient.

When a solid salt is in equilibrium with its solution, the activity of the salt in solution is constant, and the activity coefficient is inversely proportional to its molality; so that the activity coefficient of a salt whose solid phase is present may be calculated from measurements of its solubility. At first it seems that the problem of mercurous chloride, is also susceptible to the treatment just described. But the problem is more complicated, as, indeed, not only do we face the question of the variations of the activity coefficient of mercurous chloride as such in presence of other salts, which is the classical and simple case, but, besides, there is the decomposition of mercurous chloride into mercury and mercuric chloride, and the disturbance of the equilibrium by the action of other chlorides, so that it might be said that at least two phenomena are taking place at the same time—the variations of the activity coefficient of mercurous chloride in the salt solutions, and the variations of the activity coefficient of mercuric chloride under the influence of other chlorides. It seems that the problem can not be treated adequately by simplifying it and assuming that one has to deal only with the variations of the activity coefficient of a single salt whose activity remains constant. The treatment of the question from a thermodynamic point of view must take account of the chemical reactions which actually take place, for indeed, the mercuric chloride must have a "potential" of its own as well as the mercurous chloride.

Let us now turn to the consideration of the mechanism of the phenomena. We may express the equilibrium between solid mercurous chloride and its solution, the decomposition of mercurous chloride into ions, the oxidation of the mercurous ion, by the following equations:

$$\mathrm{Hg_2Cl_2\ (solid)} \rightleftarrows \mathrm{Hg_2Cl_2\ (in\ solution)} \qquad (1$$

$$\mathrm{Hg_2Cl_2\ (in\ solution)} \rightleftarrows \mathrm{Hg_2^{++}} + 2\mathrm{Cl^-} \qquad (2$$

$$\mathrm{Hg_2^{++}} \rightleftarrows \mathrm{Hg^{++}} + \mathrm{Hg} \qquad (3$$

It is known that the mercuric ion[1] never exists to a great extent in solution. Luther,[2] indeed, studied a solution of mercuric chloride saturated at 25°C; according to him, such a solution contains in mols per liter: $\mathrm{HgCl_2} = 0.26$, $\mathrm{HgCl^{-}}$* $= 0.00015$; $\mathrm{Hg^+} = 0.00033$; $\mathrm{Cl^-} = 0.00048$; $\mathrm{Hg^{++}} = 10^{-8}$; $\mathrm{HgCl_4^{--}} = 5 \times 10^{-4}$; therefore the mercuric ion produced according to (3) must react with the other ions present in the solution according to the following equations:

$$\mathrm{Hg^{++}} + \mathrm{n\,Cl^-} \rightleftarrows (\mathrm{HgCl_n})^{-(n-2)} \qquad (4$$

and

$$n''\,\mathrm{Hg^{++}} + \mathrm{n\,Cl^-} + n'\,\mathrm{M^+} \rightleftarrows [\mathrm{M_{n'}}\,\underset{n''}{\mathrm{HgCl_n}}]^{+(n'-n+2n'')} \qquad (5$$

The mercuric ion might also react with the mols of water, as expressed in the following reaction:

$$n''\,\mathrm{Hg^{++}} + \mathrm{n\,Cl^-} + n'\,\mathrm{M^+} + n'''\,\mathrm{H_2O} \rightleftarrows [\mathrm{M_{n'}}\,\underset{n''}{\mathrm{HgCl_n}}\,(\mathrm{H_2O})_{n'''}]^{(n'-n+2n'')} \qquad (6$$

In otherwise pure water mercurous chloride is soluble to the extent of 0.0028 gr. at 24° C. in one liter of water, according to Kohlrausch. If the solubility[3] of mercurous chloride were not accompanied by the oxidation of the mercurous ion and corresponded *only* to equations (1) and (2), the addition of extraneous chlorine ions into the solution would repress the decomposition of mercurous chloride into ions by favouring the combination of the mercurous ions with the chlorine ions, according to equation (2) read from right to left. That is, indeed, generally what happens with salts in solutions

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[1] Cf. D. Carnegie and F. Burt: Chem. News, 76, 174 (1897); also W. Biltz: Z. physik. Chem., 40, 199 (1902).

[2] R. Luther: Z. physik. Chem., 47, 107 (1904).

* It is suggested that the ion $\mathrm{HgCl^-}$ might simply have been dissolved mercurous chloride, $\mathrm{Hg_2Cl_2}$. However, the existence of the ions $\mathrm{HgCl^-}$ was established by H. N. Morse: Z. physik. Chem., 41, 733 (1902).

[3] The solubility of mercurous chloride is not determined without some arbitrariness. When mercurous chloride is finely divided it is 10% more soluble than when coarsely crystalline. Cf Sauer: Z. physik. Chem., 10, 301 (1904).

containing an ion in common with them. But the formation of mercury according to (3) is an undoubted fact which corresponds to other phenomena of the same sort. Behrend[1] found that mercurous iodide decomposed in solution in water into mercury and mercuric iodide. Ogg[2] also studied the last phenomena, while Abel[3] studied the phenomena corresponding to (3) and found, for the reaction shown by the equation read from left to right, that the constant of the equilibrium K is 120. Reciprocally, when a solution of mercuric nitrate[4] is placed over mercury, there is formation of mercurous nitrate.

The concentration of the mercuric ion depends on temperature, since it is found that the reaction represented by (3) from left to right is the more marked, the higher the temperature. Hence, it is inferred that temperature will influence the solubility of mercurous chloride.

Therefore, it seems fairly certain that the equations (1), (2) and (3) represent correctly what is taking place. That the mercuric ion thus formed reacts with the substances present in solution seems also very probable, and it is understood how the removal of the mercuric ion from the solution would promote the solution of mercurous chloride.

It is very likely that complexes are formed. Richards and Archibald thought there might be a complex ion, $HgCl_4^{--}$; experiments by Dawson[5] show indeed that there are complex ions in solutions containing mercurous and mercuric chloride. Sand and Breest[6] assume the formation of $HgCl_3^-$. Thus the action of the chlorine ion is clear. The presence of chlorine ions, by being favourable to the formation of complexes, tends to increase the solubility of mercurous chloride instead of diminishing it, as it would appear at first.

But the cation also has an influence on the solubility of mercurous chloride. The cation also helps to form complexes, as equations (5) and (6) show, thus favouring the removal of mercuric ions from the solution, and causing therefore a further production of mercuric ions, and ultimately a greater solubility of mercurous chloride.

The action of the cation may explain the differences in the solubility of mercurous chloride in different chloride solutions. If indeed cations differ in their tendencies toward complex formation, as this tendency increases, more mercuric ions will be removed from the solution, and ultimately the solubility of mercurous chloride will be greater.

The determinations of solubility of mercuric chloride with alkali chlorides in aqueous solutions gave evidence of the formation[7] of five double salts of CsCl and $HgCl_2$, three between KCl and $HgCl_2$, one between NaCl and

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[1] Behrend: Z. physik. Chem., 123, 199-247 (1926).

[2] Ogg: Z. physik. Chem., 27, 285 (1898).

[3] Abel: Z. anorg. Chem., 26, 361 (1901).

[4] Arthur Jacques: "Complex Ions."

[5] Dawson: J. Chem. Soc., 95, 870 (1909).

[6] Sand and Breest: Z. physik. Chem., 59, 424 (1907).

[7] Wells: Am. J. Sci., 44, 221 (1892); H. W. Foote: Am. Chem. J., 30, 339 (1903); H. W. Foote and F. L. Haigh: J. Am. Chem. Soc., 33, 459-462 (1911); cf. also H. W. Foote and L. H. Levy: Am. Chem. J., 35, 236 (1906).

$HgCl_2$ (although Bonsdorf[1] has described two double salts between NaCl and $HgCl_2$). The formulae given for these salts do not seem very certain; they are: $NaCl \cdot HgCl_2 \cdot 2H_2O$; $2KCl \cdot HgCl_2 \cdot H_2O$; $KCl \cdot HgCl_2 \cdot H_2O$; $KCl \cdot 2HgCl_2 \cdot 2H_2O$; Cs_3HgCl_5; Cs_2HgCl_4; $CsHgCl_3$; $CsHgCl_5$; $CsHg_5Cl_{11}$.

Foote and Martin[2] studied the specific electrical conductivities of solutions on one mol of CsCl, KCl, NaCl, respectively in v liters of the molten mercuric chloride at 282°C. Their results are:

	CsCl	KCl	NaCl
v	30	30	30
conductivity	44	38.5	28

while the conductivity of molten mercuric chloride alone is extremely small, if there is any. Foote and Martin explain these figures by the formation of complex ions such as $MHgCl_4^-$ and $MHgCl^{5--}$.

Thus it is shown that the different alkali metals have different tendencies toward complex formation, and the action of a chloride on the solubility of mercurous chloride may be considered, to a certain extent, as twofold: the action of the chlorine ion and the action of the cation, although these two actions exert themselves at the same time and the distinction is somewhat formal.

Let us examine more closely which different complexes might be formed.

Richards found that "the dissolving of mercuric chloride to saturation in a twice normal solution of common salt diminished but slightly the conductivity of the solution." LeBlanc and Noyes[3] measured the effect of potassium chloride and sodium chloride in solution with mercuric chloride on the freezing point and found evidence of the formation of complexes of the type $KHgCl_3$, and diminution of the number of molecules in the solution. A. Benrath[4] found that the action of sodium chloride and potassium chloride in aqueous solutions with mercuric chloride on the raising of the boiling point gives results which may be explained by the formation of complex salts. Sherrill,[5] basing his conclusions upon experiments on electromotive force, solubility, freezing point, and partition, seems to lean toward formation of complex ions of potassium chloride and mercuric chloride of the following formula $[(HgX_2)_m X_n]^{-(n)}$ where $m = 1$ and $n = 2$, for most concentrations.

Richards and Archibald considered the complexes of mercuric chloride and alkali chlorides as highly ionized. It might be possible, on the other hand, for the complexes formed to be undissociated, for the fraction of the alkali

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[1] Bonsdorf: Pogg. Ann., **17**, 115 (1829).

[2] H. W. Foote and N. A. Martin: Am. Chem. J., **41**, 454 (1909); H. W. Foote and L. H. Levy: **35**, 236 (1906).

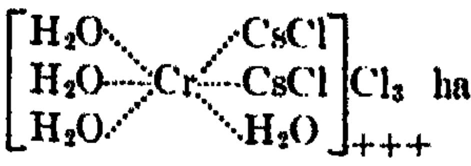
[3] M. LeBlanc and A. A. Noyes: Z. physik. Chem., **6**, 401 (1890).

[4] A. Benrath: Z. anorg. Chem., **58**, 257 (1908).

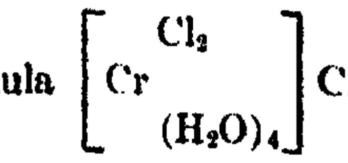
[5] Miles S. Sherrill: Z. physik. Chem., **43**, 700 (1903). An interesting discussion on the complexes between $HgCl_2$ and NaCl, and KCl, on their relative dissociation is to be found in a paper by C. Tourineux: Ann. Chim. Phys., **11**, 225 (1919).

chloride which would be taken up to form an undissociated complex would be small. The question, therfore, of knowing whether the complexes are in the ionic stage or are non-electrolytic molecules cannot be solved without some uncertainty.

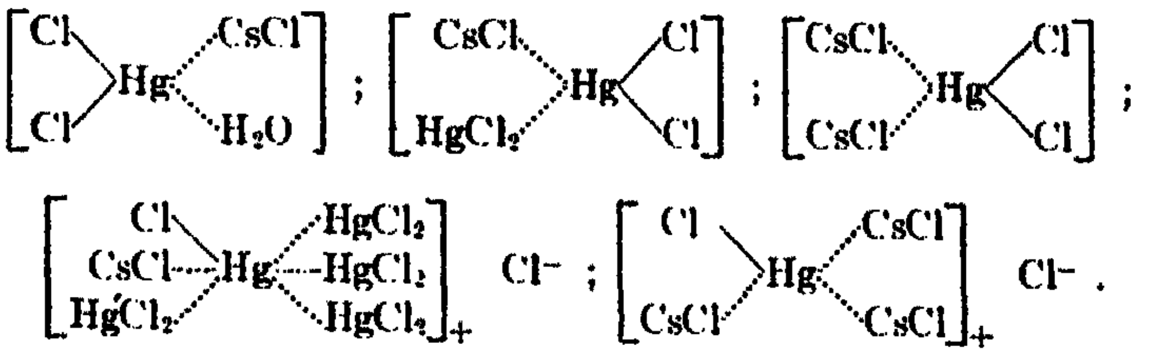
One may try with the help of Werner's conceptions about complex compounds to give a representation of the complexes formed. It can be assumed that mercury may form complexes in which mercury would have a coordination number of four or six, according to the case, and in which neutral molecules of chlorides may play the same part as do water or ammonia molecules in other complexes. For instance, in a similar way, the following formula:



has been proposed for the salt which is often given the following formula



$\left[\mathrm{Cr}\,\mathrm{Cl_2}\,(\mathrm{H_2O})_4\right]\mathrm{Cl}\cdot 2\,\mathrm{CsCl}$; that last formula seems indeed more likely to Urbain[1]; but, as Urbain points out, the substitution of salt molecules for water molecules has often been suggested, however, as, for example, to connect the double sulfates of the magnesium series to the simple sulphates with seven water molecules. Thus, the complexes between caesium chloride and mercuric chloride could be given the following formulae.[3]



In the same way, the known complexes between potassium chloride and mercuric chloride could be given formulae accounting for their properties and their composition.

It is seen, then, that some complexes would be non-electrolytic molecules, while others would form ions in solution.

That mercuric chloride forms complexes easily has been well known. H. Ley[2], for instance, in order to explain the acidity of an aqueous solution of mercuric chloride, suggested that hydrolysis takes place according to:

$$2\ \mathrm{HgCl_2} + \mathrm{H_2O} \rightleftarrows (\mathrm{HgCl})_2\mathrm{O} + 2\ \mathrm{H^+}\ 2\ \mathrm{Cl^-} \qquad (7$$

or

$$\mathrm{HgCl_2} + \mathrm{H_2O} \rightleftarrows \mathrm{HgClOH} + \mathrm{H^+} + \mathrm{Cl^-} \qquad (8$$

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[1] Urbain and Sénéchal: "Introduction à la Chimie des Complexes."

[2] H. Ley: Z. physik. Chem., 30, 226 (1899).

[3] The formula $\mathrm{CsHgCl_3.H_2O}$ seems more likely than $\mathrm{CsHgCl_3}$ given by Wells.

An aqueous solution of mercuric chloride turns methyl red to red, but, after addition of a neutral solution of an alkali chloride, the methyl red turns yellow; that reaction can be explained by the removal of mercuric chloride from the solution thanks to the formation of a complex compound between mercuric chloride and the alkali chlorides added, so that in reaction (8) the equilibrium is shifted to the left, thus diminishing the concentration of the hydrogen ions.

If we consider the polyhalidic salts of the alkali metals we see that their stability depends on the nature of the metal and is directly proportional to its atomic volume. Since many properties of the ployhalides are characteristic properties of double salts, and, since as was pointed out above, the decomposition of mercurous chloride increases when the atomic volume of the alkali metal increases, the parallelism which is found between the solubility of mercurous chloride and the stability of the polyhalide salts of the alkali metals confirms our views according to which the decomposition of mercurous chloride is followed and exalted by the formation of complexes.

It might be mentioned also, as Abegg has shown, that the tendency to the formation of higher polyhalides increases in the order Li, Na, K, Rb, Cs, which is the same order as the order of the metals in the periodic system and also the order of the decrease in solubility of the platinichlorides and other slightly soluble salts like the alums.[1] According to Abegg and Bödlander[2] the tendency which an element exhibits to form complex compounds depends largely upon its electro-affinity. The electrolytic potential is assumed to be an approximate measure of that quantity. The electrolytic potential shows a certain relationship to the atomic volume, the two quantities being roughly parallel in any given group in the periodic system. Abegg's views may be compared to J. Kendall's conceptions. Kendall[3] showed that "solubility parallels compound formation," and that, for binary inorganic mixtures, at least, "compound formation is fundamentally dependent upon diversity in character of the two components." The problem we are treating may be compared to the phenomenon of the solubility of AgCl which has been treated by Kendall[3] among many other authors. As the solubility of AgCl is explained by the complexes formed, so it may be in the case of Hg_2Cl_2 whose solubility should exceed the calculated value by an amount dependent upon the stability of the complex compounds formed between $HgCl_2$ and the added chloride, MCl or upon the attraction for one another of the constituents of the compounds formed: or in other words, upon the diversity in the positions of the radicals Hg_{++} and M_{+} in the electrode potential series. It would be expected that the solubility of Hg_2Cl_2 would increase more and more above the normal value as the radical M_{+} is more electro-positive. This is the case with the solubility of AgCl studied by Forbes[4]; in that case indeed the solubility is tremendously

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[1] Cf. Locke: Am. Chem. J., 26, 166 (1901).

[2] Abegg and Bödlander: Z. anorg. Chem., 20, 741 (1899); 39, 333 (1904).

[3] J. Kendall: Proc. Nat. Acad. Sci., 7, 56 (1921).

[4] G. S. Forbes: J. Am. Chem. Soc., 33, 1937 (1911).

increased, the order being H, Ca, Na, Sr, Ba, K, this order being exactly the electrode potential series; but with Hg_2Cl_2 the situation is somewhat different; the influence of MCl or $M'Cl_2$ on the solubility of mercurous chloride increasing in the order: Li, Ca, Ba, H, Na, K, Cs, the order of the atomic volume being Li, Na, Ca, Ba, K, Cs.

In the case of $PbCl_2$,[1] the solubility order is H, Na, K, Li, at the lowest concentrations, and H, K, Na, Li at the highest concentrations.

The electrode potential does not seem, therefore, to be more than a somewhat coarsely approximate measure of complex formation.

Some recent work on the complexes of mercury must be considered here and compared to the speculations discussed above.

Shibata and his co-workers[2] studied the complexes of mercuric salts in solution by a spectroscopic method. They found that there were complexes between mercury and most metals. According to them, the complexes correspond to the following formulae:

For univalent metals $[HgCl_3(H_2O)]^- M^+$ or $[HgCl_3(H_2O)_3]^- M^+$;
For bivalent metals $[HgCl_4]^{=} M^{++}$;
For tervalent metals $[HgCl_5(H_2O)]^{\equiv} M^{+++}$

while $HgCl_2$ did not give positive results with chlorides of Ca, Sr, Cr, Fe.

Professor P. Job[3] in a very interesting and general treatment of imperfect complexes in solutions exposed his methods developed independently of Shibata, and based on the absorption of light by the solutions considered. The results of Professor Job are interpreted on the assumptions that the law of mass action holds good for the formation of complexes and their equilibrium, and also that only one complex is formed. Thus it seems to be certain that a complex corresponding to $HgCl_3K$ exists in solution. It is remarked, however, that there might be several complexes, among them one corresponding to $HgCl_4K_2$.

F. Bourion and E. Rouyer[4] wanted to find an interpretation of a kinetic anomaly in the reduction of mercuric chloride by sodium formate. They thought that the anomaly was due to a complex between the two salts and set to study complexes by ebullioscopic determinations. They point out that Benrath[5] had deduced the formulae $HgCl_4Na_2$ and $HgCl_6K_4$ for the complexes of mercuric chloride with NaCl and KCl respectively, from his determinations of the lowering of the freezing point and of the raising of the boiling point of the solutions concerned.

Linhart[6] had pointed out that the reaction goes on after the addition of the quantity of salt corresponding to the composition of the complex, so that he concludes that the formulae given for the complexes were somewhat doubtful. When one keeps in mind that several complexes can be formed between mer-

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[1] Kendall and C. H. Sloan: J. Am. Chem. Soc., 47, 2306 (1925).

[2] Y. Shibata, T. Inouye, and Y. Makatsuka: Jour. Chem. Soc., Japan 42, 983-1000 (1921).

[3] P. Job: Compt. rend., 182, 1622 (1926); Ann. Chim., 9, 113, (1928).

[4] F. Bourion and E. Rouyer: Ann. Chim., 10, 182, 263 (1928).

[5] Loc. cit.

[6] G. A. Linhart: J. Am. Chem. Soc., 38, 1972 (1916); 39, 2501 (1917).

curic chloride and potassium chloride, possibly three, as was said above, one understands the apparent anomalies which were thought of in the preceding considerations.

The effect of HCl on the electrode potential at the contact Hg/Hg_2Cl_2 was studied very exhaustively by Carter and his co-workers,[1] who took account of the results of T. W. Richards and Archibald. The works of Sauer, and also of Tolman and Ferguson,[2] as well as that of Ellis[3] are pointed out as bearing on the question and confirming the preceding speculations and observations.

M. Randall[4] admits that the reproducibility of the measurements of the hydrogen-calomel cell is not so great as that of the hydrogen-silver chloride cell. He points out that Gerke[5] had observed that air causes an error of 0.0010 to 0.0030 volts in the potential of the hydrogen mercury calomel cell. It has been seen above, however, that the experiments of Richards and also those of Hada show that air does not affect the equilibrium $Hg_2Cl_2 \rightleftarrows HgCl_2 + Hg$. In view of the preceeding observations on the decomposition of mercurous chloride, it seems that much of the work which had been done with the calomel electrode might be somewhat invalidated.

Indeed, in the calculation of activity from electro-motive force measurements, use has been made of concentration cells without liquid junction and the following formula has been applied:[6]

$$2\,RT \ln a_{\pm} = -F\,(E - E_0)$$

but it must be remembered that the formula holds if it is assumed that the electrical energy which is evolved by such cells corresponds only to the change of free energy at constant pressure and temperature which is brought about when the electrolyte is transferred from a solution of molality m to a solution of molality m′ which is in the standard state, but where, neither the change of solubility of mercurous chloride with the concentration of the electrolyte nor the decomposition of mercurous chloride is taken into account. Of course, at low temperatures and at small concentrations, the solubility of mercurous chloride can be considered as being practically independent of the concentration of the electrolyte; but when the conditions are different from the above conditions, such is not the case. For instance, among the many works of a similar kind, I find the works of M. Randall and G. F. Breckenridge[7] who used calomel cells with electrolytes for which the molality is as great as 1.5 or 1.75 at 25°C. M. Randall[8] has pointed out very clearly indeed the distinction between the thermodynamic treatment of a problem and a treatment which explains the phenomena by proposing mechanisms. While that distinction between the sciences of principles and the explicative sciences

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[1] Carter, Lea and Robinson: J. Chem. Soc., 131, 1906; Carter and Robinson: 1912 (1927).

[2] Tolman and Ferguson: J. Am. Chem. Soc., 34, 232 (1912).

[3] Ellis: J. Am. Chem. Soc., 38, 737 (1916).

[4] M. Randall and L. E. Young: J. Am. Chem. Soc., 50, 991 (1928).

[5] Gerke: J. Am. Chem. Soc., 44, 1684 (1922).

[6] Cf. G. N. Lewis and M. Randall: "Thermodynamics," p. 333.

[7] M. Randall and G. F. Breckenridge: J. Am. Chem. Soc., 49, 1435 (1927).

[8] M. Randall: Trans. Faraday Soc., 23, 498 (1927).

is very legitimate, it seems, however, that one must take account of what actually takes place; otherwise, the application of thermodynamics becomes a mere obtention of figures which express very little if the assumptions made are not justified. For dilute solutions, on the other hand, the application of thermodynamics in the proper cases is very illuminating, as in the accurate work of Güntelberg[1] who measured the activity coefficient of HCl in solutions of LiCl, NaCl, KCl, CsCl at a total concentration of 0.1N in Cl^-, with the help of AgCl cells. His results as well as the considerations on which he based his explanations[2] show that the differences in the activity coefficients of a sparingly soluble salt in two salt solutions would be independent of the nature of the sparingly soluble salt, when the two electrolytes which constitute the mixture have an ion in common. The value of osmotic coefficients can help one to predict what takes place. Brönsted calculated the osmotic coefficients of the alkali chlorides at certain concentrations and found that

$$\varphi_{LiCl} > \varphi_{NaCl} > \varphi_{KCl} > \varphi_{CsCl}.$$

Thus it is expected that a sparingly soluble salt will be less soluble in LiCl than in NaCl, less in NaCl than in KCl, and less in KCl than in CsCl. But, as was said above, those simplifying generalities cannot be applied to mercurous chloride when the concentration and the temperature are such that the situation is much more complicated than it was assumed.

The use of the decinormal calomel electrode proposed by Richards to obviate the dangers of the decomposition of mercurous chloride shows the advantages obtained by dilution.[3]

Acknowledgment for financial assistance is made to an anonymous benefactor of this Laboratory and to the Carnegie Institution of Washington.

6. Summary

The results of the present paper may be summarized thus:

1. The decomposition of mercurous chloride in concentrated solutions of LiCl, KCl, CsCl has been studied.

2. A general treatment of the question seems to give a greater understanding of the phenomena.

3. Explanations of some irregularities of the calomel cell are given, as well as the way to remedy them.

4. Caution is required of analysts who use Hg_2Cl_2 to titrate mercury in solution.

5. The use of calomel in medicine seems to present dangers.

Wolcott Gibbs Memorial Laboratory,
Cambridge, Massachusetts.

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[1] E. Güntelberg: Z. physik. Chem., **123**, 199-247 (1926).

[2] Cf. Brönsted: J. Am. Chem. Soc., **44**, 877 (1922); **45**, 2898 (1923).

[3] It is interesting to point out that Harold A. Fales and W. A. Mudge, in a curious article [J. Am. Chem. Soc., **42**, 2434 (1920)] recommended the use of the saturated potassium chloride calomel cell.

It is suggested that 0.1N solutions of LiCl might be used for the calomel electrode instead of KCl, for there would be less danger of decomposition of mercurous chloride. The salt bridge used in cells might then be made of dilute LiCl in order to avoid the dangers of diffusion. To be sure, however, LiCl has over KCl a disadvantage resulting from the great differences in molality of the ions Li^+ and Cl^-, but, by using a dilute solution, exact corrections could be applied.

A SIMPLE CENTRIFUGAL FILTRATION DEVICE FOR PURIFICATION OF SMALL AMOUNTS OF MATERIAL BY RECRYSTALLIZATION*

BY EVALD L. SKAU**

In the purification of a chemical compound by recrystallization the effectiveness of the process depends on the completeness of the separation of the crystals from the mother liquor. Ordinary filtration is obviously very inefficient. In the first place, considerable mother liquor is inevitably retained by the crystals mechanically, for even when suction is applied, air channels tend to form. Secondly, more or less evaporation of the mother liquor takes place not only during the filtration proper but also during the previous cooling with the consequent formation of a crust or ring of impure crystals at the top of the solution. This is of course of paramount importance when volatile solvents are used or when for some reason the filtration is carried out above room temperature. Ordinary filtration has the further disadvantage: (1) that it involves considerable loss of material unless special precautions are taken; and (2) that there is a large chance for contamination of the crystals by dust particles, or by moisture in case the substance is hygroscopic or in case the filtration is carried out below room temperature. All of these factors become much more serious when small amounts of materials are being dealt with.

The centrifugal filtration tube here described overcomes in large measure all of these common difficulties and is particularly desirable: (1) since it is extremely simple; (2) since filtration even at temperatures of − 100° may be carried out with as much ease as at room temperature; and (3) since the weight of the crystals and of the mother liquor can be quite accurately determined, a fact which at once suggests a large number of applications.

It consists (see Figure 1a) of a heavy 25 to 40 mm Pyrex tube, A, closed at the bottom and having a slight constriction at B upon which the perforated glazed porcelain disc C rests. E is a stiff Nichrome wire fastened to the disc and extending up to and pressing against the rubber stopper D.

After a filter paper is placed over C and folded well down around the edges, it is pushed down upon the shoulder B, the disc fitting fairly snugly to the walls of the tube. The solid to be recrystallized is now introduced and enough solvent added to dissolve all of it at the higher temperature to be used. The stopper is then quickly inserted and the tube turned upside down in a bath a little above the required temperature. Any liquid which ran through the disc before inverting will run back while heating. When solution

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*Contribution from the Department of Chemistry, Yale University. Constructed from Part V of a dissertation prepared under the direction of Blair Saxton and submitted to the Graduate School of Yale University, June, 1925, in candidacy for the degree of Doctor of Philosophy.

** DuPont Fellow, 1924-25.

is complete the tube is cooled to the desired temperature by immersing it in a suitable bath. The tube is then quickly righted and centrifuged immediately at about 2000 r.p.m., a similar tube of the same weight having been previously placed in the opposite cup. The liquid is thus thrown into the lower chamber before the temperature has changed appreciably. The solid is left on the disc and can be lifted out with it by means of the wire E. The wire also serves the purpose of supporting the disc when the tube is inverted. It is sometimes unnecessary to cover the disc with filter paper.

fig 8 li 02

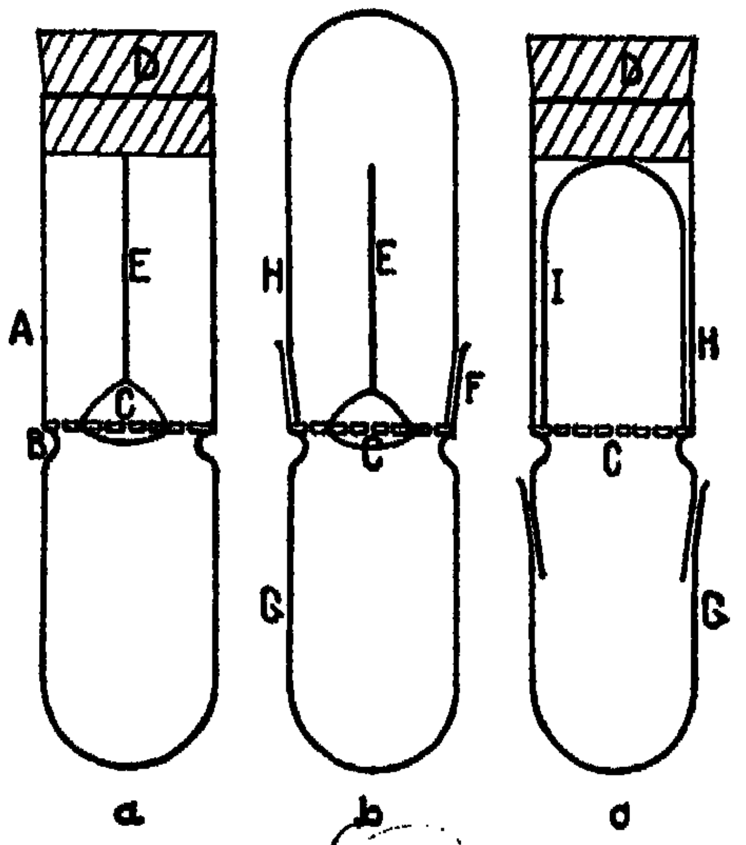

Fig. 1
Contrifugal Filtration Tubes

Two modifications of this device are also shown in the diagram. Modification *b* is all-glass and has a ground-glass joint F above the disc. In modification c the ground-glass joint F is below the disc and the inverted glass tube I fits between the disc and the stopper as shown, the wire E being omitted. The procedure is much the same as above except that in the case of modification c the solution is in tube I until immediately before centrifuging and thus the stopper cannot be attacked by the solution. This modification has the added advantage that the weights of the solid and of the mother liquor can be obtained without removing either from the apparatus since the liquid is collected in the lower section G and the crystals remain behind on the disc in the upper section H. This form is thus particularly applicable to the determination of approximate solubilities.

Application to Low-Temperature Recrystallization. Probably the most important application of this device is in the isolation of a compound from an oily liquid from which it cannot be separated by distillation, a condition often met with by the organic chemist. The ordinary methods of low-temperature filtration are very tedious and unsatisfactory but by the present method no more difficulty is encountered than in a separation at room temperature. The crystallization is carried out by inserting the centrifuge tube in one test tube fitting inside another which in turn is immersed in a suitable cooling liquid in a Dewar vessel. The sample is shaken occasionally by hand and when enough solid has separated the centrifuging is carried out in the ordinary way except for the fact that the metal centrifuge cup is previously cooled by direct immersion in the cooling liquid. The crude product so obtained may then be recrystallized from a low-boiling solvent as many times as necessary at any desired temperature below 0°.

This method can be used in all cases where the crystals separating out remain solid long enough so that they can be removed from the apparatus before melting In this way, for example, it was found possible to separate meso-2-5-dichlorohexane from a yellow oil, a crude mixture of the meso and the racemic or d-l forms. One centrifuging at about −50° followed by a single recrystallization from pentane at about the same temperature gave a perfectly white crystalline product which melted at 20° after the residual pentane had been removed by heating. The meso form had never before been isolated.[1] It is obvious that by properly controlling the temperature of the centrifuge or by lagging the temperature of the centrifuge cups, it would be possible to use this method for the isolation and purification of substances whose melting points are well below 0°.

Application to Systematic Fractional Crystallization. The large chance of contamination, the inevitable loss of material and the tediousness involved in the filtration method makes it undesirable for use in systematic fractional crystallization. In their work on lead nitrate for example, Richards and Hall[2] used decantation entirely. This is suitable in the case of an inorganic salt but is extremely inefficient when the crystals tend to form in a voluminous and absorbent mass throughout the solution as is the case with most organic compounds. In fact, an actual comparison was made in the case of meta-dinitrobenzene and it was found that to attain the same degree of purity three times as many successive recrystallizations were necessary when decantation was used as when the centrifugal filtration tube was used. The time factor is of course even greater.

Modification *b* is perhaps the most suitable form for general use for this purpose. The procedure is very simple, the crystallizing, redissolving and centrifuging being performed on all of the fractions simultaneously. The substance is first dissolved and filtered to free it from any dust or foreign matter, and then divided into say six approximately equal portions (five successive crops of crystals, using decantation, and the remaining mother liquor). These are introduced into the tubes numbered in the order of their purity "1" to "6" respectively. After the correct amount of solvent has been added to each,

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[1] For further details concerning the preparation and other properties of this compound see paper by Dr. Frank Cortese (to be published soon) to whom we are indebted for supplying the sample.

[2] Richards and Hall: J. Am. Chem. Soc., 39, 531 (1917).

as described above, the tubes are all heated, cooled and then centrifuged. In separating the tubes at the ground joint it will be found that practically all of the crystals remain in the upper part due to the taper of the joint and the rest can be readily lifted out on the disc. The liquid in the lower part of 6 is now put into the lower part of another tube, 7, that from 5 into 6 and so on fresh solvent being added to tube 1. The tubes are now reassembled and inverted[1] and the cycle repeated as before.

The crystals obtained become purer and purer with each cycle, that in tube 1 usually being the purest. When 1 is considered pure enough or has become too small in amount to work with conveniently, it may be omitted from the following cycle after which the crystals in 2 may be combined with it, having undergone the same number of recrystallizations, and so on.[2]

Summary

A "Centrifugal filtration tube" has been described for use in separating liquids from solids at a definite temperature. Its chief advantages are: (1) its simplicity; (2) its efficiency; and (3) its adaptability to separations below 0°. It is particularly applicable to systematic fractional crystallization when only small amounts of material are available. Meso-2-5-dichlorohexane has been isolated by means of this device.

Trinity College,
Hartford, Conn.

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[1] If the liquid does not run through the disc readily upon inverting, it can be hastened by alternately cooling and heating the other chamber.

[2] For a more complete discussion of systematic fractional crystallization the reader is referred to articles by Richards and Hall (loc. cit.) and by Dennis and Wyckoff: J. Am. Chem. Soc., 42, 985 (1920).

AN ALL-GLASS CIRCULATING PUMP FOR GASES*

BY ROBERT LIVINGSTON 7113

A double-acting modification of the electromagnetic pump of Porter, Bardwell, and Lind[1] has been described by Funnell and Hoover[2] in this journal. While this pump has the advantage of greater capacity and more positive action, its horizontal construction greatly increases the friction between the piston and cylinder.

To overcome this defect a vertical double-acting pump has been constructed, the design of which is indicated in the diagram. The cylinder is 35 cm long, with an internal diameter of 1.0 cm. The piston is 10 cm long, and contains several lengths of soft iron wire. The valves were made as described by Porter, Bardwell, and Lind. The solenoids are each 7.5 cm long, and are separated by fiber disks 1 cm thick. They are activated, in succession, by means of a commutator system. This arrangement permits the use of either direct or alternating current.

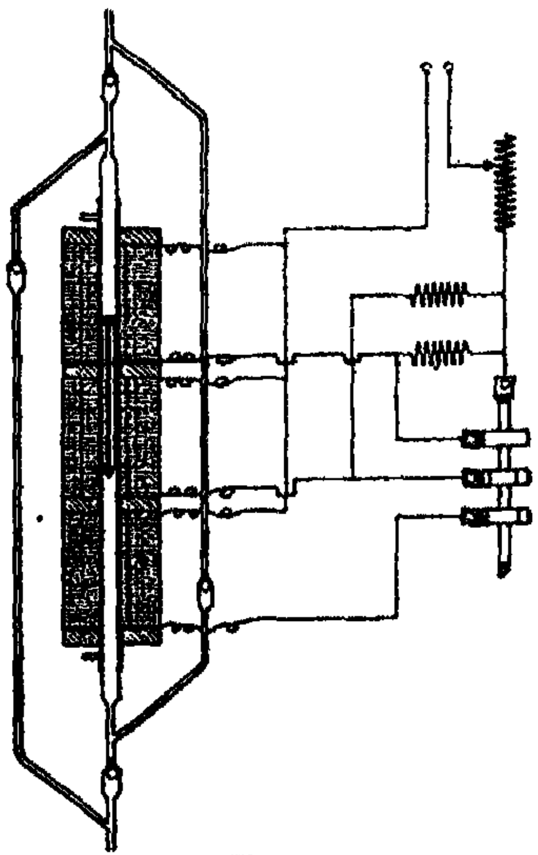

FIG. 1

When adjusted to make sixty complete strokes a minute, this pump forces air at atmospheric pressure against a head of 0.5 cm of water at a rate of 65 liters per hour. The capacity of the pump is greatly influenced by the accuracy of its construction and by the adjustment of the resistances, and could probably be increased as much as two fold by careful attention to these details.

This type of pump may be used with undiminished efficiency for gases saturated with water vapor, if the valves are kept at a temperature of 35 or 40°C. This may be easily accomplished by the use of simple resistance-wire heaters.

The ease of construction and adjustment, which Funnell and Hoover claim for their pump, applies equally well to the one described here. Pumps of all three types are equally adjustable to the same wide range of pressures. The chief advantages of the new design, relative to that of Funnell and Hoover, are lowered frictional resistance and a decreased sensitivity to the presence of saturated vapors.

Minneapolis,
Minnesota.

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* Contribution from the School of Chemistry of the University of Minnesota.

[1] F. Porter, D. C. Bardwell and S. C. Lind: Ind. Eng. Chem., **18**, 1086 (1926).

[2] W. S. Funnell and G. I. Hoover: J. Phys. Chem., **31**, 1099 (1927).

NEW BOOKS

Ice Engineering. *By Howard T. Barnes. 23 × 15 cm; pp. ii + 364. Montreal: Renouf Publishing Co., 1928.* More than twenty years ago Mr. Barnes wrote: "I have every confidence that a thorough understanding of the laws underlying the formation of ice will lead to methods, as it has already done in part, which will so temper the effects of ice in our northern rivers as to render them no longer a bar to the full development and utilisation of our vast water powers."

The chapters are entitled: equilibrium of the ice-water system, colloidal ice, the crystal structure of ice; physical constants of ice; rates of growth and melting of surface-formed ice; theories of the formation of anchor ice; frazil ice, winter ice floods; ice remedial work; ice pressure and expansion; ice navigation and ice breaking; conservation of heat in lakes and rivers for ice prevention; glacier ice and icebergs.

The author accepts Sutherland's view that liquid water contains no monohydrol even at the boiling-point, and that we have 37% trihydrol at the freezing-point, p. 6.

"In the glacier ice we find pressure cracks often filled by melted glacier ice which has freed itself of air and comes from the purest form of ice. This refrozen mass gives the deepest blues so characteristic of the blue streaks in an iceberg. The green ice of an iceberg is the compressed glacier ice before the air has been expelled or freed from the interior of the ice mass. The presence of the air molecules in the ice changes the scattering resonant ratio and gives the changed hue. It is highly probable that Prof. Raman is correct, and the color of ice is due to the large molecules, while the color of water is due to the presence of the ice molecules in solution. The glacial ice of icebergs is interesting because it shows no large crystal structure, being merely a mass of snow or frost nuclei grown to large dimensions. It is what we will call *pressure ice* as contrasted to *thermal ice* formed in a river or lake. Pressed down into a compact mass on the great ice plateau of Greenland the entangled air in amongst the snow and frost for countless ages is pressed into the ice and held in solution until the pressure is relieved as the icebergs melt. This air comes out in great quantities from iceberg fragments. The writer has shown that the amount of air carried by an iceberg is from 7 to 15% of the total mass and causes it to float much higher out of the water than ordinary ice would," p. 9.

When ice evaporates slowly, the latest heat of vaporization is about 700 calories, p. 32. When ice evaporates rapidly the corresponding figure is about 610 calories. The author believes that ice evaporates as a polymeric vapor, which is the same conclusion that Wood reached in regard to liquid mercury. The specific heat of water drops rapidly from −8° to about 40° and then increases as the temperature rises. The specific heat at 15°-16° is almost exactly one-hundredth of the specific heat between 0° and 100°, p. 38. The presence of ice molecules in water explains completely the rapid decrease in the specific heat of water as the temperature rises, as well as the maximum density point. "In the first case, superimposed on the heat energy necessary to cause an expansion of the molecules as the temperature rises, we have the heat absorbed in breaking up the molecules of ice (trihydrol) to form water-molecules (dihydrol). The relative amount of ice-molecules grows less as the temperature rises, and consequently the specific heat apparently grows less. At 37°C. there is an exact balance between the two effects, the normal increase in the specific heat, and the decrease in the heat absorbed in breaking up the ice-molecules."

"The manner in which one ice changes into another is truly remarkable. We know that water freezes slowly or that ice melts slowly, but some of these kinds of ice will change into another kind so rapidly that the reaction reminds one of an explosion. For instance, if ice I changes to ice III at −25°, the reaction takes place so suddenly that it is impossible to follow the change of pressure which takes place after the reaction. On several occasions a click in the apparatus has occurred when the transformation took place, so rapid was it," p. 90.

"The fact that ice I gives place to ice II at a certain pressure has one practical application. We have often heard of the immense pressures developed when water is allowed to freeze in a closed vessel. Burst water pipes are a familiar example of this, and there are also well-known experiments in which cannon balls have been split open by freezing water. It is of interest to inquire how much pressure might be reached in this way. The diagram furnishes an answer to the question, as it shows that if the pressure on the ice during freezing should rise to much over 2000 kgms., corresponding to 30,000 pounds per square inch, the ordinary ice would change to ice III, which has a much less volume, so that the ice would tend to shrink and the rise of pressure would be arrested. Thirty thousand pounds per square inch is, therefore, the highest pressure that can be obtained by freezing water in a closed space," p. 91.

"Anchor ice grows so rapidly during periods of excessive nocturnal radiation and low humidity that it may attain a thickness of five feet or more during the night. So compact does it become, that it is often very difficult to thrust a sounding rod through it. It is granular and plate-like in structure. Through clear water the ice looks like weeds with long tentacles rising up out of the mass. It often has great power to lift rocks and boulders up bodily, and many of these are carried far downstream attached to irregular masses of ice. The spongy character of adhering frazil crystals attached to anchor ice, or the underside of a surface sheet, causes them to accumulate slime from the water. The characteristic color of these masses is brown. When melted in a vessel the slime settles to the bottom, where it is seen to be of a very fine structure consisting probably of infusorial growth," p. 98.

"Anchor ice is, as has been pointed out, a product of the great nocturnal radiation under a clear sky whenever the weather is cold. In the early morning, however, the first light which tinges the eastern sky causes the ice to rise, before even a delicate thermometer can detect any temperature change in the water. Thousands of tons of ice are brought up from the bed of the St. Lawrence river every morning in winter in the open reaches, and are floated down stream to add their quota to the great packs at restricted points," p. 105.

"This remarkable influence of the sunrise on ice was the occasion of the writer's first conceiving the idea of using artificial heat for destroying ice. During a two weeks' observation of a single iceberg off the coast of Newfoundland, it was remarked how much cracking was heard in the period from darkness to dawn, and how during this time large pieces came off. The day witnessed no such effects, and the heat of the sun was washed off by the running water from the melting surface. At night the iceberg dried, and the surface became cold and hard again. As morning approached much fog was precipitated on the ice, and when the light first appeared the cracks started again. The sunlight was able to penetrate the ice surface, setting up strains in the huge mass which contributed to its destruction," p. 106.

"It is highly probable from the experiments now in progress that some form of selective radiation will be found of high photochemical activity, which will imitate sunlight in destroying the ice-forming power of water by breaking up the trihydrol. Already a "sunrise" lamp has been made to burn under water, emitting powerful red, green and ultraviolet rays which are active in destroying ice," p. 107.

"During the time when the water is producing frazil, which is when it is slightly supercooled, there is a tendency for ice to adhere to all bodies immersed in proportion to their thermal conductivity and surface. Thus hemp rope will grow ice on it much sooner than a metal rope. This first layer of ice is like a slim precipitate which is very tenacious. As time goes on, the ice builds up a thicker layer, more or less compact in proportion to the current of water flowing. In quiet water long needles gather and grow out until the whole rope is encased in a mantle of ice crystals and plates. In fast running water, a solid layer of clear ice is usually found, which resembles surface ice, and is thickest on the upstream side. One of the most interesting methods of determining the ice forming power of the water, is used at Holtwood, Penn., where it is the custom to hang a frayed rope in the intake of the power house. Long before other evidences of ice are present in the wheels, it is seen growing from this rope. It is stated that this simple test is much more sensitive than a thermometer, and thoroughly reliable, as a warning of approaching ice troubles," p. 195.

"In treating the ice problem, even those with the oldest experience are inclined to regard the task of ice breaking from the wrong end. Anyone who views the ice accumulation in the river toward the end of the winter thinks rightly of the impossibility of coping with such masses. Where ice is prevented from accumulating and usually the task of prevention is not an insurmountable one, these large masses cannot form. It is the work of but a few days or less for the formation of the famous ice bridge at Cap Rouge, and yet it is the work of two months to break it down again, whereas the presence of an ice breaker during the first few days and after will prevent the bridge from forming altogether, and make the task of keeping the river clear at that point a simple one," p. 229.

"The air which has been pressed into the ice under the great pressure from the masses of snow, comes out when the berg melts and often causes explosions and loud disruption. This air is of great interest since it must have been stored for thousands of years. Ice water prepared from pieces of iceberg ice will effervesce very much like soda water," p. 233.

In all, three icebergs were treated with thermit. "Only one charge of 100 pounds was placed in the first berg, but this reacted perfectly, causing a very powerful explosion of the ice, which disintegrated a great part of the large plateau. Immediately after cracks were heard which continued all during the evening, and towards morning, about 2 o'clock, a very loud cracking awoke many people in the village. On visiting the berg the next day a great part of the inside had come out between the thermit hole and the main cliffs and most of the plateau, 400 feet long, was gone. In two days the disruption thus started went on and the iceberg once so grand and firm became a poor shadow of its former self, breaking up rapidly and turning nearly completely over. No other charge was put in to complete the disruption, for the writer did not like the look of the ice and thought it more prudent to try other bergs.

"The second iceberg treated was one grounded in Jenkin's Cove in Twillingate harbor. This was selected in order to give the poeple of the village a chance to see the beautiful sight of a burning iceberg. A natural ampitheatre was provided by the high cliffs all around the cove. During the day a large charge of thermit, 500 pounds, was sunk into the ice and in the early evening just at sundown it was fired. Those who saw the spectacle will never forget the wonderful sight as the charge roared and flamed hundreds of feet into the air with the exploding ice scattering fire and sparks for hundreds of feet on either side.

"Vesuvius in eruption was the nearest approach to this unique sight. The effect on the ice was the same as before. The explosion disrupted a great deal of ice, but the intense heat wave cracked and honeycombed the mass and during the night and all the next day the berg continued to fall to pieces, rolling to one side and the other as the mass was lightened by the falling pieces. An attempt was made the next day to put a charge of high explosive on the ice to see what a sudden shock would do to the rotten ice, but a large mass fell into the sea directly in front of the dory and it was considered far from safe to venture on.

"The third experiment was made on a medium-sized berg off the North Island. This was grounded alongside of three icebergs and from its massiveness and shape served our purpose very well. It had the appearance of an inverted tea-cup. The ice was very hard and firm and showed no sign of disintegrating. Two charges were put off on the very peak of this berg, one of 60 pounds and the other of 100 pounds of thermit. Both charges exploded the ice but no ice was knocked off by the force of the explosion. This occurred about six o'clock in the evening. In the morning the writer with his party visited the spot to inspect the result of the treatment, but the iceberg had disappeared and could not be found for a long time, until sufficient evidence was found that it had not floated away from the spot because a fragment was located floating in the vicinity which contained marks of the thermit slag together with a part of the hole made for the thermit can half submerged under the water line. This hole had been cut on the top of the berg 30 feet above the water line and been blown out funnel-shaped by the explosion, easily located by this peculiar shape. The three other icebergs in this place were still in position and had not broken up. No better evidence of the peculiar nature of the heat action could be found. The writer's party left for home that night well satisfied with the results of the experiments.

"There is no question of the wonderful effectiveness of the heat treatment to control iceberg menace, for the action of the thermit heat units are most effective in the hardest and most resistant ice masses. Our experiments with high explosives verified the results obtained by the U.S. Coast Guard that they have little or no effect on these solid masses of ice. The action of the heat is quite different; it sets up the thermal expansion strain which causes innumerable cracks and fissures through which the sun and melted ice water gain access, causing the falling apart of the ice wherever the heat has been applied," p. 337.

Wilder D. Bancroft

The Determination of Hydrogen Ions. *By William Mansfield Clark. Third edition. 23 × 15 cm., pp. 717. Baltimore: Williams and Wilkins Company, 1928. Price $6.50.* In the preface of this edition, the author says, p. *ix*: "Within the past twenty years methods of determining hydrion concentration have served well in the exploration of many and divers subjects. But the period of general exploration is drawing to a close and long ago there were begun exact studies of equilibria or of kinetic events in which hydrions participate. Refinement of technique, variety of method, and elegance of formulation are in greater demand. Accordingly there have been added in this edition chapters or sections bearing upon each of these aspects, and the old text has been almost entirely rewritten to conform to the revised presentation."

In the preface also the author shows graphically how varied and extensive are the applications of the technique, the methods, and the special forms of theory dealing with his subject. In the years from 1911 to 1927 the number of papers abstracted in Chemical Abstracts and dealing with hydrogen ion concentration rose from 70 to about 1470. This interest is reflected also in the demand for this book which has led to seven printings in eight years.

There are thirty chapters dealing, for the most part with the same subjects as were found in the second edition and in about the same order. New chapter headings include: the application of spectrophotometry, colorimetry, etc.; on changes of free energy; the quinhydrone and similar half-cells; metal oxide electrodes, the gas electrode, the oxygen electrode; temperature coefficients; the theory of Debye and Hückel; elementary theory of titration; non-aqueous solutions.

The book is designed to appeal to many classes of scientific workers. It includes detailed description of apparatus, manipulative directions, theoretical and mathematical developments, thirty-eight pages of applications and eighty-six pages of bibliographical references. In spite of the abundance of material the lack of unifying generalizations is marked. There seems to be no agreement on the best way to prepare so simple an apparatus as a reliable and efficient hydrogen electrode. Many procedures are outlined as having worked well in some conditions but no one knows reasons for failures in other cases. The worker in this field must guard against innumerable sources of error, known and unknown, and trust that no new ones enter. He then joins the author in hoping for that genius who will some day present the subject, "with brilliant simplicity and withal rigidly."

The methods of approach taught in this book are of increasing usefulness. It would appear, however, that extensions of the field would be even more rapid if, for example, the buffer solutions could be made even more resistant to change. Possibly this is another way of saying that little is known about the hydrogen ion determination in concentrated solutions.

This new book is a worthy successor to the earlier editions and will, no doubt, continue to instigate and guide many investigations in many branches of science.

Herbert L. Davis

A General Discussion on Homogeneous Catalysis held by the Faraday Society, September, 1928. *25 × 16 cm; pp. 200. Aberdeen: The University Press. Price: 15 shillings, 6 pence.* The papers and discussion included in this volume on Homogeneous Catalysis give a very clear idea of the present position of the theory and practice of the subject. It brings together the views of chemists as to the meaning of the varied phenomena of catalysis. We see in this volume ideas based on kinetic and statistical theories, in militant juxta-position to those which have their origin in the theory of electrolytes and in the structural conceptions of organic chemistry. Also in some papers there can be perceived an inclination to explain the phenomena of catalysis in terms of thermodynamic conceptions.

It is too much to expect that these ideas will be fused into one comprehensive theory as a result of the discussion, for each viewpoint has been gained as a result of experience in specialised fields of chemistry, each of which requires for its development a specialised theory. However, the discussion should serve the useful purpose of breaking down whatever isolation exists between workers in different fields.

The kinetic and statistical aspect of catalysis is treated in papers by Hinshelwood, Rideal, Polanyi, Christiansen, and Bäckstrom. This section of the discussion shows the wide range of applicability of the Christiansen theory of chain-reactions to the explanation of positive and negative catalysis, and to the explanation of the effects of inert gases on the velocity of chemical change. Bäckstrom employs this theory to explain the inhibition of auto-oxidation of organic compounds in aqueous solution, and Polanyi applies it to the explanation of the inhibition of chain-reactions in gases by bromine. The work of Semenoff shows how useful is this theory in the treatment of the phenomena accompanying the inception of flame in a gaseous mixture. A paper by Hinshelwood on the influence of nitrogen peroxide on the union of hydrogen and oxygen sets forth an interesting case of trace catalysis.

Papers by Boeseken, by Rice and Sullivan, and by Moureu are concerned with catalysis in reactions in organic chemistry. Moureu shows that anti- or pro- oxygenic catalysis occurs in a large number of cases of oxidation, and to explain their action, puts forward an intermediate compound theory of catalysis. Boeseken advances the view that dislocation of chemical linkings by a catalyst is the cause of changes in the velocity of reaction and discusses the effect of the catalyst on the constants in the Arrhenius relation, $\log_e k = -A/RT = B$. Kendall and Harrison discuss the evidence for compound formation in the ester-water system.

In the introductory paper to the discussion, Lowry points out the necessity for agreement on the main features of the catalysis by acids and bases, and in particular, recognition of catalysis by neutral salts. Brönsted, Dawson, v. Euler, Harned and Åkerlöf, Lowry and Wilson, and Skrabal contributed papers to this section, and Lapworth, McBain, Giordani and others to the discussion. There was general agreement as to the impossibility of explaining the so-called acid and basic catalysis solely in terms of the concentration of hydrogen and hydrogen ions, but there was great divergence in the methods adopted in explaining the abnormalities. The catalytic effects of ions other than hydrogen and hydroxyl and even of neutral molecules was admitted, and Brönsted, in order to group all of the catalysis as acids or bases, puts forward a new theory of acids and bases. There was less agreement with regard to the explanation of the effect of concentration of electrolyte on the catalytic phenomena. There is a disinclination in some quarters to admit the usefulness of the Debye-Hückel theory in the explanation of these effects. There was agreement as to the main facts, however. If the velocity of catalysis by an acid HA is given by

$$v = k_h[H^+] + k_a[A^-] + k_m[HA],$$

then it is recognised that the coefficients, k_h, k_a, k_m, and the equilibrium constant K_{HA} are changed on the addition of electrolytes, either by an effect on the medium, or on the ionic hydration. The regularities observed in the salt effects are illustrated by a large amount of experimental data.

W. E. Garner

ERRATUM

In Fig. 2 on p. 6 of the article by Messrs. Ferguson and Funnell, change F and W, Wr., and B and W to F and F, Wr., and B and B.